Análisis de la contaminación antrópica en el Parque Natural de L'Albufera: uso de muestreadores pasivos, análisis de núcleos de sedimento y evaluación del riesgo ambiental

Doctorado en Química

Febrero 2025



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MINISTERIO
DE ECONOMÍA, INDUSTRIA
Y COMPETITIVIDAD

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

GENERALITAT VALENCIANA

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Que la graduada Yolanda Soriano Juan ha estado trabajando bajo nuestra dirección durante más de cuatro años en la elaboración de la tesis doctoral que lleva por título "**Evaluación de la contaminación antrópica en el Parque Natural de L'Albufera: uso de muestreadores pasivos, análisis de núcleos de sedimento y determinación del riesgo ambiental**" por lo que autorizamos su presentación para optar al grado de Doctora en Química con Mención internacional.

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Yolanda Soriano, Rodrigo Alvarez-Ruiz, Joseph E. Clokey, Sara Ghorbani Gorji, Sarit L. Kaserzon, Yolanda Picó (2023). **Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: An environmental risk assessment:** *Science of The Total Environment*, 903, 166594 [JCR (WOS) IF: 8.2 en el área de Ciencias Medioambientales 22/265 Q1 (primer decil)]

Yolanda Soriano, E Gimeno-García, Julián Campo, Carmen Hernández-Crespo, V Andreu Pérez, Yolanda Picó (2024). **Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: Accounting for site/area dependent factors:** *Journal of Hazardous Materials*, 470, 134168 [JCR (WOS) IF: 12.2 en el área de Ciencias Medioambientales Q1 (primer decil)]

Yolanda Soriano, E Gimeno-García, Julián Campo, Carmen Hernández-Crespo, V Andreu Pérez, Yolanda Picó (2024). **Trace elements and legacy and emerging organic contaminants concentrations datasets in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota:** *Data in Brief,* 54, 110464 [Cited Score (Scopus) SC: 1.7 en el área Multidisciplinar 32/111 Q2]

Yolanda Soriano, Emilio Doñate, Sabina Asins, Vicente Andreu, Yolanda Picó (2024). **Fingerprinting of emerging contaminants in L'Albufera natural park (Valencia, Spain): Implications for wetland ecosystem health:** *Chemosphere,* 364, 143199 [JCR (WOS) IF: 12.2 en el área de Ciencias Medioambientales Q1 (primer decil)]

Yolanda Soriano, Emilio Doñate, Sabina Asins, Vicente Andreu, Yolanda Picó (2024). **Data on the profile of organic contaminants in the L'Albufera Natural Park (2019–2020). Target and non-target screening:** *Data in Brief,* 57, 111021 [Cited Score (Scopus) SC: 1.7 en el área Multidisciplinar 32/111 Q2]

Yolanda Soriano, Eric Carmona, Javier Renovell, Yolanda Pico´, Werner Brack, Martin Krauss, Thomas Backhaus, Pedro A. Inostroza (2024): **Co-occurrence and spatial distribution of organic micropollutants in surface waters of the River Aconcagua and Maipo basins in Central Chile:** *Science of The Total Environment*, 954, 176314 [JCR (WOS) IF: 8.2 en el área de Ciencias Medioambientales 22/265 Q1 (primer decil)]

Los artículos publicados se han incluido en la tesis en el formato original de la revista. En todos ellos, **Yolanda Soriano** ha llevado a cabo la totalidad del trabajo experimental, supervisando estrechamente los experimentos, analizando los resultados y redactando los manuscritos

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La presente tesis doctoral se ha realizado gracias a la concesión de una ayuda para contratos predoctorales para la formación de doctores 2019 (PRE2019-089042) del Ministerio de Ciencia, Innovación y Universidades, que además ha financiado una estancia en el extranjero de cinco meses en el Centro Helmholtz de Investigación Medioambiental (UFZ) para la obtención de la mención internacional. El trabajo desarrollado ha sido financiado por los proyectos RTI2018-097158-B-C31 (MCIN/AEI/10.13039/501100011033 y "FEDER una manera de hacer Europa") y CIPROM/2021/032 (Programa Prometeo para Grupos de Investigación de Excelencia, Conselleria de Educación, Universidades y Empleo de la Generalitat Valenciana).

AGRADECIMIENTOS

Quiero expresar mi más sincero agradecimiento a todas las personas que me han brindado su apoyo durante la realización de esta tesis.

En primer lugar, quiero expresar mi agradecimiento al Ministerio de Ciencia, Innovación y Universidades por brindarme la oportunidad de realizar este doctorado a través de la concesión de la ayuda predoctoral para la formación de doctores. Asimismo, agradezco a la directora y al personal de la Oficina del Parque Natural de L'Albufera por su continuo asesoramiento y apoyo, sin los cuales este trabajo no habría sido posible.

Quiero expresar mi más profundo agradecimiento a Yolanda Picó, cuya guía, dedicación y apoyo fueron fundamentales en la realización de esta tesis. Sin su confianza y apoyo inquebrantable, este logro no habría sido posible. Agradezco profundamente su energía inagotable y su dedicación a la investigación, la cual me ha transmitido durante estos años. Lamentablemente, su partida ocurrió antes de que pudiera compartir con ella el fruto de nuestro trabajo, pero su legado sigue presente en cada página de este proyecto. Siempre recordaremos a Yolanda como una persona excepcional, apasionada por la ciencia y dotada de una calidez humana inigualable. Su sonrisa, su empatía y la alegría que transmitiría a diario permanecerán en nuestra memoria. Siempre estaré agradecida por su orientación y por todo lo que me enseñó. Esta tesis es, también, un homenaje a su memoria.

A Vicente, como codirector, también le agradezco por todas las correcciones intercambiadas a lo largo de este tiempo. Tu experiencia y la manera en que constantemente compartes tus conocimientos y sabiduría son invaluables. Sé que estos han sido momentos difíciles para ti, y admiro profundamente tu generosidad y compromiso al acompañarme en este proceso final a pesar de las circunstancias. Te envío mi más sincero agradecimiento.

I extend my gratitude to Werner Brack and Martin Krauss for the opportunity to research at the Helmholtz Centre for Environmental Research (UFZ) and to experience the enriching adventure of living in Leipzig. I am also thankful to Eric and Pedro for their unwavering support, and to all the colleagues at UFZ. I

look forward to sharing a beer in the future. Also, I extend my gratitude to Sarit Kaserzon and Joseph E. Clokey for their contribution to this work by providing the MPT passive samplers and assisting in the development of a significant component of this study.

Asimismo, expreso mi sincero agradecimiento a Miguel Martín y Carmen Hernández, ambos de la Universidad Politécnica de Valencia, por habernos proporcionado el corer de sedimento necesario para la extracción de los núcleos de sedimento, sin el cual este estudio no habría sido posible.

Dar las gracias también a Eugenia, Sabina, Cristina y Pedro, y a todos los compañeros y compañeras del CIDE, así como a todo el personal de la UV, por su acogida y disponibilidad, que han aportado su granito de arena para hacer posible esta tesis.

Por supuesto, también quiero agradecer a mis compañeros/as de batalla. Deseo expresar mi más profundo agradecimiento a mi compañera, pero, sobre todo, amiga Lulu. Su compañía ha sido inestimable durante los numerosos muestreos realizados en los arrozales, soportando largas horas bajo el sol y las inevitables caídas en el fango de los campos de arroz. Su energía positiva ha sido una fuente constante de motivación y apoyo, actuando como mi inagotable fuente de vitalidad a lo largo de nuestro recorrido juntas en la ciencia.

No podía olvidarme de mis chiquitinas, de mis guerreras, de mis luchadoras a pie de cañón... Vasia y Dyana, hermanas de batalla desde el primer día hasta el último. Juntas hemos salido victoriosas en cada batalla con el Orbitrap, o con los generadores del nitrógeno. Gracias por vuestra compañía en "café y salseo" de todas las mañanas, y gracias por hacer que mis últimos años de doctorado fueran posible. Gracias por estar ahí en los momentos de desafíos y por celebrar conmigo cada pequeño avance. Me llevo una amistad enorme que no entiende de fronteras ni de oficinas. No importa dónde estemos, siempre encontraremos la manera de seguir en contacto, de compartir nuestras historias y, quién sabe, tal vez de reencontrarnos algún día con un café en mano, como si el tiempo no hubiera pasado.

Daniele, mi pequeño filósofo, gracias por tus sabios consejos sobre cómo abordar la vida. Tu paz y serenidad interior era necesaria en el laboratorio (¡Cómo la echamos de menos!). Espero verte pronto, ya sea en Roma, Yecla, o en tu querida Valencia. Julián, gracias por tu infinita paciencia y comprensión. Has transformado tu chalet en un hogar lleno de calidez y acogida familiar, junto con María, y Gaia. Roy, estuviste a mi lado desde el principio, y tus anécdotas e historias siempre llenaron el despacho de alegría. Fuiste quien impulsó esos momentos inolvidables compartiendo vinos en la

bodega y esas cervesitas en el Colonial de Benimaclet. Gracias por cada sonrisa y por hacer de cada momento algo especial. También expresar mi agradecimiento a Alicia, Manuela, Jhesibel, Kaique, Javi y Emilio, así como a todas las compis de prácticas que han tenido una breve, pero intensa estancia en el laboratorio. Han contribuido significativamente a que este viaje sea inmejorable. Marcello, aunque estuviste con nosotros solo unos meses, dejaste una huella imborrable de calma, paciencia y paz. Te agradezco de corazón por esos momentos compartidos. Te llevaste a Italia dos palabras que sé que te encantaron: "petarda" y "almuerzo".

Agradezco también a todos mis amigos y amigas que me han acompañado a lo largo de este camino, brindándome su energía, apoyo y la confianza en mí misma, que en ocasiones sentí que me faltaba. A mi gente de Yecla: Natalia, mis Lauras, Rebeca, Rosa, Sheila, Vanessa, Yamilé… y a toda la Peña el Arabilejo, porque sin llegar a entender muy bien lo que hacía, siempre habéis estado ahí apoyando. Gracias por formar parte de mi vida. Además, quiero expresar mi agradecimiento a mi pequeña familia valenciana, que desde mi llegada en 2011 me hizo sentir como en casa. En especial, agradezco a Claudia, Marina, Javi, Dani, Pablo, Alex, Jorge, Jorgito, y a todos los demás, por haberme acogido como parte de su familia y hacerme sentir en un hogar lejos del mío.

Finalmente, quiero expresar mi agradecimiento a toda mi familia. En particular, a mi padre, mi referente de humildad en la vida. Gracias por cuidarme siempre que regreso a casa, por ese espacio en tu escritorio destinado a la redacción de mi tesis, y por el café recién preparado cada mañana cuando vuelvo a Yecla. Más que pequeños gestos, son recordatorios constantes de tu amor incondicional. A mi madre, por su constante preocupación por mí y por velar siempre por mi bienestar y salud mental durante estos cuatro años. Eres mi refugio en cada tormenta y mi luz en los días oscuros. Gracias por cada preocupación disfrazada de consejo y por hacerme sentir que siempre tengo un lugar seguro al que volver. Agradezco a ambos por su paciencia y fortaleza, incluso durante mis días de estrés en los que lo mejor era que nadie me hablara.

También quiero dar las gracias a mi hermano, un trabajador incansable. ¡Es difícil seguir tu ritmo con todo lo que haces! ¡Eres increíble! Gracias por brindarme tus consejos cuando más los he necesitado. Has sido una fuente constante de inspiración y fortaleza. A ti y a Esther (eres más que bienvenida en casa, y eres una más en esta familia), gracias por vuestro cariño y hospitalidad.

Y, por supuesto, a Carlos, no puedo dejar de agradecerte por estar a mi lado todos estos años. Tu infinita paciencia, tu capacidad para soportar mis cambios de humor y mis días de estrés, tus cuidados diarios y tu apoyo incondicional en los momentos más difíciles han sido invaluables. ¡Gracias por la deliciosa comida que tenías preparada cuando volvía del CIDE!

Os quiero mucho, familia. Este logro no es solo mío, es nuestro.

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PRESENTACIÓN DE LA MEMORIA

01. OBJETIVOS Y ESTRUCTURA

Las acciones cotidianas en el ámbito doméstico, conjuntamente con las operaciones industriales y agrícolas, conllevan la introducción de una amplia gama de contaminantes orgánicos en el entorno ambiental [1]. Las altas cargas de estos contaminantes orgánicos son introducidas de manera continua en el medio acuático a través de diversas vías. Las estaciones depuradoras de aguas residuales (EDARs), representan la principal fuente de vertido de contaminantes antropogénicos, ya sean domésticos o urbanos, en los medios acuáticos [2]. Eso se debe a que los métodos convencionales de tratamiento de aguas residuales no son capaces de eliminar la mayoría de estos contaminantes [3]. Además, existen contaminantes, como las sustancias perfluoroalquiladas y polifluoroalquiladas (PFASs) o pesticidas, que, aunque también se detectan en los efluentes de las EDARs, cuentan con vías alternativas de vertido al medio ambiente.

El uso de pesticidas se asocia generalmente con la producción de cultivos y otras actividades agrícolas. No obstante, los pesticidas también son utilizados en áreas urbanas. Algunos pesticidas se emplean para el control de plagas en jardines, parques y campos de golf, así como para el control de pulgas en mascotas, o la gestión de plagas de mosquitos en áreas urbanas [4]. Además, es importante destacar que los materiales de construcción pueden contener pesticidas; por ejemplo, los fungicidas se encuentran en conservantes de madera, pinturas, revestimientos de yeso o incluso mezclados con pinturas con el fin de evitar el crecimiento de biopelículas. Incluso las propias industrias dedicadas a la fabricación de pesticidas, o fármacos, también representan una fuente de contaminación por estos compuestos. Otras fuentes difusas podrían incluir variaciones espaciotemporales ocasionadas por flujos de personas, como el turismo estival o invernal [5], lixiviados de vertederos [6], deposición atmosférica, descargas a los ríos, actividades de navegación y portuarias, así como escorrentía superficial y urbana [7]. Además, la eliminación inadecuada de medicamentos o cosméticos caducados en inodoros o vertederos también puede ser una fuente de contaminación para las aguas superficiales y subterráneas. Todos estos contaminantes suelen acabar desembocando en el medio acuático.

Los humedales, clasificados entre los ecosistemas más vulnerables del planeta, se presentan como entornos propicios para el desarrollo de actividades agrícolas, dada su capacidad para proveer suelos fértiles y reservas de agua dulce de alta calidad [8]. Además, desempeñan un papel fundamental en la regulación de los ciclos naturales y el sustento de una amplia biodiversidad. A pesar de su significativa importancia ecológica y económica, estos ecosistemas acuáticos se encuentran entre los más vulnerables a las alteraciones ocasionadas por la actividad humana, tales como la sobreexplotación de sus recursos y la expansión de la agricultura intensiva. Estas actividades, entre otros efectos, provocan una considerable reducción en su extensión natural.

El Parque Natural de la Albufera, situado en la provincia de Valencia (España), constituye un caso de estudio relevante en el contexto de los humedales costeros mediterráneos, ya que el estado ecológico de esta laguna costera ha experimentado un deterioro significativo desde la década de 1970, como resultado de una serie de factores tanto naturales como antropogénicos. La sobreexplotación de los recursos hídricos y la contaminación de las masas de

agua, como se ha indicado anteriormente, son problemas preocupantes que tiene importantes consecuencias para estos ecosistemas y, en último término, para la salud humana.

Como se ha mencionado anteriormente, las principales fuentes de contaminación están asociadas con actividades urbanas, industriales y agrícolas. Además, factores socioeconómicos como el crecimiento demográfico han contribuido al incremento de contaminantes de origen humano en esta área [9], los cuales a menudo tienen como destino el medio acuático (ríos, lagos, mar, agua potable, aguas residuales, etc.).

Como consecuencia, se ha observado una presencia considerable de estos contaminantes en el Parque Natural, incluyendo contaminantes emergentes de preocupación creciente (CECs), tales como pesticidas [10], y productos farmacéuticos y de cuidado personal (PPCPs) [11,12]. Aunque han sido detectados en el medio ambiente en concentraciones mínimas (mg L^{-1}, µg L^{-1}, ng L^{-1}), aún no están sujetos a restricciones regulatorias. Es decir, los contaminantes orgánicos no siempre están sujetos a regulaciones por parte de la legislación ambiental, la mayoría de ellos no están contemplados en la lista de contaminantes prioritarios establecida por la Unión Europea (UE), y no se dispone de concentraciones admisibles reguladas en aguas superficiales para evaluar su impacto ambiental [1]. Además, algunos de estos contaminantes, han sido incluidos en la "lista de observación" de la Directiva Marco del Agua de la UE debido a sus efectos adversos en el medio acuático. A pesar de la falta de regulación oficial, surge una creciente preocupación en torno a los CECs debido a sus posibles efectos a largo plazo en los ecosistemas y organismos vivos, incluso en concentraciones bajas (desde ng L^{-1} hasta mg L^{-1}) y en exposiciones prolongadas [13].

Como se mencionó previamente, la persistencia de estos compuestos químicos, aun en concentraciones bajas, puede conllevar no solo su acumulación en diversos compartimentos del medio ambiente, sino también, puede suponer un peligro para los ecosistemas, ya que existe un profundo desconocimiento sobre su comportamiento ambiental, y sus efectos toxicológicos son desconocidos. Estos contaminantes pueden provocar la pérdida de hábitats y biodiversidad, así como efectos tóxicos en los organismos acuáticos y representar una amenaza para la salud humana [14,15]. Por ende, uno de los principales desafíos en el entorno de L´Albufera radica en la gestión de su sistema hídrico para garantizar la calidad del agua, incluyendo, la detección de contaminantes orgánicos en dicho humedal costero que, a su vez, requiere el desarrollo y optimización de técnicas analíticas, que constituyen el talón de Aquiles de la detección, ya que hablamos de compuestos que se encuentran a concentraciones traza y en algún caso se trata de compuestos degradables que, además, se transforman en el medioambiente.
Estas son las razones por las que la recopilación de datos exhaustivos sobre su presencia dentro del Parque Natural de L´Albufera es fundamental para poder desarrollar nuevos tratamientos de depuración más eficaces, con el propósito de evitar o minimizar su liberación al medio ambiente. Además, determinados compuestos se perfilan como candidatos para su inclusión en futuras regulaciones relativas a la reutilización de aguas regeneradas, dada su ecotoxicidad y presencia en diversos compartimentos ambientales, entre otros aspectos. Por lo tanto, el desarrollo y la mejora de los métodos de preparación de muestras, detección y cuantificación son imprescindibles para un mayor conocimiento y formas de seguimiento del destino de los contaminantes en el medio ambiente y en los organismos vivos.

Basándose en lo expuesto previamente, el objetivo general de la presente tesis doctoral es establecer la presencia, el destino y los impactos de los contaminantes en el medio acuático, así como estudiar la distribución espacial de una variedad de contaminantes orgánicos con el propósito de establecer conexiones con la carga de contaminación proveniente de múltiples fuentes, así como determinar si existe correlación entre la contaminación y un tipo específico de uso del suelo. Además, se busca evaluar los riesgos ambientales que los contaminantes orgánicos representan para el Parque Natural, tratando de establecer si la presencia de estas sustancias supone un riesgo para la fauna de estas áreas.
Para alcanzar este objetivo general se establecieron los siguientes objetivos específicos:

1. Desarrollo de técnicas de análisis de cromatografía líquida de alta resolución necesaria para la determinación y cuantificación simultanea de contaminantes orgánicos pertenecientes a diversas familias, así como la evaluación de la efectividad de técnicas de métodos no dirigidos (non-target) para la identificación de contaminantes en matrices ambientales complejas (agua y sedimento), para proporcionar una visión más completa del perfil de contaminantes orgánicos dentro del Parque Natural. Se evaluará, además, su distribución espacio-temporal y se vincularan con la carga de contaminantes provenientes de diversas fuentes. Para la consecución de este objetivo, la aplicación de los sistemas de información geográfica (GIS) y el análisis estadístico son fundamentales. Asimismo, se evaluará el riesgo ambiental que ciertos pesticidas representan para los organismos acuáticos mediante la predicción del riesgo, utilizando el cociente de riesgo ecológico de aguas superficiales (RQ).

2. Evaluación de la presencia de contaminantes, así como sus concentraciones, dentro del Parque Natural de la Albufera mediante el empleo de muestreadores pasivos de tubo de polietileno microporoso como herramienta complementaria al muestreo convencional. Este enfoque permitirá evaluar el estado de contaminación a medio plazo en los humedales costeros proporcionando información adicional mediante su promedio ponderado en el tiempo.

3. Estudio de la presencia y movilidad de contaminantes orgánicos en los núcleos de sedimentos del lago, estableciendo conexiones entre la edad de los sedimentos y las variaciones verticales de dichos contaminantes, así como con las características sedimentarias y la evolución histórica del lago. Esto se realizará, para estudiar su posible utilización como paleoarchivos, lo que proporcionaría información sobre el origen y el desarrollo del Antropoceno en el área del Parque.

4. Estudio sobre la coocurrencia y distribución de microcontaminantes orgánicos, tales como productos farmacéuticos, pesticidas, productos de cuidado personal, surfactantes y otros contaminantes orgánicos industriales, en las aguas superficiales de dos cuencas fluviales en el centro de Chile. Este enfoque permitirá identificar y clasificar los compuestos químicos cuantificados, categorizar sus modos de acción y correlacionar su presencia con diferentes usos del suelo.
El plan de trabajo que se diseñó para el desarrollo de los objetivos anteriormente expuestos ha sido el siguiente:

En primer lugar, se llevó a cabo una exhaustiva búsqueda bibliográfica con el propósito de profundizar en el conocimiento de la situación medioambiental de la contaminación por compuestos orgánicos, con especial énfasis en los humedales costeros mediterráneos, así como en las técnicas analíticas más recientes para la determinación del perfil de contaminación en un área determinada. Estas técnicas abarcan métodos de muestreo que difieren de los métodos convencionales, así como métodos de análisis no dirigidos, también conocidos como "non-targeted análisis" (NTA). De este modo, se ofrece una visión general de los estudios realizados hasta la fecha y se lleva a cabo una evaluación de las perspectivas futuras para este ámbito de investigación, aspectos sobre los cuales se fundamentará la presente tesis.
Para obtener una comprensión más completa de la diversidad de contaminantes ambientales y polares en diversas matrices, se recomienda la utilización de instrumentos de Espectrometría de Masas de Alta Resolución (HRMS). La Cromatografía Líquida (LC) acoplada a HRMS (LC- HRMS) se ha vuelto más accesible para los laboratorios de investigación, convirtiéndose en la herramienta más poderosa para los métodos de análisis dirigidos (targeted analysis, TA) y no dirigidos (NTA).

El análisis dirigido de compuestos conocidos suele realizarse utilizando un conjunto de estándares de referencia y sus análogos marcados con el propósito de cuantificación. Por otro lado, el screening sospechoso utiliza bases de datos o listas internas de compuestos en lugar de estándares de referencia para identificar y confirmar la presencia de analitos conocidos. Esto se basa en la precisión de masas, el tiempo de retención, y la confirmación de la estructura mediante experimentos de MS/MS.

Para ello, se seleccionaron 51 puntos de muestreo dentro del Parque Natural de L'Albufera con el propósito de obtener una comprensión integral del estado de contaminación en esta reserva natural. Con todo ello, se obtuvo una perspectiva de cuáles eran los puntos negros de contaminación antropogénica dentro del Parque Natural que podían llegar a impactar los medios acuáticos. Además, este período se corresponde con el inicio y final del ciclo de cultivo del arroz del año, durante el cual se realizaron recolecciones de muestras de agua in situ en los principales ecosistemas acuáticos, abarcando una extensa área del Parque Natural y su cuenca hidrográfica. Posteriormente, en el laboratorio, se procedió a realizar análisis de diversas variables fisicoquímicas, así como análisis de contaminantes orgánicos con el propósito de evaluar la calidad de las aguas.

Se utilizó el GIS y el análisis estadístico para observar la distribución geográfica de los contaminantes y mostrar las diferencias estadísticamente significativas entre las concentraciones

de los mismos y las diferentes áreas, incluyendo las correlaciones con las características físico - químicas. Además, se realizó una evaluación del riesgo que suponen los contaminantes orgánicos seleccionados para la fauna acuática, utilizando el RQ de aguas superficiales que suponen las concentraciones encontradas para los distintos niveles tróficos.

Además, en el desarrollo experimental de la tesis, se implementó el uso de muestreadores pasivos para evaluar la presencia de contaminantes antropogénicos en los medios acuáticos, ya que la Directiva Marco del Agua (DMA) recomienda el uso de muestreadores pasivos, además de las muestras puntuales, como una forma complementaria de obtener información cuando se espera una gran variación temporal o fluctuación de contaminantes. Entre los muestreadores pasivos disponibles, los Muestreadores Integrativos de Compuestos Orgánicos Polares (POCIS, por sus siglas en inglés) [16,17] son los más utilizados. Sin embargo, existen otros sistemas como los tubos de polietileno poroso (MTP), los muestreadores pasivos Chemcatcher [18] o muestreadores pasivos de nanotubos de carbono [19] que se han utilizado en una amplia gama de ecosistemas acuáticos loticos. Sin embargo, la aplicación de muestreadores pasivos para el seguimiento a largo plazo de contaminantes en humedales no ha sido suficientemente explorada pese a que ofrece oportunidades para caracterizar mejor las fluctuaciones de exposición y los riesgos ecológicos.

Para ello, se seleccionaron pesticidas, PPCPs, PFASs y retardantes de llama organofosforados (OPFRs) como los principales tipos de contaminantes sobre los cuales se enfocaría este estudio. La aplicación de muestreadores pasivos de MPT permitió la vigilancia a medio plazo de estas substancias en los humedales con el objetivo de caracterizar mejor las fluctuaciones y los riesgos ecológicos.
Por otro lado, y para comprender mejor el estado ecológico actual de los humedales mediterráneos, también fue necesario mirar las fuentes de contaminación preexistentes, especialmente de contaminantes persistentes que se puedan retener en los sedimentos y puedan causar impactos tóxicos si por diversas causas sufren fenómenos como la resuspensión y la removilización. Algunos estudios tratan de establecer patrones de contaminación histórica, a partir del análisis de los sedimentos de lagos, estuarios y ríos. Sin embargo, los humedales tienen diferentes tiempos de retención hidráulica, condiciones de redox y dinámicas ecológicas en comparación con los lagos. Además, los patrones de contaminación pueden ser muy diferentes de un lugar a otro. Por lo tanto, la identificación simultánea de contaminantes en registros sedimentarios depositados durante el Antropoceno ofrece la oportunidad de identificar impactos o contaminantes claves que hayan contribuido al cambio biológico. Además, el análisis de dichos sedimentos (es decir, muestras de núcleos profundos) y el análisis estadístico de tendencias temporales pueden contribuir a construir un paleoarchivo de sedimentos de humedales. Para ello, se recolectaron dos núcleos de sedimentos en las partes Norte y Sur del lago del Parque Natural de L'Albufera con el fin de evaluar la presencia y distribución vertical de los contaminantes orgánicos. Estos núcleos fueron segmentados en siete secciones, y posteriormente datados por radiocarbono. Además, se llevaron a cabo mediciones de las características fisicoquímicas de los sedimentos para establecer una correlación entre la concentración de contaminante y el contenido de carbono orgánico presente en cada sección del núcleo de sedimento.

Asimismo, dado que los datos sobre la presencia de microcontaminantes orgánicos en los ecosistemas de agua dulce de América del Sur son limitados, en octubre de 2021 se recolectaron diez muestras de agua superficial de las cuencas de los ríos Maipo y Aconcagua, en el centro de Chile, con el objetivo de investigar la coocurrencia y distribución espacial de estos contaminantes.

La presente tesis doctoral se presenta estructurada en seis secciones, e incluyen un total de seis publicaciones científicas, que recogen todos los hallazgos conseguidos durante su realización:

La **sección 1** comprende una introducción de los desafíos asociados al análisis de contaminantes orgánicos en agua superficial y sedimentos para establecer el perfil de contaminación de un área. En esta sección se exponen las metodologías más innovadoras para la extracción y detección de compuestos orgánicos en agua y sedimento, y se lleva a cabo un análisis crítico de los desafíos analíticos que implica su identificación y cuantificación en los ecosistemas acuáticos.

En la **sección 2** se presenta el perfil general de contaminación en el agua y los sedimentos del Parque Natural de L'Albufera. Esta incluye el monitoreo de aguas superficiales mediante muestra puntual de agua de aguas provenientes de acequias de arrozales, cítricos, y huertas, agua superficial del lago, y la proveniente de golas. En dicho estudio también se evalúa la distribución espacial, el modo de acción de los pesticidas detectados, el riesgo de estos contaminantes y su destino. La aplicación de estas técnicas al Parque Natural de L'Albufera permitirá avanzar en el conocimiento de la contaminación, pudiendo desarrollar un sistema de muestreo y seguimiento que permita monitorizar de forma continuada el parque y proponer soluciones y medidas paliativas.

Artículo I: "Fingerprinting of emerging contaminants in L'Albufera natural park (Valencia, Spain): Implications for wetland ecosystem health".

Artículo II: "Data on the profile of organic contaminants in the L'Albufera Natural Park (2019-2020). Target and non-target screening".
Set de datos: "Dataset of emerging contaminants in L´Albufera Natural Park (2019-2020) by target and non-target screening using high resolution mass spectrometry" sediment characteristics and risk assessment to the aquatic biota", Mendeley Data, V1, doi: 10.17632/n44rpfms7b.1

La **sección 3** se enfoca en la investigación llevada a cabo en el área de estudio del Parque Natural de la Albufera, utilizando muestreadores pasivos como herramientas complementarias para evaluar el estado de contaminación a medio plazo del humedal costero.

Articulo III: "Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: An environmental risk assessment".

La **sección 4** reúne un total de 2 artículos y una base de datos, que no se incluye en la tesis, pero que es de acceso público, en los que se llevó a cabo la identificación simultánea de contaminantes en los registros sedimentarios depositados durante el Antropoceno mediante TA y NTA con LC y HRMS que ofrecen la oportunidad de identificar los principales contaminantes. De esta manera, se busca examinar la contaminación a largo plazo en el Parque Natural mediante la datación de sedimentos y la determinación de contaminantes en diferentes épocas, con el objetivo de analizar cómo estas variables se ven afectadas por el Antropoceno y su impacto en el Parque Natural.

Artículo IV: "Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: Accounting for site/area dependent factors".

Artículo V: "Trace elements and legacy and emerging organic contaminants concentrations datasets in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota".
Set de datos: "Dataset on trace elements and legacy and emerging organic contaminants concentrations in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota", Mendeley Data, V2, doi: 10.17632/n9p7xkp3vc.2.

En la **sección 5** se incluye un estudio sobre la presencia de microcontaminantes en los ecosistemas de agua dulce en América del Sur. Este estudio se centra en evaluar la presencia y distribución de microcontaminantes orgánicos en las aguas superficiales de dos cuencas fluviales en el centro de Chile. Además, busca identificar y clasificar los compuestos químicos presentes, analizar sus modos de acción y correlacionar su presencia con los distintos usos del suelo. El estudio tiene como objetivo identificar y clasificar los productos químicos cuantificados, analizar su modo de acción y correlacionar su presencia con los diferentes usos del suelo.

Artículo VI: "Co-occurrence and spatial distribution of organic micropollutants in surface waters of the River Aconcagua and Maipo basins in Central Chile".

En la **sección 6** se recoge un resumen general de los hallazgos obtenidos en las secciones 2, 3, 4 y 5. Finalmente, se presentan las conclusiones derivadas de todos los trabajos mencionados, así como un apartado de anexos que incluye un índice de tablas, figuras, textos y abreviaturas utilizadas en el transcurso de la misma.

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02. AIMS AND STRUCTURE

Everyday activities in the domestic sphere, along with industrial and agricultural operations, lead to the introduction of a wide range of organic contaminants into the environment [1]. High loads of these organic contaminants are continuously introduced into aquatic environments through various pathways. Wastewater treatment plants (WWTPs) are the primary source of discharge for anthropogenic contaminants, both domestic and urban, into aquatic systems [2]. This is because conventional wastewater treatment methods are not capable of removing most contaminants [3]. Additionally, there are contaminants such as perfluoroalkyl and polyfluoroalkyl substances (PFASs) and pesticides, which, although also detected in WWTPs effluents, have alternative pathways of release into the environment. The use of pesticides is generally associated with crop production and other agricultural activities. However, these compounds are also used in urban areas. Some them are employed for pest control in gardens, parks, and golf courses, as well as for flea control in pets and mosquito management in urban settings [4]. It is also important to note that construction materials can contain pesticides; for example, fungicides are found in wood preservatives, paints, plaster coatings, or even mixed with paints to prevent biofilm growth. Additionally, industries involved in the production of pesticides or pharmaceuticals are significant sources of contamination by these compounds. Besides, other diffuse sources of organic contaminants may include spatiotemporal variations caused by human activity, such as seasonal tourism [5], landfill leachates [6], atmospheric deposition, river discharges, navigation and port activities, as well as surface and urban runoff [7]. The improper disposal of expired medications or cosmetics in toilets or landfills can also be a source of contamination for surface and groundwater. These contaminants often ultimately reach aquatic environments.

Wetlands, classified among the most vulnerable ecosystems on the planet, are particularly susceptible as they provide fertile soils and high-quality freshwater reserves, making them favorable environments for agricultural activities [8].

Moreover, they play a crucial role in regulating natural cycles and supporting a wide range of biodiversity. Despite their significant ecological and economic importance, these aquatic ecosystems are among the most vulnerable to disruptions caused by human activities, such as resource overexploitation and the expansion of intensive agriculture. These activities have led to a substantial reduction in their natural extent. The Albufera Natural Park, located in the province of Valencia, Spain, serves as a significant case study within the context of Mediterranean coastal wetlands. The ecological condition of this coastal lagoon has undergone considerable deterioration since the 1970s due to a combination of natural and anthropogenic factors. The overexploitation of water resources and pollution of water bodies is a concerning issue with serious implications for the ecosystem and, ultimately, human health.

As previously mentioned, the primary sources of pollution are linked to urban, industrial, and agricultural activities. Additionally, socioeconomic factors such as population growth have contributed to the increase in human-derived contaminants in this area [9], which often end up in aquatic environments, including rivers, lakes, seas, drinking water, and wastewater. As a result, a significant presence of these contaminants has been observed in the Natural Park, including emerging contaminants of increasing concern (CECs) such as pesticides [10], and

pharmaceuticals and personal care products (PPCPs) [11,12]. Although detected in the environment at minimal concentrations (mg L^{-1}, µg L^{-1}, ng L^{-1}), these substances are not yet subject to regulatory restrictions. Specifically, organic contaminants are not always regulated under environmental laws, and most are not listed as priority pollutants by the European Union (EU). Furthermore, there are no established permissible concentrations in surface waters to assess their environmental impact [1]. Some of these contaminants have been included in the EU Water Framework Directive's 'watch list' due to their adverse effects on aquatic environments. Despite the lack of official regulations, there is a growing concern about CECs due to their potential long-term effects on ecosystems and living organisms, even at low concentrations (ranging from ng L^{-1} to mg L^{-1}) and with prolonged exposure [13].

As mentioned above, the persistence of these chemical compounds, even at low concentrations, can lead not only to their accumulation in various environmental compartments but also pose a risk to ecosystems. This risk is compounded by a significant lack of understanding regarding their environmental behavior and unknown toxicological effects. These contaminants can result in habitat loss and reduced biodiversity, exert toxic effects on aquatic organisms, and ultimately represent a threat to human health [14,15].

Therefore, one of the primary challenges in managing the L'Albufera environment is overseeing its water system to ensure water quality. This includes detecting organic contaminants in this coastal wetland, which requires the development and optimization of analytical techniques. These techniques are crucial for detecting trace-level compounds, some of which are degradable and transform in the environment. Consequently, comprehensive data collection on their presence within the L'Albufera Natural Park is essential for developing new, effective purification treatments to prevent or minimize their release into the environment. Additionally, certain compounds are emerging as candidates for inclusion in future regulations concerning the reuse of treated water due to their ecotoxicity and presence in various environmental compartments, among other factors. Thus, the advancement and refinement in sample preparation, as well as detection and quantification methods are vital for a better understanding and monitoring of the fate of contaminants in the environment and living organisms.

Based on the aforementioned, the general objective of this doctoral thesis is to determine the presence, fate, and impacts of contaminants in the aquatic environment. It aims to study the spatial distribution of various organic contaminants to establish links with pollution loads from multiple sources, and to determine if there is a correlation between pollution and specific types of land use. Additionally, the thesis seeks to assess the environmental risks posed by organic contaminants in the Natural Park and to evaluate whether the presence of these substances poses a threat to the area's wildlife.

To achieve this general objective, the following specific objectives were established:

1. Development of high-resolution liquid chromatography techniques: this involves the development of techniques necessary for the simultaneous determination and quantification of organic contaminants from various families. Additionally, it includes the evaluation of the effectiveness of non-target methods for identifying contaminants in complex environmental

matrices (water and sediment). This approach aims to provide a comprehensive profile of organic contaminants within the Natural Park, addressing their spatiotemporal distribution and linking them to pollution loads from diverse sources. The application of Geographic Information Systems (GIS) and statistical analysis is fundamental to achieving this goal. Moreover, the environmental risk posed by certain pesticides to aquatic organisms will be assessed by predicting risk through the calculation of the ecological Risk Quotient (RQ).

2. Assessment of contaminant presence and concentrations: this involves evaluating the presence and concentrations of contaminants within the Albufera Natural Park using microporous polyethylene tube passive samplers as a complementary tool to conventional sampling. This approach will enable the assessment of medium-term contamination levels in coastal wetlands, providing additional information through time-weighted averages.

3. Study of contaminant presence and mobility in sediment cores: this goal focuses on examining the presence and mobility of organic contaminants in sediment cores from the lake. It involves establishing connections between sediment age and vertical variations in contaminants, as well as correlating these with sediment characteristics and the historical evolution of the lake. This study intends to explore the potential use of sediments as paleoarchives to provide insights into the origins and development of the Anthropocene.

4. Study of the co-occurrence and distribution of organic micropollutants, including pharmaceuticals, pesticides, personal care products, surfactants, and other industrial organic contaminants, in the surface waters of two river basins in central Chile. This approach enabled the identification and classification of the quantified chemical compounds, the categorization of their modes of action, and the correlation of their presence with different land uses.
The work plan designed for the development of the aforementioned objectives was as follows: Firstly, an extensive literature review was conducted to deepen in the understanding of the environmental situation, with particular emphasis on Mediterranean coastal wetlands, as well as the most recent analytical techniques for determining contamination profiles in specific areas. This review covered sampling methods that differ from conventional approaches, as well as non- target analytical methods. The aim was to provide a comprehensive overview of existing studies and evaluate future research prospects in this field, which will form the foundation of this thesis.

To gain a comprehensive understanding of the diversity of environmental and polar contaminants across various matrices, the use of High-Resolution Mass Spectrometry (HRMS) instruments is recommended. Liquid Chromatography (LC) coupled with HRMS (LC-HRMS) has become increasingly accessible to research laboratories and is now a powerful tool for both targeted and non-targeted analytical methods. Targeted analysis of known compounds is typically performed using a set of reference standards and their labeled analogs for quanti-

fication. In contrast, non- targeted screening employs databases or internal compound lists rather than reference standards to identify and confirm the presence of analytes. This approach relies on mass accuracy, retention time, and structural confirmation through MS/MS experiments.

For this study, 51 sampling sites within the Albufera Natural Park were selected to gain a comprehensive understanding of contamination levels in this natural reserve. This approach provided insights into areas with significant anthropogenic pollution that could impact aquatic environments. Additionally, the sampling period coincided with the start and end of the annual rice cultivation cycle, during which in-situ water samples were collected from major aquatic ecosystems across an extensive area of the park and its watershed. Subsequently, laboratory analyses were conducted on various physicochemical variables and organic contaminants to assess water quality.

GIS and statistical analysis were employed to examine the spatial distribution of contaminants and identify statistically significant differences in contaminant concentrations across different areas, including correlations with physicochemical characteristics. Furthermore, an assessment of the ecological risk posed by the selected organic contaminants to aquatic fauna was conducted using the RQ for surface waters, based on the concentrations found at various trophic levels.

In the experimental development of the thesis, passive samplers were implemented to assess the presence of anthropogenic contaminants in aquatic environments. This approach aligns with the water Framework Directive recommendation to use passive samplers in addition to discrete samples as a complementary method for obtaining information when significant temporal variation or fluctuations in contaminants are anticipated.

Among the available passive samplers, Polar Organic Chemical Integrative Samplers (POCIS) [16,17] are among the most widely used. However, other systems such as porous polyethylene tubes (MTP), Chemcatcher passive samplers [18], and carbon nanotube passive samplers [19] have been employed across various lotic aquatic ecosystems. Despite this, the application of passive samplers for long-term monitoring of contaminants in wetlands has not been extensively explored, although it offers opportunities to better characterize exposure fluctuations and ecological risks. For this study, pesticides, PPCPs, PFASs, and organophosphorus flame (OPFRs) were selected as the primary contaminants of focus. The use of passive samplers MPT facilitated medium-term monitoring of contaminants in wetlands to better characterize exposure fluctuations and ecological risks.

Additionally, to gain a comprehensive understanding of the current ecological status of Mediterranean wetlands, it was necessary to examine pre-existing sources of contamination, especially persistent contaminants that may be retained in sediments and cause toxic impacts if resuspended or remobilized. Some studies aim to establish historical contamination patterns by analyzing sediments from lakes, estuaries, and rivers. However, wetlands have different hydraulic retention times, redox conditions, and ecological dynamics compared to lakes, and contamination patterns can vary significantly from one location to another. Therefore, the simultaneous identification of contaminants in sediment records deposited during the Anthropocene provides an opportunity to identify key impacts or contaminants contributing

to biological change. Additionally, analyzing these sediments (i.e., deep core samples) and conducting statistical analysis of temporal trends can contribute to constructing a paleoarchive of wetland sediments. To this end, two sediment cores were collected from the northern and southern parts of the Albufera Natural Park Lake to assess the presence and vertical distribution of organic contaminants. These cores were segmented into seven sections and subsequently dated using radiocarbon methods.

Furthermore, measurements of the physicochemical characteristics of the sediments were conducted to establish a correlation between contaminant concentration and organic carbon content in each sediment core section.

In addition, given the limited data on the presence of organic micropollutants in freshwater ecosystems in South America, ten surface water samples were collected from the Maipo and Aconcagua River basins in central Chile in October 2021. The aim was to investigate the co-occurrence and spatial distribution of these contaminants.
This doctoral thesis is structured into six sections and includes a total of six scientific publications that encompass all the findings obtained during its development.

Section 1 provides an introduction to the challenges associated with the analysis of organic pollutants in surface water and sediments to establish the contamination profile of a given area. In this section, the most innovative methodologies for the extraction and detection of organic compounds in water and sediment are presented, along with a critical analysis of the analytical challenges involved in their identification and quantification within aquatic ecosystems.

Section 2 presents the general contamination profile of the water and sediments in the L'Albufera Natural Park. This section includes the monitoring of surface waters through point sampling from watercourses linked to rice paddies, citrus groves, and vegetable gardens, as well as from the lake's surface water and the "golas" (channels). The study also evaluates the spatial distribution, mode of action of the detected pesticides, the associated risks of these contaminants, and their environmental fate. The application of these techniques to the L'Albufera Natural Park will enhance understanding of its contamination levels, enabling the development of a sampling and monitoring system that ensures continuous oversight of the park and supports the proposal of mitigation strategies and remedial measures.

Publication I: "Fingerprinting of emerging contaminants in L'Albufera natural park (Valencia, Spain): Implications for wetland ecosystem health".

Publication II: "Data on the profile of organic contaminants in the L'Albufera Natural Park (2019-2020). Target and non-target screening".

Dataset: "Dataset of emerging contaminants in L´Albufera Natural Park (2019-2020) by target and non-target screening using high resolution mass spectrometry" sediment characteristics and risk assessment to the aquatic biota", Mendeley Data, V1, doi: 10.17632/n44rpfms7b.1

Section 3 focuses on the research conducted in the study area of the L'Albufera Natural Park, employing passive samplers as complementary tools to assess the mid-term contamination

status of the coastal wetland.

Publication III: "Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: An environmental risk assessment".

Section 4 comprises two articles and a publicly accessible database (not included in the thesis) in which the simultaneous identification of contaminants in sedimentary records deposited during the Anthropocene was carried out. This was achieved using targeted and non-targeted analyses with LC and HRMS, offering the opportunity to identify key contaminants. The aim is to examine long-term contamination in the Natural Park through sediment dating and the determination of contaminants across different time periods, in order to analyze how these variables have been influenced by the Anthropocene and its impact on the park. This section is organized into two articles.

Publication IV: "Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: Accounting for site/area dependent factors".

Publication V: "Trace elements and legacy and emerging organic contaminants concentrations datasets in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota".
Dataset: "Dataset on trace elements and legacy and emerging organic contaminants concentrations in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota", Mendeley Data, V2, doi: 10.17632/n9p7xkp3vc.2

Section 5 presents a study on the presence of microcontaminants in freshwater ecosystems in South America. This study focuses on evaluating the presence and distribution of organic microcontaminants in the surface waters of two river basins in central Chile. Additionally, it aims to identify and classify the quantified chemical compounds, analyze their modes of action, and correlate their presence with different land uses. The primary goal of the study is to classify the detected chemicals, examine their mechanisms of action, and establish correlations between their presence and the surrounding land use practices.

Publication VI: "Co-occurrence and spatial distribution of organic micropollutants in surface waters of the River Aconcagua and Maipo basins in Central Chile".

Section 6 provides a general summary of the findings from Sections 2, 3, 4, and 5. Finally, the conclusions drawn from all the aforementioned studies are presented, along with an appendix section that includes an index of tables, figures, texts and abbreviations used throughout the thesis.

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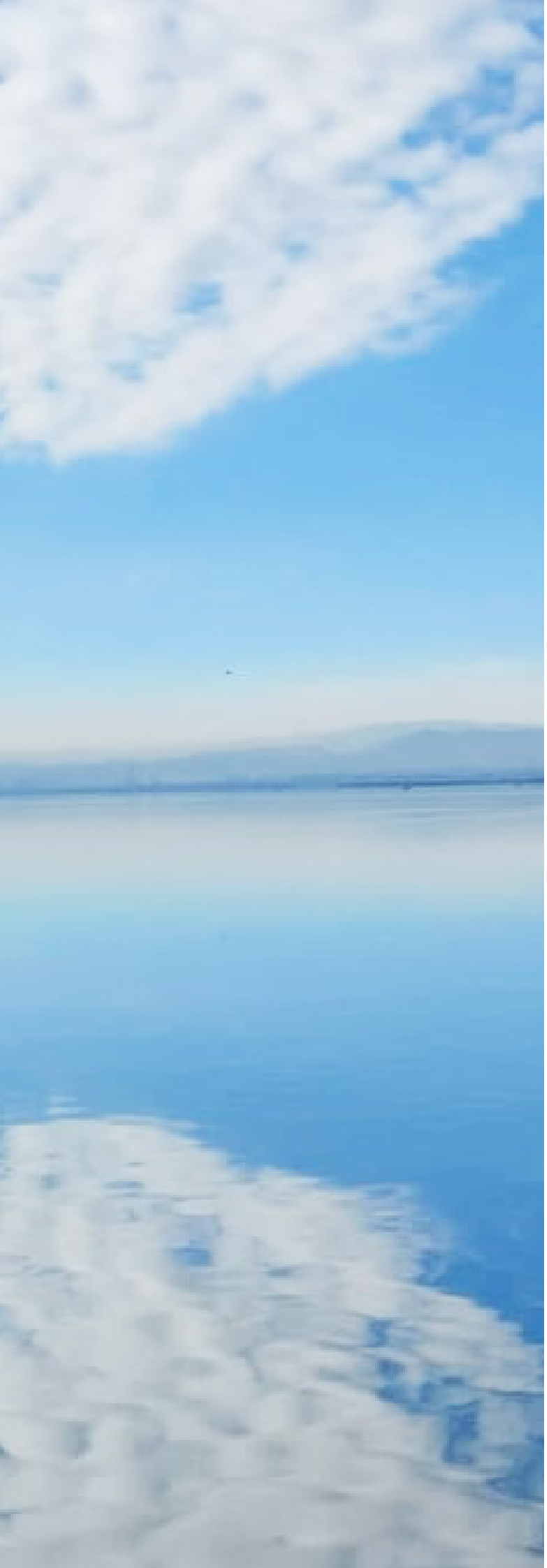
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SECCIÓN 1

Introducción

El crecimiento de la población y el desarrollo de la industrialización están ligados a un período geológico fluctuante conocido como el "Antropoceno", en el que los contaminantes de origen humano interactúan de manera dramática con el cambio climático, afectando a la biodiversidad y al medio ambiente [1,2]. Esto ha llevado a la presencia generalizada de contaminantes de preocupación emergente (Contaminants of Emerging Concern o CECs) en los entornos acuáticos [3]. Estos CECs incluyen principalmente productos farmacéuticos y de cuidado personal (PPCPs) [4,5], sustancias perfluoroalquiladas y polifluoroalquiladas (PFASs) [6–8], retardantes de llama organofosforados (OPFRs) [9,10] y pesticidas [11,12], que se encuentran distribuidos globalmente y ejercen efectos perjudiciales sobre los organismos acuáticos. Además, incluso en concentraciones bajas, estos CECs representan una amenaza significativa para la integridad de los ecosistemas acuáticos [13].

Muchos de estos compuestos, en su mayoría de origen antropogénico, se introducen en el medio acuático a través de las descargas continuas de las plantas de tratamiento de aguas residuales (WWTPs), lixiviados de vertederos y escorrentía agrícola [14–18]. Por lo tanto, los ecosistemas acuáticos cercanos a áreas urbanizadas reciben y retienen cantidades significativas de contaminantes de diversas fuentes, incluyendo descargas directas o indirectas, aportes fluviales y deposición atmosférica. En consecuencia, para comprender de manera integral los impactos de los CECs en los ecosistemas acuáticos, es imprescindible realizar evaluaciones exhaustivas de las concentraciones de estos contaminantes en dichos sistemas.

Dentro de los ecosistemas acuáticos, los humedales destacan como sistemas ecológicos particularmente interesantes debido a su notable biodiversidad y a los diversos servicios ecosistémicos que proporcionan [19]. Estos ecosistemas naturales ofrecen una gran variedad de servicios ambientales, entre ellos, la mitigación de inundaciones, la conservación de la biodiversidad, la purificación del agua y oportunidades recreativas, entre otros. Su importancia ecológica y socioeconómica los convierte en un recurso valioso [20,21]. Se reconocen a nivel mundial como puntos críticos de biodiversidad y proporcionan importantes servicios ecosistémicos que pueden ser clasificados en: I) hidrológicos (protección de aguas subterráneas, control de calidad y contaminación del agua, mitigación de inundaciones); II) bioquímicos (mantenimiento de la calidad del agua y control de la contaminación); III) ecológicos (apoyo a las redes tróficas, hábitats para la reproducción, etapas migratorias y áreas de descanso); IV) físicos (control de sedimentación y erosión); V) económicos (apoyo a la pesca, pastoreo y agricultura); y VI) sociales (valor cultural, contribución al paisaje local y regional, oportunidades recreativas y fines educativos) [22].

La mayoría de los datos sobre contaminantes orgánicos (OCs) en humedales provienen de métodos de muestreo puntual, que ofrecen una imagen instantánea de la distribución espacial de la contaminación. Sin embargo, este enfoque puede resultar inadecuado para detectar la presencia de sustancias específicas o las fluctuaciones en sus concentraciones a lo largo del tiempo [23,24]. En contraste, el muestreo pasivo ha ganado popularidad para el monitoreo espaciotemporal de CECs en el medio acuático [25,26].

En los últimos años, se ha observado la aplicación exitosa de muestreadores pasivos en el monitoreo de aguas superficiales, ya que ofrecen numerosas ventajas sobre las metodologías convencionales, como su capacidad para calcular un promedio ponderado en el tiempo (TWA)

de la concentración de CECs y su costo razonable para campañas de monitoreo a largo plazo. Además, los muestreadores pasivos ofrecen el potencial de evaluar la biodisponibilidad al medir la fracción libremente disuelta, que representa la forma más biodisponible de los contaminantes. En regiones sujetas a influencia de mareas, el muestreo convencional puede enfrentar dificultades debido a las rápidas fluctuaciones en las condiciones de flujo. Asimismo, los límites de detección mejorados que ofrece la tecnología de muestreo pasivo permiten evaluaciones más precisas de las concentraciones en los sitios, especialmente a medida que los estándares regulatorios evolucionan hacia niveles recomendados más bajos para ciertos contaminantes, como los PFAS en el agua potable. Sin embargo, dado que las regulaciones existentes se basan en métodos de muestreo convencionales, el muestreo pasivo debe considerarse como complementario en lugar de un reemplazo para los enfoques tradicionales [27–29].

Además, la introducción del término "Antropoceno" ha estimulado la investigación sobre la contaminación a largo plazo, considerando que los núcleos de sedimentos pueden funcionar como archivos históricos [30–32]. Por esta razón, y para comprender la condición ecológica actual de los humedales mediterráneos, es imprescindible examinar las fuentes históricas de contaminación, en particular los contaminantes persistentes que pueden estar retenidos en los sedimentos y que podrían generar efectos tóxicos si se movilizan bajo diversas circunstancias. Por ello, los archivos sedimentarios han sido considerados para reconstruir la contaminación histórica en ecosistemas acuáticos por contaminantes orgánicos hidrofóbicos, hidrofílicos y persistentes [33].

Sin embargo, una vez obtenida la distribución vertical de contaminantes, interpretar los patrones puede representar un desafío. Por lo tanto, en sitios carentes de programas de monitoreo a largo plazo, el examen de núcleos de sedimentos datados presenta oportunidades para abordar lagunas en los registros históricos de contaminación mediante la estimación de tendencias temporales de los contaminantes retenidos en ellos [30]. Estudios recientes han empleado núcleos de sedimentos para evaluar tendencias temporales a largo plazo de contaminantes tanto tradicionales como emergentes [34–36].

En los últimos años, la evolución de la espectrometría de masas de alta resolución (HRMS, por sus siglas en inglés) acoplada a cromatografía de gases o líquidos (GC o LC, respectivamente) ha abierto una ventana para detectar cientos de compuestos inesperados o desconocidos en el medio ambiente, ofreciendo un perfil de contaminación más integral [37]. Este tipo de análisis no dirigido (Non Target Analysis o NTA) es complejo y lleva tiempo, pero actualmente se considera una de las estrategias más prometedoras para avanzar en el conocimiento sobre los niveles de contaminación ambiental. Esta técnica es ampliamente reconocida como una herramienta poderosa para el cribado de diversas familias de contaminantes en ambientes acuáticos, abarcando estrategias de cribado tanto dirigidas como no dirigidas [38]. Estas metodologías han demostrado su eficacia como instrumentos prometedores para mejorar nuestra comprensión de los perfiles de compuestos emergentes, como productos de transformación (TPs), metabolitos, sustancias desconocidas o aquellas omitidas en los esfuerzos de monitoreo rutinarios que pueden estar presentes en los sistemas ambientales [39]. Hasta la fecha, los estudios que utilizan HRMS han experimentado una creciente aplicación en la identificación de diversos compuestos químicos orgánicos en el medio ambiente [40–42].

En resumen, la complejidad de los humedales, la variabilidad de los contaminantes orgánicos, las limitaciones en las técnicas de análisis y cuantificación, la falta de datos de referencia disponibles y los impactos de las actividades antropogénicas representan los principales desafíos en el estudio de los CECs,

Por esta razón, este trabajo ofrece un resumen integral de los datos existentes sobre los niveles actuales de los CECs estudiados y documentados en los ecosistemas acuáticos. Asimismo, incide en que los avances en las metodologías analíticas facilitarán la ampliación de nuestra información y comprensión sobre los ecosistemas acuáticos, con un enfoque particular en los humedales, reconocidos por sus importantes contribuciones a los servicios ecosistémicos.

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SECCIÓN 2

Perfil general de contaminación en el Parque Natural de L'Albufera: análisis de agua y sedimento

ARTICLE 01

Fingerprinting of emerging contaminants in L'albufera natural park (Valencia, Spain): implications for wetland ecosistem health

Chemosphere 364 (2024) 143199

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Fingerprinting of emerging contaminants in L'Albufera natural park (Valencia, Spain): Implications for wetland ecosystem health

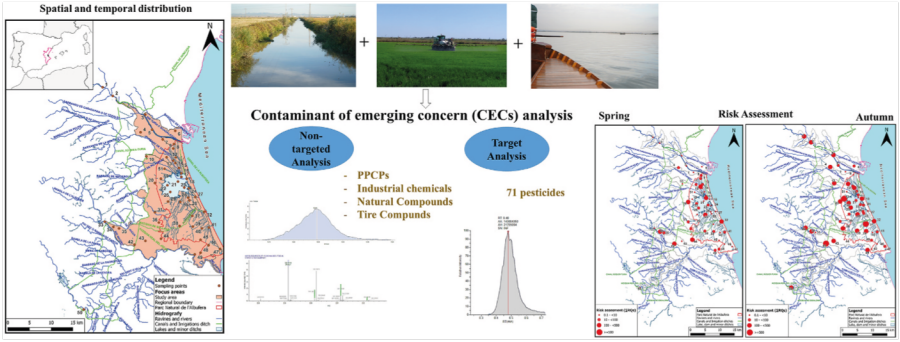
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HIGHLIGHTS

- L'Albufera Natural Park is polluted by more than 159 synthetic organic substances.
- Fungicides are the key pollutants in water and sediments both by target analysis and NTS.
- Pharmaceuticals in water and industrial products in sediments are the other major pollutants by NTS.
- Assessment only of target compounds showed important ecological risk.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Magali Houde

Keywords:
Non-target screening (NTS)
Sediments and surface water pollution
Spatial distribution
Ecological risk assessment
Mode of action (MoA)

ABSTRACT

Wetlands are crucial ecosystems that are increasingly threatened by anthropogenic activities. L'Albufera Natural Park, the second-largest coastal wetland in Spain, faces significant pressures from surrounding agricultural lands, industrial activities, human settlements, and associated infrastructures, including treated wastewater inputs. This study aimed at (i) establishing pathways of emerging pollutants entering the natural wetland using both target and non-target screening (NTS) for management purposes, (ii) distinguishing specific contamination hotspots through Geographic Information System (GIS) and (iii) performing basic ecological risk assessment to evaluate ecosystem health. Two sampling campaigns were conducted in the spring and summer of 2019, coinciding with the start and end of the rice cultivation season, the region's primary agricultural activity. Each campaign involved the collection of 51 samples. High-resolution mass spectrometry (HRMS) was employed, using a simultaneous NTS approach with optimized gradients for pesticides and moderately polar compounds, along with complementary NTS methods for polar compounds, to identify additional contaminants of emerging concern (CECs). Quantitative analysis revealed that fungicides comprised a substantial portion of detected CECs, constituting approximately 50% of the total quantified pesticides. Tebuconazole emerged as the predominant fungicide, with the highest mean concentration (>16.9 μg L^{-1}), followed by azoxystrobin and tricyclazole. NTS tentatively identified 16 pesticides, 43 pharmaceuticals and personal care products (PPCPs), 24 industrial compounds, and 12 other CECs with high confidence levels. Spatial distribution analysis demonstrated significant contamination predominantly in the southwestern region of the park, gradually diminishing towards the

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https://doi.org/10.1016/j.chemosphere.2024.143199
Received 10 April 2024; Received in revised form 17 August 2024; Accepted 26 August 2024
Available online 28 August 2024
0045-6535/© 2024 Published by Elsevier Ltd.

north-eastern outlet. The composition of contaminants varied between water and sediment samples, with pharmaceuticals predominating in water and industrial compounds in sediments. Risk assessment, evaluated through risk quotient calculations based on parent compound concentrations, revealed a decreasing trend towards the outlet, suggesting wetland degradation capacity. However, significant risk levels persist throughout much of the Natural Park, highlighting the urgent need for mitigation measures to safeguard the integrity of this vital ecosystem.

1. Introduction

The increasing worldwide release of contaminants of emerging concern (CECs) of anthropogenic origin into aquatic ecosystems is causing serious contamination problems in groundwater and surface water resources (Petrie et al., 2015). These chemicals have been associated with adverse biological effects, even at low concentrations, despite many being unregulated (Tian et al., 2021b). Detecting CECs in environmental matrices is a key challenge for environmental analysts (Pena-Pereira et al., 2021; Fisher et al., 2022). Many CECs can be found in a variety of environmental matrices, including water (Tian et al., 2020; Soriano et al., 2023; Wu et al., 2023), soil (Tian et al., 2017; Chiaia-Hernández et al., 2020; da Silva et al., 2021), sediment (Li et al., 2022; Carr et al., 2023; Chen et al., 2024), and aerosols (Ouyang et al., 2017). These compounds include pesticides, perfluoroalkyl substances (PFASs), organophosphorus flame retardants (OPFRs), pharmaceuticals and personal care products (PPCPs), and so on, which are being increasingly detected in surface water along with other regulated anthropogenic chemicals. It is important to screen and assess these CECs in the aquatic ecosystems to guarantee water quality. However, it is currently impossible to achieve this using only traditional target analysis methods. These methods select certain compounds, leaving thousands of others that have not been preselected will be undetectable. The absence of an available reference standard chemical is one of the obstacles to comprehensive target screening (e.g., transformation products, unknown chemicals). Target analysis introduces bias into the results, choosing only specific pollutants and hindering the establishment of an accurate pollution profile. Over the last decade, with the development of high-resolution mass spectrometry (HRMS), non-target screening (NTS) has demonstrated its efficacy in assessing CECs as a versatile instrument for simultaneous analysis of multiple contaminant classes and identification of new and emerging contaminants (Chiaia-Hernández et al., 2017; Tian et al., 2020; Fisher et al., 2022). This approach provides a more comprehensive understanding of contaminant profiles, particularly in urban waters (Du et al., 2020), surface water (Albergamo et al., 2019), wastewater (Gosset et al., 2021; Wiest et al., 2021) and reclaimed water (Kolkman et al., 2021; Martínez-Piernas et al., 2021). As a complementary method to target screening, the NTS approach can increase the quantity of chemical substances requiring attention (Liu et al., 2024). The use of HRMS allows for the precise acquisition of precursor and product ions concurrently in a single injection, which assists with molecular structure elucidation to identify thousands of analytes (Feng et al., 2022). One of the strengths of the NTS is its ability to qualitatively identify unexpected or unknown substances without requiring a reference standard chemical. These methodologies have demonstrated their potential as effective tools for enhancing our understanding of profiles associated with CECs, including transformation products (TPs), metabolites, unknown substances, or those not included in the routine monitoring work, which may be present in environmental systems (Wang et al., 2020). Among the various aquatic ecosystems, wetlands have been among the least studied using NTS, despite their significant capacity to degrade organic pollutants and purify water.

While some studies focus on NTS just to establish the capacity to transform chemical contaminants in artificial wetlands (Maurer et al., 2020; Tadić et al., 2024), those devoted to natural ones are scarce (Kang et al., 2020, 2023). Kang et al. (2020) studied the biodegradability potential of pesticides in Upo Wetland, Korea, an area surrounded by agricultural lands, using NTS methods. The results showed that fungicides were the predominant CECs detected in the wetland. NTS identified 48 transformation products (TPs), providing new insights into the degradation pathways of CECs. The authors concluded that natural wetlands could function as eco-friendly reactors, degrading CECs and transforming pesticides into less harmful, lower-risk compounds (TPs). Later, Kang et al. (2023) compared pesticide transformations between simulated river and wetland systems identified 97 TPs for 15 pesticides, and showed the higher capacity of wetlands to degrade contaminants. However, despite agriculture being a primary impact on most wetlands, it is not the only influence, and no study has yet provided a comprehensive profile of the main CECs, including TPs, in these ecosystems.

Therefore, our study has aimed to apply a combination of target and NTS of the most intense ions detected in a natural wetland to establish the contamination profile of these aquatic ecosystems including expected and unexpected contaminants and their TPs. The selected case study was L'Albufera Natural Park (Valencia, Eastern Spain), a characteristic Mediterranean wetland significantly affected by both climate change and anthropogenic pressures. Coastal wetlands rank among the world's most valuable ecosystems, primarily attributable to the array of ecosystem services they provide (Ricaurte et al., 2017). These services include providing habitat for invertebrates, shorebirds, and mammals, as well as offering cultural and recreational opportunities (Estrela-Segrelles et al., 2021). Additionally, coastal wetlands contribute to carbon sequestration, helping to mitigate climate change effects (Calder et al., 2019; Morant et al., 2020; Saintilan et al., 2019). Despite their value, coastal wetlands are particularly vulnerable and can be considered ecosystems under significant threat from various anthropogenic activities. Agriculture has exerted the most detrimental influence on L'Albufera, primarily attributed to the substantial expansion of rice cultivation and production during the 18th century, resulting in the loss of 83% of the lagoon's surface area (Onandia et al., 2015). Consequently, pesticides have become a primary contributor to the accelerated pollution of aquatic ecosystems, exacerbating eutrophication through excessive nutrient inputs.

One advantage of this wetland is that it has already been widely studied and there is previous information. Several studies have already established the presence of different CECs within the aquatic ecosystems of specific regions within L'Albufera Natural Park, employing targeted methodologies (Pico et al., 2012; Calvo et al., 2021; Sadutto et al., 2021; Soriano et al., 2023). However, these studies collectively provided only a partial view of a relatively low number of pre-selected pollutants, sampled from a limited number of points mostly located in the northern part of the Park. The findings highlighted the significance of pesticides in the area and served as a basis for the experimental design of this study. Nevertheless, they offer only a partial profile of the pollutants present, lacking information on the other unexpected main substances and the distribution of pollution throughout the Natural Park. This study provides 51 sampling points that cover practically the entire Natural Park, trying to establish correlations between CEC concentrations and land uses. To achieve this overarching goal, the following specific objectives were established: (i) to identify the pathways through which CECs enter the natural wetland, using targeted analysis of pesticides and NTS to establish the profile of main contaminants and their temporal variations for management purposes; (ii) to determine the spatial distribution of CECs using geographical information systems (GIS) and statistical analyses to identify contaminants hotspots; and (iii) to

conduct both individual and cumulative risk assessments based on the CECs' action modes to establish the ecosystem health. To our knowledge, this is the first study of NTS in L'Albufera wetland, which would provide insights into future environmental monitoring strategies for the risk assessment of chemicals.

2. Materials and methods

2.1. Reagents and chemicals

Seventy-one reference standards for the target pesticides analyzed quantitatively were purchased from Sigma-Aldrich (Madrid, Spain) with purity >98 % (Supplementary material, Table S1). These target pesticides were selected because they are highly used in rice fields and the use of some of them has been previously reported in the Natural Park. Additionally, two isotope-labeled internal standards (chlorpyrifos-d_{10} and chlorfenvinphos-d_{10}) were obtained from Sigma-Aldrich. Water, methanol, formic acid, ammonium formate, and ammonium fluoride were all UHPLC-MS grade purchased from Fisher Chemicals (Denmark). All extraction reagents and chemicals, unless stated differently, were of analytical grade. Further details on other reagents and chemicals can be found in Text S1.

2.2. Study area and sampling

L'Albufera Natural Park, located on the Mediterranean coast south of Valencia city, is renowned for its stunning biodiversity. Stretching across approximately 21,120 ha, this park encompasses a mosaic of ecosystems, including freshwater lagoons, marshlands, dunes, and rice paddies. Agriculture exerts the most significant pressure on L'Albufera Natural Park. To give an idea, L'Albufera of Valencia is a shallow coastal lagoon with an average depth of 1 m. It covers an area of 23.94 km^2 and is surrounded by 223 km^2 of rice fields. Rice cultivation has been practiced in the region for centuries and is the dominant activity. Additionally, a significant portion of the land in the basins discharging water to the natural park is dedicated to horticultural and fruit cultivation (mostly orange orchards and vineyards). Primarily found in the park's interior, these agricultural areas are also extended across a substantial portion of the sandy barrier separating the marsh from the sea on the southern side (see Fig. 1A for land uses). The area has a network of channels and ditches that facilitate the irrigation of the cultivars. The Park also supports local fishing, the industrial belt surrounding Valencia, and several towns and villages (see Fig. 1B for soil sealing and irrigation channels). Sampling dates were selected according to the representative months of the rice cultivation period since it is the prevalent activity in the area: at the beginning of the cultivation (May–June) and during harvest (September-early October). Notably, no rain or storms affected the sampling area at least two weeks before the two campaigns.

Pesticide application in rice cultivation is aligned with the crop's biological cycle. Rice planting usually occurs between May and June, with small temporal deviations depending on weather conditions and individual farmer practices. The cultivation process begins with the application of herbicides, such as bensulfuron methyl, molinate, and bentazone, to control weed growth. The initial herbicide application generally occurs five to six weeks after sowing, necessitating a water

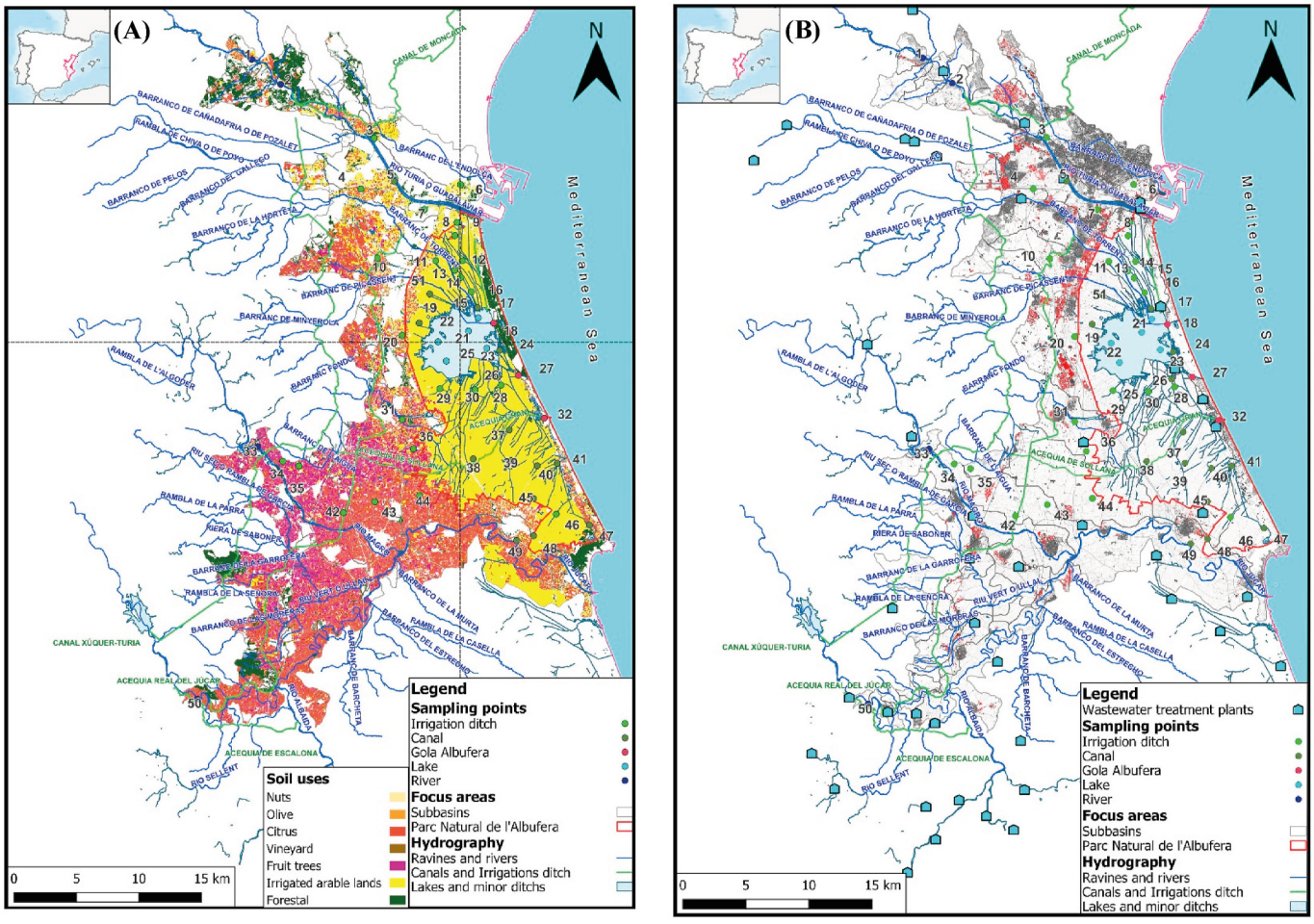


Fig. 1. Map of the sampling points: (A) agricultural land uses and hydrography and (B) soil sealing and hydrography.

level flooding of 2–3 cm in the fields. The first sampling period corresponds to these applications.

Subsequently, fungicides are applied, sometimes even by helicopter, while the fields remain flooded. The application of pesticides, especially fungicides is more prevalent during July to September. Fungicides are applied only once rice plants have reached a certain growth stage to mitigate or prevent the proliferation of pests, especially Pyricularia. In addition, certain fungicides usually represent the last biocidal agents used before harvest. Insecticides and fungicides are administered as a preventive or palliative measure, allowing for a treatment period covering the entire crop cycle that can extend from April to September. The second sampling period selected was September, just before harvesting the rice.

Sampling locations were selected after a geospatial analysis, considering factors such as water sources, land use patterns, human activities, and the influence of wastewater treatment plants, and the Turia and Jucar Rivers (the boundaries of the study area), to delineate the area into landscape functional sectors. Subsequently, a random sampling design was implemented to ensure comprehensive coverage of influences and potential sources affecting the area (See Fig. 1A and **B** for sampling locations and influences). According to this random design samples proceed from 51 sampling points distributed in both rivers (4, points 1,2, 49, 50), irrigation channels (39), Albufera Lake (5, points 17, 21–23, 25), and outlets to the Mediterranean Sea (3, points 18, 27, 32). The 39 irrigation channels were influenced by the following land uses: citrus orchards (12), horticultural cultivations (6), and rice fields (21). The spatial location of the points considering the four transects that divide the Park from the center of the lake (see Fig. 1A) are: Northwest (points 1–5, 7–8, 10–11, 13–15, 19–22 and 51), Northeast (points 29, 31, 33–36, 42–44 and 50), Southwest (23, 24, 26–28, 30, 32, 37–41) and Southeast (45, 46, 48–49). Grab water samples were collected during both sampling periods, while sediment samples were collected only during the first period due to the more stable contamination profile of sediments. One hundred and thirty samples, 100 of water, and 30 of sediment were taken. At each sampling point, 1 L of grab surface water samples were collected in amber polyethylene terephthalate bottles from the middle of the water column. Sediment samples, taken from the top 10 cm, were collected using a Van Veen grab sampler with a 0.5 L capacity. Both water and sediment samples were transported to the laboratory in a portable refrigerator at 4 °C and stored at −20 °C until analysis.

Sediment samples were freeze-dried (-65 °C; with a vacuum between 1 and 4 mTorr) for 72 h using a Sentry 2.0 lyophilizer from VirTis SP Scientific manufacturer (Gardiner, NY, USA). Lyophilized samples were stored at −20 °C. Then, the freeze-dried sediments were sieved to collect the finest fraction (<125 μm). Sediment samples were lyophilized using a Sentry 2.0 lyophilizer from VirTis SP Scientific manufacturer (Gardiner, NY, USA).

Also, the following water quality parameters were measured in situ: pH, temperature (T, °C), oxidation-reduction potential (ORP, mV), conductivity (CE, dS m^{-1}), Total Dissolved Solids (TDS, mg L^{-1}), NaCl (mg L^{-1}), Resistivity (Ω) and dissolved oxygen (DO, % and mg L^{-1}). These values were obtained using a portable multiparametric meter (model HI9829, HANNA Instruments).

2.3. Sample treatment and extraction. Grab water extraction and sediment extraction

First, grab water samples were thawed for 24 h at room temperature in darkness, followed by filtration of 250 mL using a 0.45 μm glass fiber filter under vacuum (Advantec MFS, Dublin, CA, USA). Then, 50 μL of isotopically labeled internal standards mixed at a concentration of 1 μg mL^{-1} was spiked into each sample. The samples were extracted using the method previously reported by Carmona et al. (2017) that involves Solid Phase Extraction (SPE) using Strata-X Cartridges (Phenomenex Strata-X-33 μm Polymeric Reversed Phase (200 mg/6 mL)) (See internal standards combination in footnote to Table S1).

Concerning sediment extraction, the samples were extracted using the citrate buffered Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method previously reported by Masiá et al. (2015) for moderately polar compounds, such as pesticides. While polar compounds were extracted using the method previously reported by Carmona et al. (2017) that involves solid-liquid extraction (SLE) with a McIlvaine-ethylenediaminetetraacetic acid (EDTA) buffer followed by solid phase extraction (SPE).

2.4. LC-MS/MS analysis

Target and non-target analyses were conducted to investigate pesticides and other compounds in the grab water and sediment samples. Target and NTS of contaminants were performed using reversed-phase liquid-chromatography (LC) separation employing a Vanquish Flex UHPLC consisting of a binary pump, a split sampler, and a column compartment and HRMS using Thermo Scientific™ Orbitrap Exploris™ 120 high-resolution mass spectrometer equipped with a heated electrospray ionization (HESI) source.

Three injections were conducted for each sample:

- The first injection utilized a gradient for moderately polar compounds. The MS analysis was operated under the positive ion and in full MS followed by Data Dependent Acquisition (DDA) of MS^2 mode. The full MS scan was performed with 60 000 FWHM resolution and narrow mass windows at 5 ppm and MS^2 scan with resolution at 15 000 FWHM. The DDA performs priority targeted analysis against a list of 71 pesticides, and, if no signal of the positive list was detected, secondary, it performs NTS considering peak intensity as the dependent parameter for the four most intense ions.
- The second injection involved a gradient optimized for polar compounds in positive ionization mode, conducting full MS followed DDA of the MS^2 of the four most intense ions with the same resolution as in the previous one.
- The third injection used a gradient optimized for negative ionization of polar compounds, followed by DDA of the MS2 for the four most intense ions at the same resolution as the previous injection.

Further information on instrument parameters is described in the supplementary material, Text S2. Targeted compounds were manually analyzed using the vendor software TraceFinder (version 4.1, Thermo Scientific). NTS results were evaluated using Compound Discoverer 3.2 (Thermo Fisher Scientific, Software for HRMS data treatment) implementing the workflow for environmental samples, and using mzCloud (On-line) as MS-library. The selected workflow was "Environmental w Stats Unknown ID w Online and Local Database Searches" which involves performing mzCloud and ChemSpider searches to identify unknown compounds. The results were analyzed and identified using peak picking and integration, retention time alignment, unknown compound detection, isotope and adduct peak grouping, unknown compound grouping, blank subtraction (excluding any sample/blank ration <5), and database searching filtering *m/z* cloud matches with scores <80. After these initial steps, MS/MS matches were manually reviewed to eliminate compounds only with parent ion fragment features, ensuring accurate matches to the library with the MS/MS spectrum.

2.5. Ecological risk assessment

The ecological risks associated with the 43 and 59 pesticides detected by target analysis in surface water and in sediments, respectively, were assessed using the Risk Quotient (RQ_i) according to Eq. (1) (Anagnostopoulpou et al., 2022; Wei et al., 2022). The RQ_i of each pesticide was calculated using the following equation:

$$RQ_i = \frac{MEC_i}{PNEC_i} \quad (1)$$

Where MEC is the measured environment concentration of each pesticide in surface water samples (ng L^{-1}) or in sediment samples (ng g^{-1}), and PNEC is the Lowest Predicted No Effect Concentrations (ng L^{-1} or ng g^{-1}). In this study, the average concentration and the maximum concentration measured for each pesticide in surface water were used as MEC_i to assess the general risk and to evaluate the worst-case scenario, respectively. $PNEC_i$ values were extracted from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php) and corresponded to the lowest value predicted by QSAR models or obtained experimentally. The results were evaluated based on the following criteria:

- $RQ_i > 1$ high ecological risk, necessitating appropriate risk reduction measures (Wei et al., 2022).
- $0.1 \leq RQ_i \leq 1$ medium ecological risk, signifying the need for further monitoring of the sources of risk.
- $RQ_i < 0.1$ low ecological risk, the exposure to that chemical is unlikely to produce adverse effects.

Furthermore, previous studies based on no synergistic or antagonistic risks for pesticides (Barbieri et al., 2021), suggested that the combined effects of total pesticide risk (RQ_{Total}) in water samples can be calculated by the sum of their individual RQ_i (Ma et al., 2016; Zheng et al., 2016) to have a complete view of water pollution by pesticides in the area and the associated ecotoxicological risk, applying an additive model. The calculation is made by adding the individual RQ values (RQ_i) of the compounds found in a specific sample or with the same mode of action. The RQ_{Total} was calculated using the following equation:

$$RQ_{Total} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i} \quad (2)$$

This additive model allows the assessment of ecotoxicological risk derived from the co-occurrence of various pesticides in a specific location with some limitations, as it does not consider unpredictable synergistic or antagonistic effects (Barbieri et al., 2021).

2.6. Quality assurance/quality control

Procedural blanks for every batch of samples (without sample, while other experimental steps from extraction to instrumental analysis were like those of the other samples) were prepared to check for possible contamination from reagents, tubes, or equipment. Background contamination values was subtracted from concentrations found in blanks. Analytical blanks, consisting of methanol, and control samples, which were fortified with known concentration of target compounds, were analyzed every 10 injections to ensure accuracy. Precautions were implemented to mitigate potential contamination from personnel, organic solvents, equipment, and glassware. All glass laboratory materials were meticulously cleaned using HPLC-grade water and methanol. blank samples were prepared for the target and non-target analysis. For non-target analysis, solvent and procedural blanks were analyzed between samples to ensure instrument stability. The Limit of Detection (LOD) of the analytical method for pesticides was calculated based on a signal-to-noise ratio of 3 (S/N = 3), and the Limits of Quantification (LOQ) was defined as 3 × LOD. Calibration curves in the linear response range with good correlation ($r^2 \geq 0.991$) were achieved. The LOD of the pesticides ranged from 0.05 to 1 ng L^{-1} and from 0.1 to 1 ng g^{-1} in water and sediment samples already stated in previous publications (Carmona et al., 2017; Lorenzo et al., 2019; Masiá et al., 2015). If the measured concentrations in the samples were "non detects", the values were set as LOD/2.

2.7. Statistical analysis

Statistical methods were used to confirm relationships between compounds and environmental factors. For this purpose, the statistical package IBM SPSS version 29 was used. To find the possible differences between (i) sampling periods, (ii) type of water and (iii) land uses and concentration of pesticides and values of physicochemical parameters analysis of variance (ANOVA) and Tukey's multiple range test ($\alpha = 0.05$) were used. Significant differences were not underestimated due to the substitution of not detected by the LOD/2 because LODs are very low, and pesticides are quite frequent in the samples. Then, the added value is irrelevant. Pearson's bivariate correlation analyses were performed at 95% and 99% significance levels to correlate the compounds with the physicochemical parameters of water. Spearman's Rho was used for variables with non-normal data distribution. To confirm the weight and dependence of the observed interactions between pesticide concentration and water physicochemical parameters multiple stepwise linear regression analysis, discriminant analysis, and categorical PCA were utilized.

2.8. GIS

The data used to generate GIS layers came from official sources and fieldwork. They were integrated using QGIS 3.28, projected according to official standards (ETRS-1989 reference system). The first step was to obtain the sub-basins that discharged water into L'Albufera Lake. To achieve this, the sub-basin layer was downloaded from the Confederación Hidrográfica del Júcar (https://aps.chj.es/down/SHP/F851_Subcuencas_1_25000_DGA_CEDEX.zip), which delimited the study area.

The hydrography layer (https://aps.chj.es/down/SHP/F850_Rios_1_25000_DGA_CEDEX.zip), was obtained from the same source and complemented with the hydrography extracted from the Cartografía Oficial de la Comunitat Valenciana, scale 1:5000, encompassing the irrigation channels and L'Albufera lake (https://geocataleg.gva.es/#/search?uuid=spaicvBcv05Serie2015&lang=spa).

The boundaries of L'Albufera Natural Park were downloaded from the RAMSAR layer (https://www.mapama.gob.es/app/descargas/descargafichero.aspx?f=humedalesramsar.zip), provided by the Spanish Ministry for Ecological Transition and Demographic Challenge (MITECO). For land uses and soil sealing, the layer provided by the Instituto Cartográfico Valenciano called Cartography of Land Use in the Valencian Community (COSCV) was used (https://geocataleg.gva.es/#/search?uuid=spaicv0403_COSCV&lang=spa). This layer facilitated the categorization of agricultural and forestry uses based on the original categories provided. For soil sealing, a distinction was made between total sealing and agroindustrial buildings. Finally, graphical representations of the data obtained in this study were developed to ensure clear and accurate visualization of the information.

3. Results and discussion

3.1. Occurrence of contaminants in L'Albufera natural park

3.1.1. Target analysis

The minimum, maximum, and mean concentrations, along with the detection frequency of the target pesticides in the surface water of L'Albufera Natural Park are shown in Table 1. Over half of the target pesticides (43 out of 71) were detected in the surface waters of L'Albufera Natural Park. The pattern of pesticides reflects the land uses reported in Fig. 1A, mostly dominated by rice fields (del Barrio Fernández et al., 2012; Jorge-García et al., 2023; Martín et al., 2020; Saccò et al., 2020) and to a lesser extent the surrounding citrus orchards. Agricultural practices in this region vary year to year because they must be adapted to the climate conditions and pesticide concentrations depend on their application and degradation rates. It should be considered that herbicides are commonly less persistent than fungicides. Rice cultivation

Table 1
Minimum, maximum, and mean concentration in ng L^{-1} of the detected individual pesticides and frequency of detection in the investigated surface water samples.

Pesticide	Concentration ng L^{-1}							
	Spring (May–June)				Autumn (September–October)			
	Min	Max	Mean[a]	Frequency[b]	Min	Max	Mean[a]	Frequency[b]
Acetamiprid	0.05	275.14	21.40	88	0.05	288.30	30.91	82
Atrazine[c]	0.05	15.04	1.45	67	0.05	5.61	1.26	67
Atrazine-desethyl	0.15	22.56	3.30	47	0.15	24.78	3.95	49
Atrazine-desisopropyl	0.15	14.34	2.43	37	0.15	9.41	1.29	22
Azoxystrobin	0.05	557.89	131.49	96	0.60	5064.40	668.95	100
Bensulfuron methyl	0.25	62.53	3.35	18	0.25	44.48	4.44	29
Buprofezin	0.05	1.23	0.10	4	0.05	10.18	0.26	4
Carbendazim[c]	0.10	37.32	7.34	92	0.10	11.38	2.92	57
Carbofuran	0.20	1.54	0.25	4	0.20	6.06	0.39	4
Chlorfenvinphos[c]	0.05	405.08	38.91	20	0.05	389.65	165.89	61
Chlorpyriphos	0.10	152.27	17.84	39	0.10	143.74	48.84	73
Clothianidin	–	–	–		0.75	243.23	5.70	2
Diazinon[c]	0.03	8.17	0.48	29	0.03	48.85	1.65	37
Difenoconazole	0.08	252.17	7.97	37	0.08	107.70	12.78	59
Dimethoate	0.10	110.26	5.55	47	0.10	1.25	0.14	4
Diuron	0.03	27.36	4.13	86	0.03	40.70	4.38	84
DMPF	0.03	2.10	0.13	10	0.03	3.46	0.31	22
Fenthion sulfoxide	0.05	1.30	0.11	10	0.05	6.20	0.22	8
Fluvalinate	0.25	183.81	7.44	14	0.25	3617.56	93.82	10
Hexythiazox	0.13	2.68	0.26	8	0.13	44.80	1.21	6
Imazalil	0.06	388.98	29.01	22	0.06	292.23	85.97	96
Imazamox	0.05	5.31	0.22	12	0.05	4.12	0.19	6
Imidacloprid	0.25	183.81	7.23	25	0.25	17106.90	387.59	90
Isoproturon[c]	0.05	1.28	0.10	8	0.05	4.24	0.52	33
Malathion	–	–	–		0.10	52.46	3.28	12
Metoalachlor[c]	0.05	37.62	1.26	27	0.05	3.26	0.17	6
Molinate[c]	0.25	30.73	2.50	20	–	–	–	
Omethoate	0.25	395.84	12.55	8	0.25	399.44	32.70	12
Prochloraz	0.05	26.82	2.65	55	0.05	86.55	14.33	59
Propanil[c]	–	–	–		0.50	294.48	13.60	10
Propazine	0.13	322.24	6.80	16	0.13	337.54	141.90	73
Pyriproxyfen	0.05	41.60	1.43	20	0.05	10.28	0.34	8
Simazine[c]	0.13	59.59	1.93	18	0.13	11.45	2.31	55
Tebuconazole	0.10	1112.04	175.92	92	0.10	16935.31	1104.15	98
Terbumeton	0.05	31.85	1.92	59	0.05	20.53	1.82	57
Terbumeton-desethyl	0.05	186.64	30.93	90	0.05	207.20	37.00	96
Terbuthylazine	0.05	360.70	48.18	75	0.05	339.08	142.95	88
Terbuthylazine-2-hydroxy	0.88	67.09	16.08	86	0.13	420.24	18.98	94
Terbuthylazine desethyl	0.15	49.28	1.75	18	0.15	11.45	2.41	57
Terbutryn[c]	0.20	71.51	22.96	78	0.20	52.37	17.71	80
Thiabendazole	0.05	1182.26	61.52	88	0.05	389.32	33.00	96
Thiamethoxam	0.50	26.15	1.00	2	0.50	6032.80	127.21	6
Tricyclazol	0.05	199.34	21.10	80	0.05	182.34	24.54	90

DMPF (N'-(2,4- Dimethylphenyl)-N-methylformamidine).
In italics, pesticide detected only in water samples.
[a] Mean calculated considering values nd as LOD/2.
[b] not including compounds with values nd. Detection frequencies (expressed in %). 51 and 49 sampling points considered in spring and autumn respectively to calculate detection frequency.
[c] Compounds currently prohibited for their use in Europe. The exceptional use of propanil is annually allowed in Spain.

in L'Albufera of Valencia starts with the treatment with herbicides to ensure proper rice growth, followed by fungicides to avoid several infections, as mentioned in the experimental section. However, the interval between these treatments has been progressively shortening each year. Additionally, water containing pesticides from various treatments remains stagnant in rice fields until it is drained. During draining, pesticide-laden water primarily flows into the canals and arrives at the lake. Additionally, there may be contamination from spray and plane drift, but the drainage from the rice fields is an important source. In spring pesticide concentrations are lower than in autumn. However, some pesticides, such as acetamiprid, diuron, prochloraz, terbumeton (mostly as terbumeton desethyl), tebutryn and tricyclazole, were detected at low concentrations across a high number of samples, with similar average concentrations observed in both spring and autumn. Relevant pesticides were considered those with average concentrations >50 ng L^{-1} and a frequency >50 % of the samples. In spring, the most relevant pesticides were azoxystrobin (average concentration 131.49 ng L^{-1} in 90 % of the samples), tebuconazole (average concentration 175.92 ng L^{-1} in 92 % of the samples), and thiabendazole (61.56 ng L^{-1} in 88 % of the samples). Tebuconazole and azoxystrobin are related to rice cultivation whereas thiabendazole is mostly used in citrus. This could indicate the influence of citrus cultivation on the pesticide profile in spring when rice cultivation starts in the park. Furthermore, carbendazim was detected in spring at apparently higher concentration and frequency than in autumn (even though the statistical analysis did not provide statistically significant differences) and molinate was found only in spring. In autumn, the main detected pesticides were clofenvinphos (average concentration 165 ng L^{-1} in 61% of the samples), imazalil (average concentration 85.97 ng L^{-1} in 96% of the samples), propazine (average concentration 141.9 ng L^{-1} in 73% of the samples), terbuthylazine (average concentration 141.2 ng L^{-1} in 88% of the samples), tebuconazole (average concentration 1104 ng L^{-1} in 98% of the samples), and azoxystrobin (average concentration 668 ng L^{-1} in 100% of the samples). Additionally, chlothianidin, malathion, and

propanil were only detected in autumn. Simazine appeared more frequently, and thiamethoxam was present at high concentrations, though it was only detected in 6 samples. Thiabendazole has already been previously reported by Calvo et al. (2021) and Celma et al. (2022) in surface water samples from coastal lagoons or estuaries collected across the Spanish Mediterranean including L'Albufera Natural Park. Furthermore, it was detected in all samples in the Júcar River Hydrographical Basin (Spain) (Fonseca et al., 2019). Thiabendazole is a fungicide primarily utilized in fruit and vegetable agriculture owing to its antifungal properties, although it also holds potential as a pharmaceutical agent for treating fungal infections (Fonseca et al., 2019). The concentrations of imidacloprid, tebuconazole, and azoxystrobin observed in our study were also higher than those reported in previous studies inside the natural park (Calvo et al., 2021; Soriano et al., 2023). In comparison to other studies, imidacloprid and tebuconazole have been frequently detected in surface water, groundwater, and marine ecosystems (Bride et al., 2021; Elfikrie et al., 2020; Peng et al., 2018). Tebuconazole is typically applied as a post-emergence fungicide, commonly sprayed from mid-July until rice harvest, contingent upon the severity of Pyricularia infection during the cultivation year. In addition, tebuconazole was employed post-harvest in citrus crops. Hence, tebuconazole concentrations remain elevated during both the spring and autumn seasons.

Azoxystrobin is a predominant pesticide, presented at nearly all sampling points (n = 49, Table 1) in both sampling campaigns. The concentration of azoxystrobin was notably higher during the autumn sampling (maximum concentration of 5.01 μg L^{-1}) than during the spring sampling (131.5 ng L^{-1}). Phytosanitary products formulated with 25% w/v azoxystrobin are exceptionally authorized in the area for their aerial application to combat Pyricularia and Helminthosporium in rice commonly at the recommended dose of 200–400 L ha^{-1} of the phytosanitary (ORDEN 3/2019). It is usually authorized in July (avaasaja.org). Azoxystrobin has been frequently documented in surface water (Battaglin et al., 2011; Rodrigues et al., 2013). Tian et al. (2021a) reported azoxystrobin concentrations ranging from 130 to 3900 ng L^{-1} in agricultural watersheds, consistently present during all sampling events. These substances were introduced as alternatives to older, more toxic fungicides like prochloraz and tebuconazole, or carbendazim, which was recently banned (Andreu Sánchez, 2008).

Fig. 2 illustrates the seasonal variation of pesticides in L'Albufera Natural Park, displaying cumulative concentrations for various subgroups across different seasons at each point. Although differences were not statistically significant, there are observable differences between spring and autumn. Fig. 2 shows that the concentrations are up to 10 times higher in autumn than in spring (see the different scales between the two seasons). In autumn, fungicides are the most important pesticide group in the rice-dominated sites, while insecticides are the most prominent pesticides in the citrus-dominated sites. In contrast, in spring, the concentrations of insecticides, herbicides, and fungicides are in the same range.

Consequently, during autumn, the concentration of fungicides exceeds that of herbicides and insecticides. The post-emergence fungicides, namely prochloraz, tebuconazole, and tricyclazole, are typically applied from mid-July until the rice harvest period. The use of

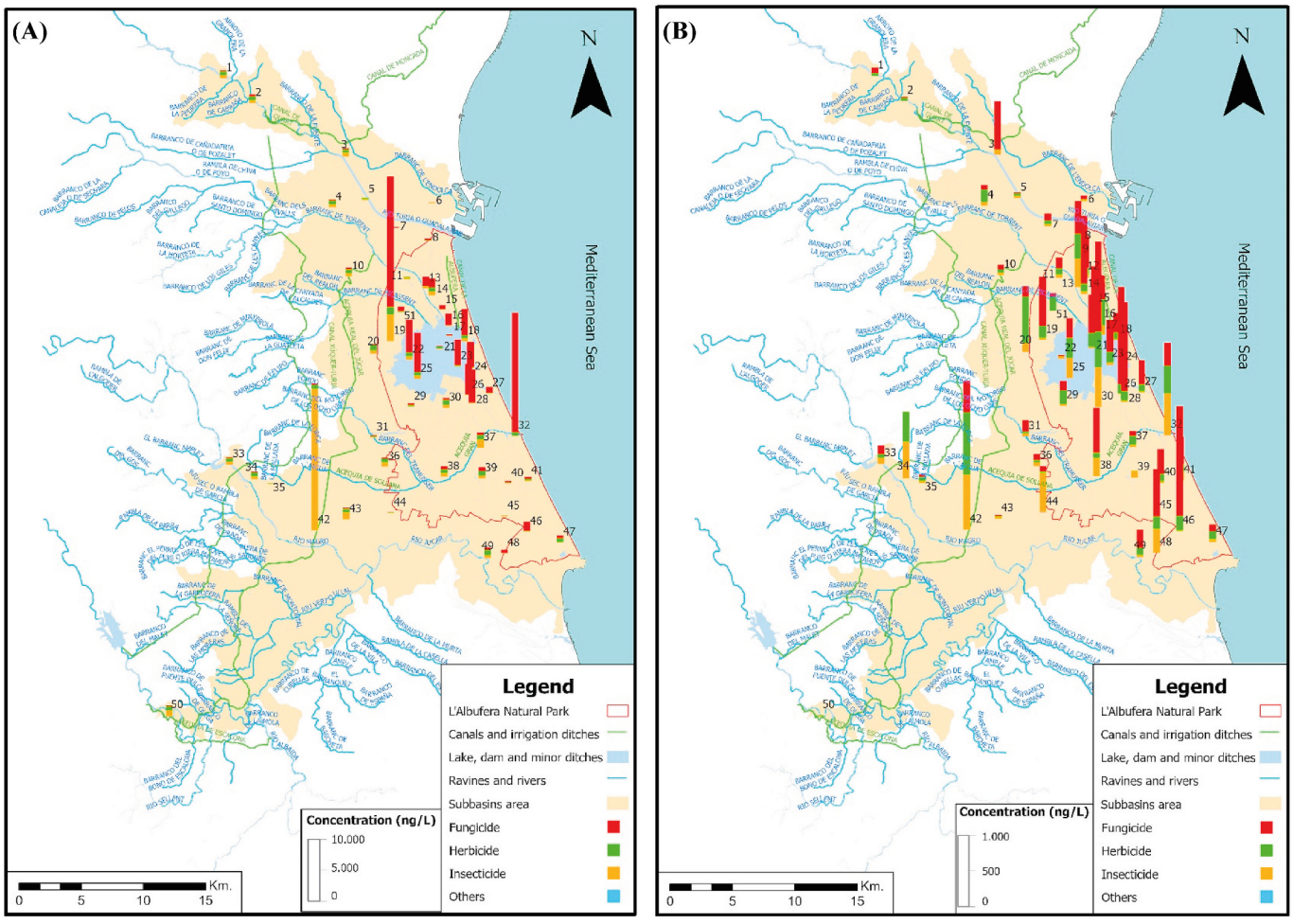


Fig. 2. Cummulative concentrations (total sum of the measured concentrations) of fungicides, insecticides, herbicides and other (A) spring and (B) Autumn. The figures are not to the same scale.

tricyclazole was sanctioned by the Ministry of Agriculture of Spain for both terrestrial and aerial application, under an exceptional authorization spanning from July 15th to October 28th (MAPA, 2016). Application protocols permitted its administration twice within a single treatment, with an interval of 15–20 days between applications. The average concentration of acetamiprid was higher in autumn than in spring. Acetamiprid is applied in early July, directly onto the soil surface during the 7-day dry period. Additionally, three banned neonicotinoids —clothianidin, thiamethoxam, and imidacloprid— whose authorization expired on January 31, 2019, April 30, 2019, and December 1, 2020, respectively, were also found in the samples. These deadlines are close to the sampling period, and it is possible that they were excessively used to deplete the stock before or immediately after the ban. Pesticides such as carbendazim and thiabendazole were found at higher concentrations in spring than in autumn. These pesticides are not typically utilized in rice cultivation but are commonly applied post-harvest in other crops such as citrus (oranges and tangerines) and potatoes, which are also cultivated within the confines of the Natural Park (Calvo et al., 2021). This could account for the higher concentrations of both substances observed in spring compared to autumn. After performing ANOVA analysis, no statistical differences were observed between sampling seasons for any compound.

Some pesticides identified in the study area are currently prohibited by the European Commission, constituting 24% of the detected pesticides (10 out of 42), as indicated by the asterisks in Table 1. Propanil was exclusively detected during the autumn campaign following rice cultivation. Despite propanil was withdrawn from the EU market in 2008 (EC, 2008), its detection is still possible because the Spanish Government annually issues an exceptional authorization for the use of this active substance in rice crops during the growing season (May to July) (Spanish Ministry of Agriculture, 2017). Barbieri et al. (2021) previously documented higher concentrations of this herbicide in the surface waters of the Ebro Delta. Other studies have also detected propanil in the surface waters of the Ebro Delta (Köck et al., 2010; Kuster et al., 2008). Among the other prohibited pesticides, atrazine, carbendazim, chlorfenvinphos, and terbutryn are among the most frequent pesticides in the area. The presence of the banned pesticides in the surface waters of L'Albufera Natural Park is unexpected and could potentially be attributed to their leaching from soils/sediments. However, pesticides such as chlorfenvinphos, chlorpyrifos, diazinon, and terbutryn are characterized by high log Kow values (>3) and they are not expected to be found in the aqueous phase as they are likely to sorb onto suspended particles and accumulate into sediments. However, in our study, these pesticides were detected in surface water during both sampling campaigns.

Environmental quality standards (EQS) in surface water are established for several pesticides, including atrazine, clorfenvinphos, chlorpyrifos, diuron, isoproturon, simazine and terbutryn (*Directive, 2008/105/EC*). Chlorfenvinphos and chlorpyrifos exceeded the maximum allowable concentrations (300 and 100 ng L^{-1}, respectively) in both seasons. Chlorfenvinphos also surpassed the annual average EQS (100 ng L^{-1}) in autumn, and chlorpyrifos averaged 32 ng L^{-1}across both seasons, exceeding its EQS (30 ng L^{-1}). The latest watch list includes imazalil, prochloraz, tebuconazole, and azoxystrobin, which currently lack EQS. Notably, tebuconazole and azoxystrobin levels were high in both seasons, while imazalil and prochloraz consistently showed low concentrations. According to the criteria of the IUPAC Pesticides database (PPBD) (https://sitem.herts.ac.uk/aeru/iupac) (see Table S1), the DT50 values for aqueous hydrolysis indicate the compound's persistence: <30 days means it is not persistent, 30–100 days is moderately persistent, 100–365 days is persistent, and over 365 days is very persistent. Similarly, for water-sediment degradation, thresholds are: <30 days is fast, 30–100 days is moderately fast, 100–365 days is slow, and over 365 days is stable. Then, tebuconazole is classified as moderately persistent in water (DT50 42 days) and the average concentration in water is > 1000 ng L^{-1}. The illicit use of existing stock, even though not a common practice, cannot be dismissed since, for example, recently the police closed a warehouse in Albufera Park selling without authorization phytosanitary products, many of them banned for 13 years (Aparicio).

The results show that bensulfuron methyl, dimethoate, imazamox, and tricyclazol, which were detected exclusively (compounds in italics in Table 1), are characterized by high polarity, water solubility, mobility, and low Kow values (the relevant data for all compounds are provided in Table S1). The exception is diuron, which has inconsistent data: some sources classify it as low-water soluble (42 μg L^{-1}) (Liu, 2005), while others consider it relatively soluble (35 mg L^{-1}) with a log Kow of 2.8 (Thomas, 2009). Supporting the latter, diuron is reported to have a Kd of 8.9 L kg^{-1} in freshwater (House et al., 1997), 4 L kg^{-1} in saline water, and a Koc of around 250 L kg^{-1} (Thomas et al., 2002) indicating it is mostly found in the dissolved phase and weakly sorbed to sediments. The pesticides found in the water reflect the current pattern of use.

The minimum, maximum, and mean concentrations, along with the frequency of detection for target pesticides in surface sediments of L'Albufera Natural Park, are shown in Table 2. More than half of the target pesticides (59 out of 71 pesticides, 83 %) were detected at least in one sampling point in the surface sediments of L'Albufera Natural Park. A greater number of pesticides were detected in sediments compared to surface water, even though with a lower frequency of detection across various sampling points. Sixteen pesticides marked in italics in Table 2 and including cyhalothrin (at the highest concentration 536.1 ng g^{-1} d. w.) were reported only in sediments. Cyhalothrin was also detected in others wetlands sediments at lower concentrations than those identified in our study (Álvarez-Ruiz et al., 2020; McMurry et al., 2016). This compound together with azinphos methyl, azinphos ethyl, coumaphos, dichlofenthion, ethion, ethofenprox, fenitrothion, methiocarb, parathion methyl, parathion-ethyl, propazine and tolclofos methyl are characterized by high Log Know (non-polar substances) insoluble in water. On the contrary acetochlor and alachlor are moderately soluble in water but highly non-polar. Furthermore, bentazone, ethion a propiconazole are persistent in sediments with DT50 > 1 years. The concentrations of cyhalothrin in sediments observed in this study were lower than those reported in the Gualeguay Basin (Mac Loughlin et al., 2022). Compounds detected exclusively in sediments are low-water soluble, little mobile, and with high Know (compounds in italics in Table 2). The exception is the presence of metabolites and/or degradation products of amitraz, carbofuran and fenthion quite water-soluble (e.g., 2,4-dimethylaniline (DMA) and N, N-dimethylformamide (DMF), carbofuran-2-OH, and fenthion sulfone, marked in capital letters in Table 2) attributable to a slower degradation and higher microbial activity leading to more transformation mechanisms. For example, fenthion sulfone was detected with a maximum concentration of 84.5 ng g^{-1}. Fenthion sulfone is a final metabolite of fenthion, and its presence may indicate residues from an old treatment. Picó et al. (2020) already reported the presence of this pesticide only in sediment samples. These compounds could reflect old use of these pesticides especially for those compounds that are found only in sediments and are highly persistent.

Among the compounds detected in both water and sediment, ten compounds - acetamiprid, carbendazim, imazalil, prochloraz, tebuconazole, terbuthylazine (as their metabolites), thiabendazole and thiamethoxan - exhibited the highest frequency of detection (>50 % of the samples) and at mean concentrations >50 ng g^{-1} d.w. Tebuconazole was detected at the highest average concentration (182 ng L^{-1}), followed by prochloraz (106 ng L^{-1}) and imazalil (93 ng L^{-1}) with frequencies that were 60, 80 and 83 %, respectively. These compounds are known to persist in sediments with DT50 > 1 year. Some of these pesticides have been previously documented in sediments from the Natural Park of the Albufera of Valencia, albeit at concentrations lower than those identified in our study (Calvo et al., 2021; Soriano et al., 2024). The ten banned pesticides found in waters also appear in sediments. Atrazine has been previously detected in various studies. In estuarine sediments, quantified levels ranged from 5.93 to 50 ng g^{-1} dw (Cunha et al., 2022), while

Table 2
Minimum, maximum, and mean concentration in ng g^{-1} of the detected individual pesticides and frequency of detection in the investigated surface sediment samples (May–June period).

Pesticide	Concentration ng g^{-1} d.w.			
	Min	Max	Mean[a]	Frequency[b]
Acetamiprid	0.15	129.56	47.38	53
Acetochlor	0.20	84.33	10.49	13
Alachlor	0.25	81.60	9.64	13
Atrazine[c]	0.08	85.37	21.08	27
Atrazine-Desethyl	0.15	26.80	2.77	10
Atrazine-Desisopropyl	0.15	13.61	0.97	10
Azinphos-ethyl	0.20	100.94	20.62	23
Azinphos-Methyl	0.15	61.26	9.03	17
Azoxystrobin	0.25	427.86	34.81	10
Bentazone	0.50	42.92	5.66	12
Buprofezin	0.20	129.33	23.35	20
Carbendazim[c]	0.10	48.17	29.59	77
Carbofuran	0.08	57.25	10.56	23
CARBOFURAN-3-OH	0.08	105.24	11.76	13
Chlorfenvinphos[c]	0.08	171.34	42.59	33
Chlorpyriphos	0.08	86.15	22.52	33
Clothianidin	0.05	2.66	0.20	13
Coumaphos	0.25	123.78	16.66	13
Cyhalothrin	0.15	536.10	27.81	17
Diazinon[c]	0.05	56.89	19.69	37
Dichlofenthion	0.10	58.66	5.96	17
Difenoconazole	0.25	48.72	2.29	4
DMA	0.25	14.62	0.73	3
DMF	0.05	47.49	9.40	30
DMPF	0.05	70.47	6.32	17
Ethion	0.05	73.62	5.07	20
Etofenprox	0.30	233.05	23.50	10
Fenitothrion	0.20	146.46	15.51	23
Fenthion (water detected as fenthion sulfoxide)	0.25	43.37	4.07	10
FENTHION SULFONE	0.13	84.49	15.95	23
Fenthion sulfoxide	0.23	34.27	3.94	23
Fluvalinate	0.13	164.28	5.60	3
Hexythiazox	0.10	91.24	17.77	23
Imazalil	0.15	241.85	92.35	80
Imidacloprid	0.05	196.91	54.12	40
Isoproturon[c]	0.05	67.82	13.24	27
Malathion	0.25	54.16	15.57	30
Methiocarb	0.05	19.36	1.49	20
Metoalachlor[c]	0.13	69.47	28.59	47
Molinate[c]	0.13	69.47	15.40	23
Omethoate	0.25	46.06	12.52	30
Parathion-ethyl	0.10	64.44	9.59	17
Parathion-methyl	0.20	352.85	55.43	30
Prochloraz	0.30	266.15	106.51	60
Propanil[c]	0.13	84.38	25.76	33
Propazine	0.13	72.11	8.35	13
Propyconazole	0.25	74.80	15.11	37
Pyriproxyfen	0.20	164.78	36.24	23
Simazine[c]	0.50	66.20	11.28	17
Tebuconazole	0.17	495.18	182.26	83
Terbumeton	0.10	56.96	18.45	33
Terbumeton-desethyl	0.05	29.51	1.66	37
Terbuthylazine	0.25	38.28	13.16	40
Terbuthylazine-2-hydroxy	0.05	51.13	31.37	90
Terbuthylazine desethyl	0.17	57.04	35.54	77
Terbutryn[c]	0.17	119.15	61.42	57
Thiabendazole	0.25	234.57	74.72	93
Thiamethoxam	0.10	111.77	77.31	87
Tolclofos-methyl	0.25	88.90	10.45	23

DMA (2,4- dimethylaniline), DMF (N, N-dimethylformamide), DMPF (N'-(2,4-Dimethylphenyl)-N-methylformamidine).
In italics, pesticides are detected only in sediment samples.
In capital letters, parent pesticides and/or degradation products detected only in sediment samples.
[a] Mean calculated considering values nd as LOD/2.
[b] not including compounds with values nd. Detection frequencies (expressed in %). 30 sampling points considered to calculate detection frequency.
[c] Compounds currently prohibited for their use in Europe. The exceptional use of propanil is annually allowed in Spain.

in marine sediments in the Ebro Delta (Spain) and the Northern Adriatic (Italy), it was found with maximum concentrations of 39.2 ng g^{-1} dw and 980 ng ng^{-1} dw, respectively (Carafa et al., 2007; Ferrer et al., 1997). Compounds found in both, water and sediment (compounds in bold in Tables 1 and 2) are moderately polar to non-polar, moderately to low-water soluble, with high Kow, and low mobility. Notable exceptions include neonicotinoids (acetamiprid and imidacloprid), metolachlor, molinate, and omethoate, which are highly water-soluble and more polar. It has been reported that these pesticides degrade faster in water through photolysis and hydrolysis but persist longer in sediments (Huang et al., 2020; Peris et al., 2022). Furthermore, omethoate could also be a degradation product of dimethoate. Terbuthylazine that is detected at low concentrations but high frequencies together with its metabolites (terbuthylazine-2-hydroxy and terbuthylazine desethyl). The high frequency of terbuthylazine-2-hydroxy can be explained since it is a persistent compound with DT50 > 1 year.

The pesticides detected align well with those documented in prior studies conducted in L'Albufera Nature Park (Calvo et al., 2021; Soriano et al., 2023). Numerous investigations have previously reported pesticides in the surface water of irrigation channels and rice fields within the Natural Park (Gamón et al., 2003; Vázquez-Roig et al., 2010). The occurrence of these pesticides in surface water during the two sampling campaigns may be attributed to their widespread agricultural and urban applications.

3.1.2. Non-target analysis (NTS)

To identify non-target compounds, a NTS method was devised using Compound Discoverer 3.2 (CD). The NTS approach with the 'Environmental with Stats Unknown ID and Online Database Searches' presents limitations, particularly for identifying transformation products absent from existing libraries. Fig. 3 shows the compounds detected using NTS along with their frequency of appearance in surface water in both seasons and sediments (for their physicochemical and other related properties see Table S2). The compounds detected in water during spring were the same as in autumn, except for pyrimethanil and ricine (only in autumn), and pyraclostrobin, paclobutrazol, and carboxin (only in spring). However, detection frequencies fluctuated between the two seasons. The analysis unveiled 72 compounds in surface water, including tebuconazole, imazalil, pyriproxyfen, difenoconazole, azoxystrobin, diazinon, prochloraz, terbutylazine desethyl and tebutryn also detected in the target analysis. These compounds span various categories, including pesticides (18, but only 9 different of the target analysis), pharmaceuticals (41) industrial compounds (8), and others (5) [Food constituent (2), rubber components (1) and illicit drugs (2)].

Nine additional pesticides were detected in water in addition to those in the target analysis, mainly phenylureas (monouron, pencycuron, tebuthiuron) and their degradation products (monodesmethyl isoproturon, the parent compound found in the target), along with fungicides (metalaxyl, pyraclostrobin, and carboxin). Among these, phenylureas, except for pencycuron, are herbicides, while pencycuron acts as a fungicide, particularly recommended for Pyricularia. Hence, the frequency of detection in spring surface waters was slightly higher than that documented in autumn. Additionally, paclobutrazol, a member of the triazole family of plant growth regulators, was detected. This compound protects various crops from environmental stresses such as drought, chilling, and heat radiation. This completes the water pesticide profile, revealing that although the target analysis covers many currently used pesticides, others remain undetected if NTS approaches are not applied. The pharmaceuticals detected included antibiotics (monensin and azithromycin), antihypertensive (telmisartan, valsartan, olmesartan, candesartan, irbesartan, propranolol and losartan), antiarrhythmic (flecainide), analgesics and anti-inflammatory (phenazonem, niflumic acid, palmitoyl ethanolamide, benzydamine, flufenamic acid and diclofenac), antipyretics (quinine), anthelminthic and immunomodulatory agent (levamisole hydrochloride), anticonvulsant (10-Hydroxycarbazepine), antidepressant (venlafaxine and amitriptyline),

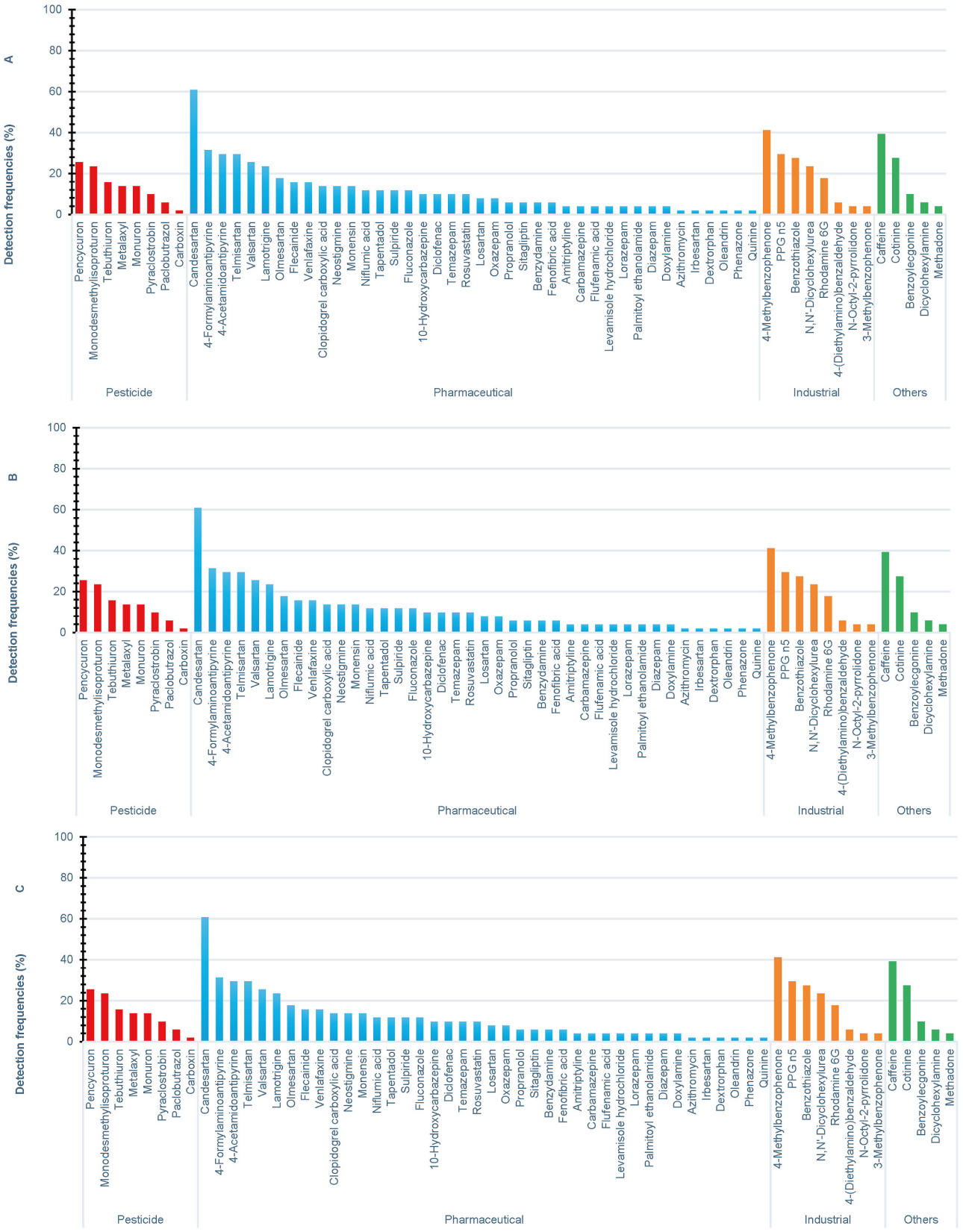


Fig. 3. Frequency of detection (expressed in %) in A) Spring B) Autumn for surface water, and C) sediments. 51 and 49 sampling points considered in spring and autumn respectively to calculate detection frequency. 30 sampling points considered to calculate detection frequency in sediment. For water samples, "Others" includes: dicyclohexylamine (tire compound), Methadone (illicit drug), benzoylecgonine (illicit drug) caffeine (food constituent) and cotinine (food constituent). For sediment samples, "Others" includes: citral (biocide), DEET (biocide), pinocembrin (natural compound), arachidonic acid, lauric acid (natural compound), daidzein (natural compound) and palmitoleic acid (natural compound). PEG: polyethylene glycols. DEET: N, N-dietil-*meta*-toluamida

antiepileptic (carbamazepine and lamotrigine), antifungal (fluconazole), antihistamine (doxylamine), metabolite of analgesic (4-Formylaminoantipyrine and 4-Acetamidoantipyrine), narcotic analgesic (tapentadol), antipsychotic (sulpiride), sleep aid (temazepam), lipid-regulating agent (fenofibric acid), treat anxiety (oxazepam), lipid-lowering agent (rosuvastatin), enzyme inhibitor (neostigmine), natural compound (ricinine), glucose-lowering drug (sitagliptin), antiplatelet agent (clopidogrel carboxylic acid), neuroprotective agent (dextrorphan), anxiolytic (lorazepam and diazepam), and cardiac glycoside (oleandrin). These compounds were highly detected in urban watersheds and positively correlated with population density. Therefore, it is evident that these pharmaceutical residues end up in the aquatic environment due to incomplete removal during the discharge of sewage effluents. This conclusion is supported by the findings of Yang et al. (2022); Eysseric et al. (2022); Tian et al. (2021a) and Watanabe et al. (2008). Two substances found were classified as pharmaceuticals: oleandrin and ricine, which likely come from plants growing in the area. Oleander (*Nerium oleander*), is commonly planted along roadsides and as hedges to separate different cultivation plots (DECRETO 259/2004).

Similarly, ricine (*Ricinus communis*) is a notorious invasive species present in the canals and channels of the Natural Park (Ferrer Merino and Donat, 2011), which is currently under eradication efforts. Quinine, commonly used to treat malaria, is also a flavoring agent in tonic water and bitter lemon drinks (approximately 80 mg per serving), which likely explains its presence in the environment.

Industrial chemicals (n = 8), which include industrial raw materials and additives, such as 3- and 4-methylbenzophenone (UV-curing ink), benzothiazole (raw material), N, N′-dicyclohexylurea (a byproduct of different reactions), 4-(diethylamino) benzaldehyde (raw material) and N-octyl-2-pyrrolidone (chemical intermediate). Furthermore, compound Discoverer 3.2 offers an option to analyze polymeric compounds like polypropylene glycols (PPG), which have limited availability of standards. In this study, PPG n5 was detected in fourteen out of fifty-one surface water samples with a match score percentage exceeding 80% with mzCloud in spring. Furthermore, the MS/MS obtained for this compound contains the most important fragments attributed to this polymer. This finding is significant because the presence of PPG in water samples is expected due to its wide range of applications. Eysseric et al. (2022) also identified five PPGs ranging from pentapropylene glycol to nonapropylene glycol in surface water samples. Just as Anagnostopoulpou et al. (2022) detected PEG n8 and PEG n5 in water samples from 18 lakes of Central Greece. The "other" category encompasses a diverse range of anthropogenic molecules, including caffeine, cotinine, illicit drugs such as benzoylecgonine and methadone, as well as one compound derived from tire degradation. These results are similar to those of Tian et al. (2021a) who detected cotinine tebuthiuron and metalaxyl in streams in agricultural watersheds. Ccanccapa-Cartagena et al. (2019) also detected tapenadol in surface water in a Mediterranean River basin.

In sediments, industrial compounds and pesticides were the most frequently detected chemical classes (Fig. 3). The 41 compounds identified in sediments were classified into similar categories than water: pesticides (n = 12, including imazalil, azoxystrobin, bentazone, difenoconazole and propiconazole, which were also detected in the target analysis), PPCPs (n = 5) industrial chemicals (n = 17) and others that included natural compounds (n = 5) and biocides (n = 2). The contamination fingerprint in sediments is quite different from those in waters. In water pharmaceuticals characterized by high water solubility and high polarity were the main contaminants detected by NTS. The most significant group of compounds found in the sediment were those coming from the industry. The only compound that was also found in water was PPG n5. Additionally, other polyethylene glycols (PEG) and PPGs were identified in sediments. These compounds are used in a variety of products, such as textiles, glass, resins, paper, pharmaceuticals, and rubber (Jang et al., 2015). Several million tons of PEGs are produced worldwide yearly (Huang et al., 2020). Furthermore, PEGs have been identified as the primary aerobic degradation metabolites of alcohol ethoxylates (Sparham et al., 2008). PPG and PEG like other surfactants are water soluble and are related to sewage-impacted ecosystems as L'Albufera. These compounds are important contaminants in sediment due to their pronounced lipophilic nature, which allows them to easily adsorb onto particles and accumulate in aquatic sediments (Terzic and Ahel, 2011; Li et al., 2022). The most prominent PEGs identified ranged from 6–13, consistent with findings from other studies (Terzic and Ahel, 2011). Knowledge of the environmental distribution of these compounds is limited. However, AEO and PEG levels ranging from 9 to 12 200 μg kg^{-1} in marine sediments and suspended solids have been reported, while total concentrations in surface waters were consistently below 50 μg L^{-1} (Corada-Fernández et al., 2011; Traverso Soto et al., 2013).

Other industrial products that occurred in a considerable number of samples are N-butylbenzenesulfonamide, benzenesulphonamide, 4-ethoxy ethylbenzoate, hexadecanamide –the carboxamide derived from palmitic acid–, phthalates, organophosphorus flame retardants, and laurolactam –an organic compound from the group of macrocyclic lactams mainly used as a monomer in engineering plastics, such as nylon-12 and copolyamides. Previous studies (Abdel-Wahab et al., 2023; Chokwe and Okonkwo, 2019; Gao et al., 2020; Zhang et al., 2021) have also reported the presence of these compounds in sediments at concentrations of several hundreds of ng g^{-1}.

In the 1970s, the Albufera of Valencia suffered an environmental crisis due to uncontrolled discharges of urban, industrial and agricultural origin and reduced flow from the Júcar River (Soria, 2006). Considering that sediments could reflect long term contamination, these could explain the presence of these contaminants. Nowadays, a network of wastewater treatment plants has been built in the area, improving the water quality and avoiding the release of substances from industry.

The detected pesticides were predominantly herbicides (clomazone, benthiocarb, and pendimethalin), though fungicides (tridemorph, fludioxonil), rodenticides (cumatetralyl) and a rowth regulator (ancymidol). Compounds such as pendimethalin, tridemorph, fludioxonil and cumatetralyl present a log Kow ≥3.4 and low water solubility, which indicates that compounds are highly non-polar and tend to accumulate in sediments. However, this does not explain the ancymidol, clomazone, bendiocarb behavior. The presence of certain compounds in sediment can be explained by the fact that the sediment naturally contains negatively charged particles.

In the case of PPCPs there are 5 compounds, three of which were also found in water (fecainide, tapentadol, and benzydamide), while the other two (fenofibrate and triclocarban) were not. All of them have a Log Kow >3 and particularly fenofibrate and triclocarban have a log Kow>5 and are considered water insoluble.

Similarly, natural compounds coming from the degradation of sediment organic matter such as various fatty acids (lauric, palmitoleic, and arachidonic), isoflavones (daizein and pinocembrin), as well as insect repellents like DEET and citral, have been commonly detected in sediment studies (Terzic and Ahel, 2011). Fatty acids have been found by several investigators in several sediments (Kvenvolden, 1967). These compounds, alongside contaminants, configure a distinct fingerprint in sediment compositions, contrasting with the predominantly polar compounds found in water.

3.2. Spatial distribution of the contaminants

A map depicting the spatial distribution of the sum of concentrations of the target pesticides (Fig. 2. Fig. S1 is equal to Fig. 2 but for sediment) is created to illustrate the overall target pesticide contamination levels of L'Albufera Natural Park. Higher pesticide concentrations are predominantly observed in the southern region compared to the north, which correlates with the more intensive agricultural activity in the area. From the perspective of the entire Natural area (Fig. 2), the highest concentrations of pesticides are observed in autumn in points 19, 32,

and 42. Point 42, an irrigation ditch located in the southwest that collects water from the citrus orchards, exhibited the highest measured environmental concentrations of insecticide imidacloprid (17.1 μg L^{-1}). The cumulative concentration of the 26 detected pesticides is 42.2 μg L^{-1}, in addition to imidacloprid, thiametoxam is at concentrations >1000 ng L^{-1}. Eight additional pesticides, including insecticides (acetamiprid, chlorfenvinfos, clothianidin), fungicides (difenoconazole and imazalil) and herbicides (propazine, terbuthylazine and terbumeton-desethyl) are at concentrations >100 ng L^{-1}. Point 19, located in a northwest irrigation ditch collecting water from rice fields, showed the highest concentrations of the fungicide tebuconazole (17.0 μg L^{-1}). The sum of the concentrations of 30 detected pesticide at this site was 45.0 μg L^{-1}. Fluvalinate and azoxystrobin are also at concentrations >1000 ng L^{-1}. Eight additional pesticides, insecticides (chlorfenvinfos, chlorpyrifos, omethoate), fungicides (imazalil), and herbicides (propanil, propazine, terbuthylazine and terbumeton-desethyl) are at concentrations >100 ng L^{-1}. Point 32 located in the southeast is the second point with the highest concentration of tebuconazole (15.5 μg L^{-1}), which is one of the mouths to the see of one of the longest irrigation channels influenced also in the low part by rice cultivation. The sum of the 21 detected pesticides concentration is 36.6 μg L^{-1}, in addition to tebuconazole azoxystrobin is at concentrations >1000 ng L^{-1}. Two herbicides propanil and terbumeton desethyl are at concentrations >100 ng L^{-1}. The presence of neonicotinoid insecticides in the case of citrus orchards and the specific rice fungicides terbuthylazine and azoxystrobin at high concentrations mark the difference between both cultivars. These points were also among those highly polluted in spring. The northernmost points (1, 2 and 3) located in the Turia River and points 4, 10, and 20, taken from irrigation ditches, showed high concentrations, though nearly ten times lower than those in the southern region. This area is characterized by the cultivation of nuts, olives, and citrus. In autumn, the predominant pesticides were herbicides, followed by insecticides and fungicides, with a notable increase in fungicides during the spring. In the southwest, the points were taken through the Magro River (a tributary of the Jucar River), and points 33 to 35, 42 (one of the most concentrated), 43, and 49 showed the same pattern as those of the Turia River. In the northern part of the Natural Park, points 5–9, 11, 12, and 51 are under Valencia city and its metropolitan area influence (see the soil sealing map Fig. 1B). The relation of these low concentrations with the soil sealing maps is clear and the decrease of concentrations is due to the restricted use of pesticides in cities. Instead, points located nearer the lake (Points 13, 14, 16 and 18 taken in the rice field irrigation channels) present higher concentrations dominated by fungicides. The same happens in the South of the lake (Points 22–28, 30 and 32).

Pesticide concentrations in the southern region were generally higher than in the north. However, in the southern part, points 35, 40, 41, 44–45, and 48 also presented low concentrations of pesticides more difficult to explain, even though point 45 is near the city of Sueca, and influence by a belt of villages and towns in the area (see Fig. 1B). These points are also characterized by the sporadic presence of nematicides and acaricides, as observed in Sites 31, 42, 44, and 45.

The pattern of pesticide detection in autumn exhibited similarities to that observed in spring. From a site-specific perspective during spring, the highest measured environmental concentrations of fungicide were observed at point 46, an irrigation channel that collects the outflows of the rice field (1.50 μg L^{-1}) followed by point 26 (1.40 μg L^{-1}) and point 30 (1.20 μg L^{-1}).

The elevated concentration of fungicides at point 46 can be attributed to the presence of thiabendazole (1.20 μg L^{-1}), a fungicide primarily used on crops such as citrus (oranges and tangerines) and potatoes, cultivated within the Natural Park (Calvo et al., 2021). Conversely, the heightened levels of fungicides at points 26 and 30 were attributed to tebuconazole (1.10 μg L^{-1}), a post-emergence fungicide typically applied from mid-July until the rice harvest, hence resulting in greater concentrations during autumn than in spring. These points are situated along rice field canals. The high concentration of insecticide in point 42 was due to the chlorfenvinphos (386.6 ng L^{-1}), an organophosphate insecticide utilized to control root-flies, rootworms, and other soil pests in citrus crops (Végh et al., 2023). Moreover, it is associated with treatments for insects affecting potatoes, olives, broccoli, and livestock (Belenguer et al., 2014). Curiously, chlorfenvinphos was also detected in the Júcar River, a typical Mediterranean Basin, as one of the predominant pesticides in terms of presence and concentration (Belenguer et al., 2014).

Fig. 4 depicts the quantity of compounds detected in water samples categorized by families using NTS. Point 8, characterized by a combination of agricultural (rice field) and urban land uses, exhibited the highest number of compounds detected via NTS, totalling 50 compounds, followed closely by point 12, where 43 compounds were detected. Furthermore, for this reason, point 8 contains the largest number of pharmaceutical compounds (38 pharmaceuticals detected in spring). Point 8 is situated downstream of the Pinedo Wastewater Treatment Plant (WWTP), which likely accounts for its relatively elevated levels of pharmaceuticals, attributed to wastewater discharges. In the northern territory, the quantity of pharmaceuticals detected surpassed that of pesticides. This coincides with the results reported by where the level of PPCPs was higher in the South part of the lake than in the North (Soriano et al., 2023). Point 50 was identified as having the fewest compounds detected through NTS, with only two compounds present. This low detection rate is likely due to its location along the Júcar River, which is situated far from urban and agricultural centers. Dicyclohexylamine was the sole tire-derived compound detected at points 11, 26, and 41 during spring, exhibiting a distinct pattern compared to autumn, where it was identified at points 8, 19, 36, and 48. No compounds were detected at sampling points 4, 12, 19, 22, 27, and 47 in spring. In autumn, no compounds were found at points 4, 10, 12, 14, 19, 22, 27, and 47. The distribution of pesticides in sediments follows a pattern like that observed in water. The most heavily contaminated sediments are found in the riverbeds, as well as in the sediments from irrigation channels and the lake affected by rice cultivation. The pattern of pesticide contamination in sediments differs from that in water, showing a predominance of non-polar compounds. Regarding NTS, sediments are predominantly contaminated with industrial compounds. At several points, several compounds ≥20 were detected by NTS. This occurred at point 8 in the North, under the influence of the city of Valencia and its industrial belt. Points 21, 24–26 and 28 are in the lake and the rice fields of the South. Additionally, points 36, 37, 29, 40, 45 and 48 are in the southeastern area characterized by small towns. They showed a similar pattern to water.

In sediments, higher concentrations of contaminants are predominantly associated with rice fields and the lake, whereas water from rivers and irrigation channels for horticultural and citrus crops typically exhibits lower concentrations. The highest concentrations sum was 2482 ng g^{-1} at point 48 followed by 2004 ng g^{-1} at point 37 corresponding to an abandoned field and rice irrigation channels. The number of pesticides detected were 31 and 18, respectively. Predominant pesticides with concentrations higher than 100 ng g^{-1} were tebuconazole, prochloraz, imazalil, and azoxystrobin in point 37. This pattern is typical of those pesticides used in rice cultivation. Chlorfenvinphos, imazalil, imidacloprid, parathion methyl, pyriproxyfen, tebuconazole, tebutryn and thiabendazole were the most important in point 48, corresponding to an abandoned field. The presence of these pesticides is likely attributable to historical contamination from former fruit orchards, with insecticides being the predominant class of pesticides.

The statistical analysis applied to this spatial assessment in water is also shown in the Supplementary Material (**Text S3**) to determine possible sources of contaminants. An ANOVA test was conducted to determine if there were any differences based on the type of water source used, such as river, lake, outlets, citrus orchards irrigation channels, horticultural irrigation channels, and rice field irrigation channels. The results of the text showed that were differences for bensulfuron methyl, tebuconazole, and terbumeton-desethyl. Specifically,

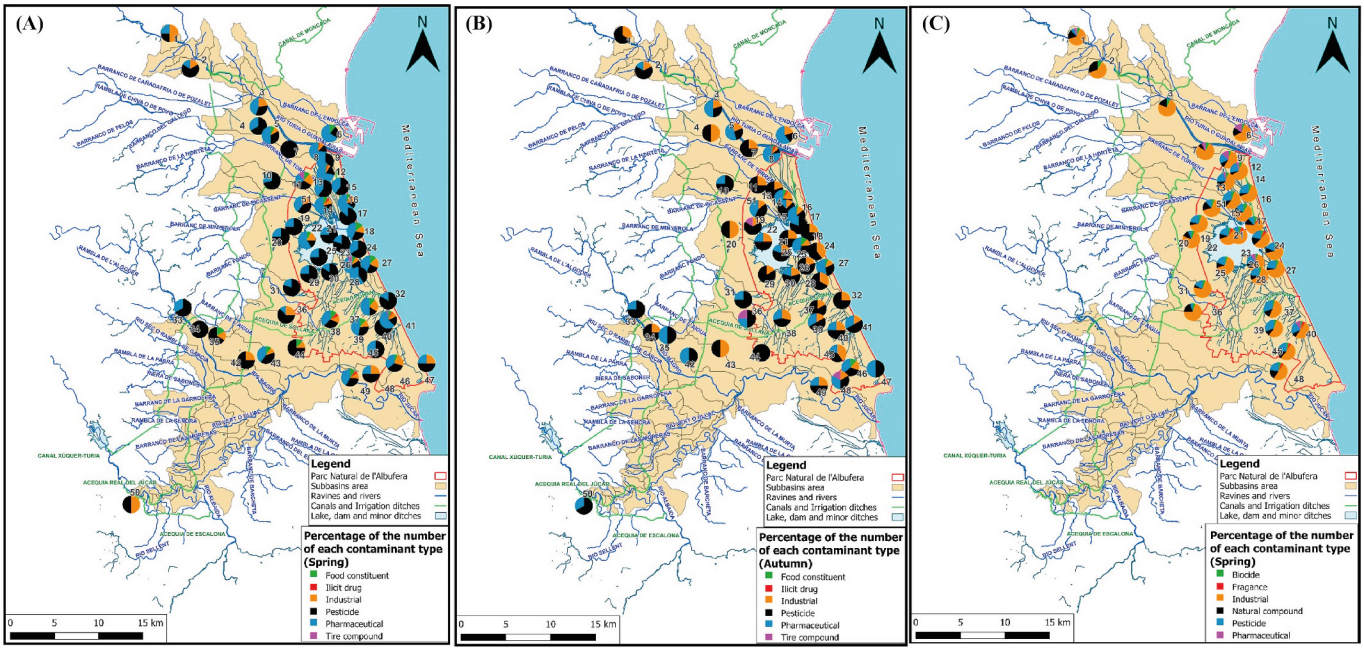


Fig. 4. Distribution of the percentage of the number of the different types of contaminants detected by NTS in (A) water in spring (B) water in autumn and (C) sediments.

the water from Albufera Lake showed higher concentrations than the other water sources for bensulfuron methyl. This herbicide is used for the control of a variety of perennial weeds in rice. Furthermore, this compound could be highly persistent in water. For tebuconazole, the concentrations in water from the lake inlet differed significantly from those in river water and citrus irrigation channels. Additionally, terbumeton-desethyl showed a distinct concentration pattern in water from the outlets compared to river waters.

Statistical analysis reveals significant differences in the levels of bensulfuron methyl, diuron, isoproturon, and tricyclazole among various water uses—wild vegetation, citrus, horticulture, rice fields, and lakes. The most pronounced disparities are observed for bensulfuron methyl, paralleling variations across different water sources. Diuron displays significant discrepancies between waters used for orchard irrigation and those for riparian vegetation and citrus crops. Isoproturon exhibits similar patterns. Tricyclazole demonstrates distinct behavior in waters used for rice crops compared to those for citrus irrigation. The remaining compounds do not exhibit significant differences in either water types or water uses. Among the intrinsic water characteristics—temperature (ranging from 15.6 to 28.6°C), TDS (ranging from 7.3 to 8996 mg L^{-1}), electrical conductivity (ranging from 0.36 to 11.8 dS m^{-1}), NaCl (ranging from 1.074 to 3997 mg L^{-1}), dissolved oxygen (ranging from 40 to 107 % and from 3.2 to 11.42 mg L^{-1}) and millivolts (electrical potential) (ranging from −141.5 to −18.4) —the ones most correlated with the detected compounds indicate a strong influence of salinity-related factors on their dynamics. Commonly it is observed higher concentrations with increased salinity. This is evident in the multiple stepwise linear regression models, particularly for diuron, DMPF, malathion, molinate, prochloraz, terbuthylazine-2-hydroxy, and tricyclazole. However, the PCA results are not highly reliable, explaining only 31.39% of the variance. Notably, a distinct group of compounds—including buprofezin, thiamethoxam, clothianidin, imidacloprid, terbuthylazine, imazalil, propazine, chlorfenvinphos, chlorpyrifos, and difenoconazole—appears to be unaffected by the studied water characteristics.

Regarding NTS, significant differences were only observed for ricinine among water sources or uses. Ricinine exhibited notable disparities between inlet waters and those in rice fields, as well as between waters for citrus crops and rice fields. This discrepancy is likely due to ricinine being an invasive species, particularly prevalent in irrigation ditches and canals associated with rice cultivation.

Among the 72 compounds detected by NTS, 36 exhibited either significant ($P = 0.005$) or highly significant ($P = 0.001$) correlations with intrinsic water parameters, including temperature (ranging from 15.6 to 28.6 °C), millivolts (electrical potential), TDS, electrical conductivity, and NaCl. Millivolts (mV) emerged as the parameter most correlated with almost all compounds (77.78%). Like target compounds, the electrical characteristics of water and salt content primarily influence the dynamics of these compounds, albeit to a lesser extent than temperature and TDS. Electrical conductivity, which measures the water's ability to conduct electric current, is directly related to the concentration of ions in solution. Elevated conductivity generally signifies an increase in dissolved salts, minerals, and other water-soluble substances. This influence is further corroborated by the multiple stepwise linear regression models obtained. From the correlations obtained and the variables refined by the models, the results gave a PCA highly significant, which explain the 84.90 % of the variance (dimension 1 explain the 71.70 % and dimension 2 the13.20 %). PCA shows two distinct groups of compounds according to their course: (i) carbamazepine, cotinine, dicyclohexylamine, flecainide, irbesartan, metalaxyl, olmesartan, tapentadol, valsartan, and venlafaxine, predominantly associated with TDS, and (ii) 10-hydroxycarbazepine, azithromycin, benzydamine, fenofibric acid, lamotrigine, methadone, niflumic acid, oxazepam, rhodamine 6G, rosuvastatin, sulpiride, and temazepam, primarily linked to mV. Pesticides are often marketed as mixtures. However, pencycuron and paclobutrazol are commercialized as individual ingredients, and metalaxyl, pyraclostrobin, and carboxin could be commercialized alone or as a mixture with other pesticides such as folpet, captan or thiram (little determinable by LC-MS).

3.3. Ecological risk assessment

3.3.1. Risk assessment according to RQ_i

The RQ index was used to evaluate the impact of pesticides on the ecosystem of L'Albufera Natural Park. For this purpose, the maximum (worst-case scenario) and average concentrations of pesticides were

compared with their corresponding predicted minimum no-effect concentration (PNEC), obtained from the NORMAN ecotoxicology database. The results, summarized in Table 3, show that, in spring, 13 out of the 43 pesticides detected in L'Albufera Natural Park exhibited high ecological risk when considering the maximum concentration. While, chlorpyrifos, fluvalinate, and omethoate also posed a high ecological risk in surface water (RQ > 1) when considering the mean concentration (as highlighted in bold in Table 3). In contrast, autumn data indicated that 17 out of the 43 pesticides exhibited high ecological risk in surface water when evaluated against maximum concentrations. Moreover, acetamiprid, azoxystrobin, chlorfenvinphos, chlorpyrifos, fluvalinate, imidacloprid, omethoate, tebuconazole, and terbuthylazine were identified

Table 3
Risk Quotient (RQ) for the worst-case (RQ_{max}) and the normal (RQ_{mean}) contamination scenarios in the two sampling campaigns and in sediments.

Pesticides	PNECsurface water[a]	Spring campaing		Autumn campaing		PNECsed[a]	Sediment	
	µg L^{-1}	RQ_{max}	RQ_{mean}	RQ_{max}	RQ_{mean}	ng g^{-1}	RQ_{max}	RQ_{mean}
Acetamiprid	0.0240	**11.5**	0.89	**12.0**	**1.28**	0.18	719.78	263.20
Acetochlor	–	–	–	–	–	0.15	562.00	69.90
Alachlor	–	–	–	–	–	3.30	24.73	2.92
Atrazine*	0.6000	<0.1	≪0.1	≪0.1	≪0.1	0.20	426.87	105.42
Atrazine-desethyl	0.2600	<0.1	<0.1	<0.1	<0.1	1.66	16.15	1.67
Atrazine-deisopropyl	0.3900	<0.1	≪0.1	<0.1	≪0.1	1.66	8.20	0.58
Azinphos ethyyl	–	–	–	-	-	0.02	4588.39	937.42
Azinphos methyl	–	–	–	-	-	0.03	1914.40	282.33
Azoxystrobin	0.2000	0.66	0.12	**25.3**	**3.35**	11.50	37.21	3.03
Bensulfuron methyl	0.01	–	–	–	–	–	–	–
Buprofezin	0.9900	≪0.1	≪0.1	<0.1	≪0.1	72.40	1.79	0.32
Carbendazim	0.4400	<0.1	<0.1	<0.1	≪0.1	5.57	8.65	5.31
Carbofuran	0.0160	<0.1	<0.1	0.38	<0.1	0.07	817.86	150.84
Carbofuran 3-hydroxy	–	–	–	-	–	56.70	1.86	0.21
Chlorfenvinphos*	0.1000	**4.05**	0.39	**3.90**	**1.66**	1.62	105.77	26.29
Chlorpyriphos	0.0005	**331.0**	**38.8**	**312.5**	**106.1**	0.11	783.20	204.73
Chlotianidin	–	–	–	**3.04**	<0.1	0.01	204.85	15.40
Coumaphos	–	–	–	-	–	0.04	3094.47	416.42
Cyhalotryn	–	–	–	-	–	0.18	2978.35	154.50
Diazinon*	0.0100	0.82	<0.1	**4.89**	0.1	0.29	196.16	67.91
Difenoconazole	0.7600	0.33	<0.1	0.14	<0.1	–	–	–
Dichlofethion	–	-	–	–	–	0.39	150.41	15.28
Dimethoate	0.0700	**1.5751**	<0.1	<0.1	≪0.1			
Diuron	0.0700	0.39	<0.1	0.58	<0.1			
DMA	–	–	–	–	–	41.90	0.35	0.02
DMF	–	–	–	–	–	93.20	0.51	0.10
DMPF	10.3	–	–	–	–	78.40	0.90	0.08
Ethion	–	–	–	–	–	0.27	272.67	18.76
Etofenprox	–	–	–	–	–	0.85	274.18	27.65
Fenitrotion	–	–	–	–	–	0.20	732.30	77.54
Fenthion	–	–	–	–	–	0.31	139.89	13.13
Fenthion sulfone	–	–	–	–	–	0.10	844.88	159.51
Fenthion sulfoxide	0.24	–	–	–	–	0.05	685.37	78.88
Fluvalinate	0.0033	**55.7**	**2.26**	**1096.2**	**28.4**	82.40	1.99	0.07
Hexythiazox	0.0250	0.11	<0.1	**1.79**	<0.1	7.65	11.93	2.32
Imazalil	0.8700	0.45	<0.1	0.34	<0.1	232.00	1.04	0.40
Imazamox	0.4500	<0.1	≪0.1	≪0.1	≪0.1	–	–	–
Imidacloprid	0.0130	**14.1**	0.56	**1315.9**	**29.8**	0.04	4688.31	1288.66
Isoproturon*	0.3000	≪0.1	≪0.1	<0.1	≪0.1	1.97	34.42	6.72
Malathion	0.006	–	–	**8.74**	0.55	0.00	90259.06	25949.99
Methiocarb	–	–	–	–	–	0.02	806.67	62.18
Metoalachlor*	0.2000	0.19	≪0.1	<0.1	≪0.1	3.17	21.91	9.02
Molinate*	3.8000	≪0.1	≪0.1	–	–	21.70	3.20	0.71
Omethoate	0.0040	**99.0**	**3.14**	**99.9**	**8.18**	0.01	5483.90	1490.06
Parathion ethyl	–	–	–	–	–	1.52	13.00	1.90
Parathion methyl	–	–	–	–	–	1.20	294.04	46.19
Prochloraz	1.5600	≪0.1	≪0.1	≪0.1	≪0.1	0.30	887.18	355.02
Propanil*	0.200	–	–	**1.47**	≪0.1	1.78	47.40	14.47
Propazine	0.1800	**1.79**	<0.1	**1.88**	0.79	2.54	28.39	3.29
Pyriproxyfen	0.0015	**27.7**	0.96	**6.85**	0.23	0.65	253.51	55.75
Simazine*	1.0000	<0.1	≪0.1	<0.1	≪0.1	7.82	8.46	1.44
Tebuconazole	0.2400	**4.63**	0.73	**70.6**	**4.60**	5.48	90.36	33.26
Terbumeton	1.7000	<0.1	≪0.1	<0.1	≪0.1	34.90	1.63	0.53
Terbumeton-desethyl	0.0650	**2.87**	0.48	**3.19**	0.57	0.64	46.11	2.60
Terbuthylazine	0.0600	**6.01**	0.80	**5.65**	**2.38**	2.68	14.28	4.91
Terbuthylazine-2-hydroxy	–	–	–	–	–	0.03	1704.35	1045.83
Terbuthylazine desethyl	–	–	–	–	–	2.14	26.65	16.61
Terbutryn*	0.0650	**1.10**	0.35	0.81	0.27	2.38	50.06	25.81
Thiabendazole	1.2000	0.99	<0.1	0.32	<0.1	105.00	2.23	0.71
Thiamethoxam	–	–	–	–	–	0.12	931.45	644.23
Tolclofos methyl						2.99	0.00	3.50
Tricyclazol	0.4700	0.42	<0.1	0.39	<0.1			

[a] Lowest PNEC extracted from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php).
-: data not available;

as posing high ecological risk based on mean concentrations, increasing the number of compounds with RQ > 1 from three in spring to nine in autumn. Tian et al. (2021a) reported that the concentrations of azoxystrobin was much higher than the PNEC, resulting in risk quotients much greater than 1, indicating chronic exposures to multiple compounds at levels considered hazardous to organisms. During autumn, malathion was detected at six sampling points, reaching a maximum concentration of 54.5 ng L^{-1}. This pesticide was also detected in surface sediments with a similar concentration. Malathion presented high ecological risk considering the maximum concentration. The toxicity of malathion to aquatic invertebrate is consistent with other studies about ecotoxicological risk assessment of polar pesticides in surface water samples (Affum et al., 2018; Köck-Schulmeyer et al., 2012).

Chlorpyrifos, for instance, demonstrated the highest RQi value during spring under worst-case contamination scenarios (maximum concentration), as well as under normal conditions (mean concentration). Conversely, imidacloprid exhibited the highest RQ value during autumn under worst-case contamination scenarios (maximum concentration), while chlorpyrifos exhibited the highest RQi value under normal conditions (mean concentration). The elevated concentrations of imidacloprid detected could potentially inflict harm upon the ecosystem within aquatic Mediterranean ecosystems. These high levels of imidacloprid may have significant implications for the invertebrate communities. The insecticide imidacloprid exhibited notable toxicity towards the macroinvertebrates *Simocephalus* sp. and *Gammarus* sp (Calvo et al., 2021). Additionally, a study conducted by Rico et al. (2018) reported that the genus Chironomini exhibited the highest sensitivity among invertebrates when exposed to imidacloprid. Furthermore, there is a necessity for conducting risk assessment studies concerning pollutant mixtures. In instances where pesticides share a common MoA, the potential effects on joint toxicity should be considered. Furthermore, the RQ values for sediments were considerably higher for all compounds, often exceeding 10, highlighting the need for comprehensive analysis in sediment studies as well.

The cumulative risk index for pesticide mixtures (RQmix) across spring and autumn in surface water is illustrated in Fig. 5. The data reveal that the risk quotient is generally higher in autumn compared to spring. The results showed that, in autumn, points 19 and 42 had the highest cumulative risk index of pesticide mixtures. The sum of exposure to the detected pesticides present at each sampling point may suggest environmental concern for some biota. These results highlight the importance of examining the whole mixture of pesticides to assess the ecological risk.

3.3.2. *Risk assessment according to the RQi of the modes of action of detected compounds*

In our study, out of the 106 detected compounds in water samples using target and NTS, 77 of them (73%) could be assigned to at least one specific mode of action (MOA) (see Fig. 6). Compounds that interact with the nervous system were the most prominent category (21), followed by photosynthesis inhibition compounds (8), sterol biosynthesis inhibition compounds (6) and compounds inhibiting angiotensin receptor or enzyme and protein biosynthesis (5). The 21 neuroactive compounds mainly consisted of pesticides and pharmaceuticals. Additionally, 35 out of the 43 detected target pesticides could be assigned to at least one specific MOA (Fig. S2), where compounds that interact with

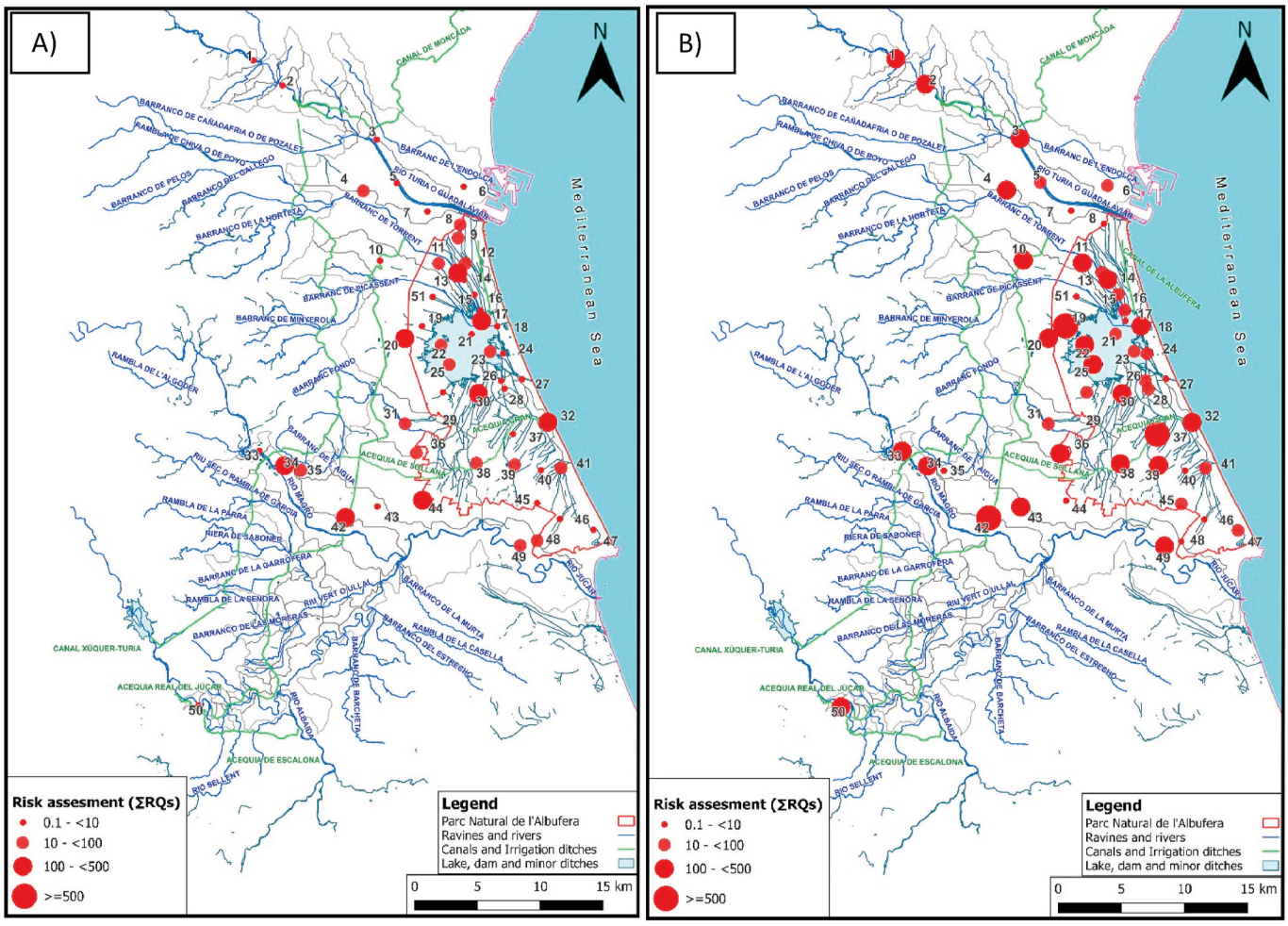


Fig. 5. ΣRisk Quotients (RQmix) at each sampling point in (A) water in spring (B) water in autumn.

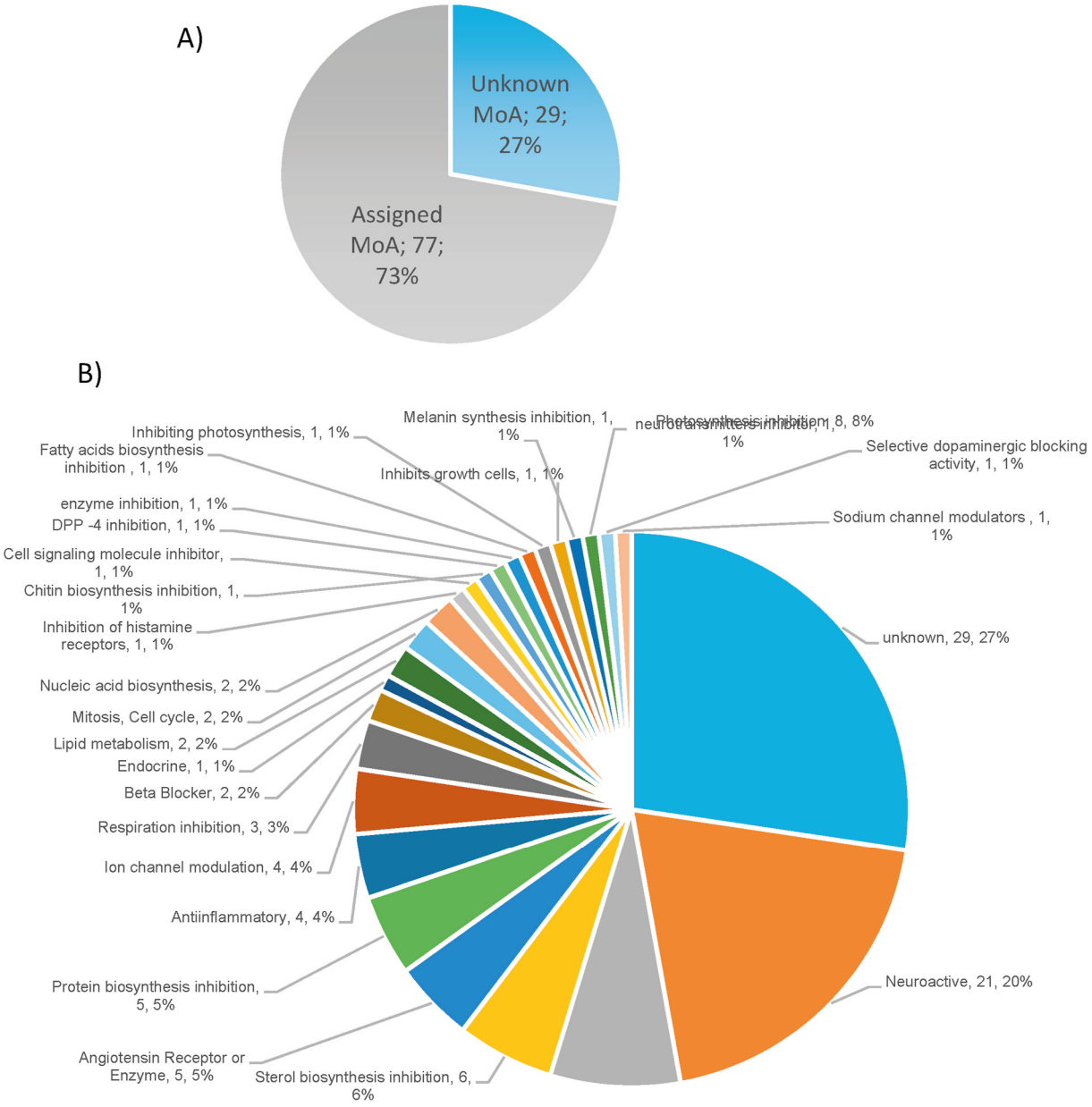


Fig. 6. Mode of action (MOA) information for detected compounds in target and non-target analysis. A: fraction of assigned and unknown MOAs. B: pie-chart of MOA information of the detected target and non-target.

the nervous system were again the most prominent category (12), followed by photosynthesis inhibition compounds (8).

The cumulative risk assessment, which evaluates the sum of RQs for substances sharing a common mode of action across both spring and autumn seasons in surface water, is detailed in Table 4. According to the results, the sum of the RQs of compounds that affect the endocrine system, modulate sodium channels, or are neuroactive are >1 in spring. In autumn, the sum of the RQs of neuroactive and sodium channel-modulating compounds is also >1. In addition, compounds inhibiting photosynthesis, sterol synthesis, or respiration also give RQs >1. In both seasons, the mode of action that poses the greatest risk to aquatic biota is neuroactive compounds. This type of risk assessment through light on the effects of mixtures, especially for those compounds that have the same MOA. However, this risk assessment, up to the moment also has limitations, such as the difficulty in determining the endpoint measured to calculate the PNEC or the lack of information about potential interactions (antagonism, synergism, and potentiation). Despite these limitations, assessing risk through modes of action offers valuable insights into the potential effects of contaminants and their likelihood of affecting aquatic ecosystems.

4. Conclusions

It is necessary to understand the spatiotemporal variability of different pesticides and others compounds to characterize their impacts and to develop informed monitoring and mitigation strategies. This study shows that pesticides transform when discharged into aquatic environments and that their use is changing due to climate variations. Long-term monitoring and big data are essential to address these factors. The consistent detection of fungicides throughout the year and the highest pesticide concentrations in autumn suggest the worst-case scenario timings for pesticide pollution to stakeholders. The successful integration of targeted analysis with non-target screening, utilizing high-resolution mass spectrometry, has revealed significant anthropogenic impacts on both surface water and sediment samples. The findings indicate that pesticides, likely originating from agricultural areas, were

Table 4
∑ RQ according to the mode of action of the different compounds.

MoA	Spring campaign		Autumn campaign		Compounds
	RQ_{max}	RQ_{mean}	RQ_{max}	RQ_{mean}	
Chitin biosynthesis inhibition	0.0012	0.0001	0.0103	0.0003	Buprofezin
Endocrine	27.7307	0.9555	6.8533	0.2275	Pyriproxyfen
fatty acids biosynthesis inhibition	0.1881	0.0063	0.0163	0.0009	Metoalachlor
Lipid metabolism	0.0081	0.0007	–	–	Molinate
Melanin synthesis inhibition	0.4241	0.0449	0.3880	0.0522	Tricyclazol
Mitosis, Cell cycle	0.0848	0.0167	0.0259	0.0066	Acetochlor
					Alachlor
					Carbendazim
Neuroactive	462.1196	43.9031	1761.2384	147.9177	Acetamiprid
					Carbofuran
					Chlorfenvinphos
					Chlorpyrifos
					Clothianidin
					Diazinon
					Dimethoate
					Ethion
					Fenitrothion
					Fenthion
					Fenthion sulfoxide
					Fipronil
					Imidacloprid
					Malathion
					Methiocarb
					Omethoate
					Parathion methyl
					Spinetoram
					Spinosad
					Thiamethoxam
Photosynthesis inhibition	8.3005	0.9056	9.6274	3.3086	Atrazine
					Bentazone
					Diuron
					Isoproturon
					Propanil
					Propazine
					Simazine
					Terbumeton
					Terbuthylazine
Protein biosynthesis inhibition	0.0118	0.0005	0.0092	0.0004	Bensulfuron methyl
					Imazamox
Respiration inhibition	1.6427	0.1676	25.6464	3.3723	Azoxystrobin
					Thiabendazole
Sodium channel modulators	55.7006	2.2556	1096.2303	28.4288	Bifenthrin
					Cyhalothrin
					Etofenprox
					Flumethrin
					Fluvalinate
Sterol biosynthesis inhibition	5.4296	0.7785	71.0969	4.7254	Difenoconazole
					Imazalil
					Prochloraz
					Propiconazole
					Tebuconazole
Unknown	4.2022	0.8583	5.9047	0.9084	Achrinatrin
					Atrazine-desethyl
					Atrazine-deisopropyl
					Carbofuran-3-hydroxy
					Coumaphos
					Dichlofenthion
					DMA
					DMF
					DMPF
					Fenthion sulfone
					Hexythiazox
					Parathion ethyl
					Terbumeton-desethyl
					Terbuthylazine-2-hydroxy
					Terbuthylazine desethyl
					Tebutryn
					Tolclofos-methyl

detected at all sampling sites. In contrast, pharmaceutical products were predominantly found near WWTPs, suggesting that contaminant profiles may be more complex than anticipated based solely on land use patterns.

This study analyses the spatial distribution and pollution levels of pesticides and other compounds identified by NTS in the surface water of L'Albufera Natural Park. The field study demonstrates that contamination in the area is driven by the type of crops cultivated mostly due to orchard fields in the boundaries of the Park and to rice fields inside the Park near the lake. It could be concluded that the pharmaceuticals identified as priority contaminants in the area could be mostly derived from the treated wastewater released to the park through different channels. The results of the multiple stepwise linear regression models and PCA demonstrate that the course of pesticides and the other organic contaminants in water samples are influenced by the physico-chemical properties of the water. Furthermore, the ecological risk assessment of our findings indicates that certain zones exhibiting a significantly elevated hazard quotient should be prioritized for monitoring and management. Further investigation is essential to reduce anthropogenic contaminants from entering aquatic environments and assess regulatory needs. It is imperative to implement agroecological practices that support water and soil quality in a Natural Park of great ecological value but in unfavorable conservation status.

CRediT authorship contribution statement

Yolanda Soriano: Writing – review & editing, Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. **Emilio Doñate:** Writing – review & editing, Visualization. **Sabina Asins:** Writing – review & editing, Visualization. **Vicente Andreu:** Writing – review & editing, Resources, Methodology. **Yolanda Picó:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be published in "Data in Brief".

Acknowledgments

This study was supported by the Prometeo program for research groups of excellence (CIPROM/2021/032) of the Conselleria d'Educació, Universitats i Ocupació (Generalitat Valenciana). Y. Soriano acknowledges her pre-doctoral contract by the grant PRE2019-089042 funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". Also supported by the project SERENA (Soil ecosystem services and soil threats modelling and mapping) – EJP-SOIL (Horizon 2020-European Union-grant agreement 862695). We also thank the director and the staff of the Office of the Natural Park of L'Albufera for their continuous advice and support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143199.

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ARTICLE 01

SUPPLEMENTARY MATERIAL:

Fingerprinting of emerging contaminants in L'albufera natural park (Valencia, Spain): Implications for wetland ecosistem health

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Table S1. Characteristics of the pesticides analysed in the present study

Compounds	Pesticide type	Samples[a]	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
												W	S	
Acetamiprid	Insecticide	W, S	135410-20-7	$C_{10}H_{11}ClN_4$	222.67	2950 (high)	0.8 (low)	132-267 (mobile moderate)	0.7	0.94	3	4.7	1.6*	Neuroactive
Acetochlor	herbicide	S	34256-82-1	$C_{14}H_{20}ClNO_2$	268.77	282 (moderate)	4.24 (high)	156 (moderately mobile)	n/a	1.67	20	40.5	19.7	Mitosis, Cell cycle
Alachlor	herbicide	S	15972-60-8	$C_{14}H_{20}ClNO_2$	269.77	240 (moderate)	3.09 (high)	335 (moderately mobile)	0.6	0.80	39	-	2	Mitosis, Cell cycle
Acrinathrin (adduct)	Insecticide	-	101007-06-1	$C_{26}H_{21}F_6NO_5$	541.44	0.0022 (low)	6.3 (high)	48231 (non mobile)	n/a	-0.92	538	6.5	18.6	Unknown
Atrazine	herbicide	W, S	1912-24-9	$C_8H_{14}ClN_5$	215.7	35 (low)	2.70 (moderate)	100 (moderately mobile)	1.7	2.57	4.3	-	80	Photosynthesis inhibition
Atrazine-desethyl	herbicide	W, S	6190-65-4	$C_6H_{10}ClN_5$	187.63	2700 (high)	1.51 (low)	110 (moderately mobile)	-	3.24	-	-	170*	Unknown
Atrazine-desisopropyl	herbicide	W, S	1007-28-9	$C_5H_8ClN_5$	173.60	980 (high)	1.15 (low)	130 (moderately mobile)	-	-	-	-	-	Unknown
Azinphos-ethyl	Insecticide	S	2642-71-9	$C_{12}H_{16}N_3O_3PS_2$	345.4	4.5 (low)	3.18 (high)	1500 (slightly mobile)	n/a	1.40	101	-	50*	Unknown
Azinphos-methyl	Insecticide	S	86-50-0	$C_{10}PN_3H_{12}S_2O_3$	317.3	28 (low)	2.96 (moderate)	1112 (slightly mobile)	5.0	1.42	40	-	10*	Unknown
Azoxystrobin	fungicide	W, S	131860-33-8	$C_{22}H_{17}N_3O_5$	403.4	6.7 (low)	2.5 (low)	207 to 594 (slightly mobile)	n/a	3.10	Low risk	6.1	205	Respiration inhibition
Bensulfuron methyl	herbicide	W	83055-99-6	$C_{16}H_{18}N_4O_7S$	410.4	67 (moderate)	0.79 (low)	409 (mobile moderate)	5.2	0.91	1.6	18.5	48	Unknown
Bentazone	herbicide	S	25057-89-0	$C_{10}H_{12}N_2O_3S_1$	240.3	7112 (high)	-0.46 (low)	55.3 (mobile)	3.5	1.95	21	80	716	Photosynthesis inhibition
Bifenthrin	Insecticide	-	82657-04-3	$C_{23}H_{22}ClF_3O_2$	422.88	0.001 (low)	6.6 (high)	236610 (non mobile)	n/a	-2.66	1703	8	161	Unknown
Buprofezin	Insecticide	W, S	69327-76-0	$C_{16}H_{23}N_3OS$	305.44	0.637 (low)	4.5 (high)	5363 (non mobile)	n/a	1.21	509	16.8	49	Chitin biosynthesis inhibition
Carbendazim	fungicide	W, S	10605-21-7	$C_9H_9N_3O_2$	191.21	8 (low)	1.48 (low)	225 (mobile moderate)	4.2	2.21	25	7.9	**33.7**	Mitosis, Cell cycle
Carbofuran	Insecticide	W, S	1563-66-2	$C_{12}H_{15}NO_3$	221.26	322 (moderate)	1.8 (low)	86.5 (moderately mobile)	n/a	2.36	12	6.1	9.7	Neuroactive
Carbofuran-3-hydroxy	Insecticide	S	16655-82-6	$C_{12}H_{15}NO_4$	237.25	6207 (high)	1.45 (low)	682 (slightly mobile)	-	-0.53	-	-	-	Unknown

Compounds	Pesticide type	Samples[a]	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
												W	S	
Chlorfenvinphos	Insecticide	W, S	470-90-6	$C_{12}H_{14}Cl_3O_4P$	359.6	145 (moderate)	3.80 (high)	680 (slightly mobile)	n/a	1.72	250	7	37*	Neuroactive
Chlorpyrifos	Insecticide	W, S	5598-13-0	$C_9H_{11}Cl_3NO_3PS$	350.6	1.05 (low)	4.70 (high)	5509 (non mobile)	n/a	0.58	1374	5	36.5	Neuroactive
Chlothianidin	Insecticide	W, S	210880-92-5	$C_6N_5H_8SO_2Cl$	249.8	340 (moderate)	0.90 (low)	123 (moderately mobile)	11.1	3.74	3[ξ]	40.3	56.4	Unknown
Coumaphos	Insecticide	S	56-72-4	$C_{14}H_{16}ClO_5PS$	362.8	1.5 (low)	4.13 (high)	-	-	-	-	-	-	Unknown
Cyhalofop-butyl	herbicide	-	122008-85-9	$C_{16}H_{12}FNO_4$	357.38	0.44 (Low)	3.32 (high)	5247 (non mobile)	n/a	-0.69	7.5	0.15	0.1	Unknown
Cyhalothrin (adduct)	Insecticide	S	91465-08-6	$C_{23}H_{19}ClF_3NO_3$	449.85	0.005 (low)	5.5 (high)	283707 (non mobile)	n/a	-2.09	4982	-	57*	Unknown
Diazinon	Insecticide	W, S	333-41-5	$C_{12}H_{21}N_2O_3PS$	304.35	60 (moderate)	3.69 (high)	609 (some mobile)	2.6	1.51	500	4.3	10.4	Neuroactive
Dichlofenthion	nematicide	S	97-17-6	$C_{10}H_{13}Cl_2O_3PS$	315.15	0.245 (low)	5.14 (high)	18 (mobile)	-	2.14	3000	-	6*	Unknown
Difenoconazole	fungicide	W, S	119446-68-3	$C_{19}H_{17}Cl_2N_3O_3$	406.26	15.0 (low)	4.36 (high)	3760 (slightly mobile)	1.1	0.83	330	2.8	133*	Sterol biosynthesis inhibition
Dimethoate	Insecticide	W	60-51-5	$C_5H_{12}NO_3PS_2$	229.3	25900 (high)	0.75 (low)	2 (mobile)	n/a	2.18	8	12.6	15.5	Neuroactive
Diuron	herbicide	W	330-54-1	$C_9H_{10}Cl_2N_2O$	233.09	25 (low)	2.87 (moderate)	813 (bit mobile)	n/a	2.65	9.45	8.8	48	Photosynthesis inhibition
DMA (amitraz metabolite)	herbicide	S	95-68-1	$C_8H_{11}N$	121.18	-	-	-	4.9	-	-	-		Unknown
DMF (amitraz metabolite)	Insecticide	S	68-12-2	C_3H_7NO	73.09	-	-	-	-0.3	-	-	-		Unknown
DMPF	Insecticide	W, S	33089-74-6	$C_{10}H_{14}N_2$	162.23	-	-	-	-	-	-	-		Unknown
Ethion	Insecticide	S	563-12-2	$C_9H_{22}O_4P_2S_4$	384.48	2 (low)	5.07 (high)	10000 (Not mobile)	-	-	586	-	150*	Neuroactive
Etofenprox	Insecticide	S	80844-07-1	$C_{25}H_{28}O_3$	376.49	0.0225(low)	6.9 (high)	17757	n/a	-0.30	-	5.7	13.3	Unknown
Fenitrothion	Insecticide	S	122-14-5	$C_9H_{12}NO_5PS$	277.2	19 (low)	3.32 (high)	2000 (slightly mobile)	n/a	0.48	29	1.1	1.57	Neuroactive
Fenthion	Insecticide	S	55-38-9	$C_{10}H_{15}O_3PS_2$	278.3	4.2 (low)	4.84 (high)	1500 (slightly mobile)	n/a	1.26	154	22	96	Neuroactive
Fenthion-sulfone	Insecticide	S	3761-42-0	$C_{10}H_{15}O_5PS_2$	310.3[β]	190.4[β]	2.05[β] (low)	235 (moderately mobile)	n/a	-	-	n/a	n/a	Unknown
Fenthion-sulfoxide	Insecticide	W, S	3761-41-9	$C_{10}H_{15}O_4PS_2$	294.3[β]	3.72[β] (low)	1.92[β] (low)	183 (moderately mobile)	n/a	-	-	n/a	n/a	Neuroactive
Fipronil	Insecticide	-	120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$	437.15	3.78 (low)	3.75 (high)	727 (slightly mobile)	n/a	2.06	321	54	68	Neuroactive

Compounds	Pesticide type	Samples[a]	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
												W	S	
Flumethrin	Insecticide	-	69770-45-2	$C_{28}H_{22}Cl_2FNO_3$	509.09	-	-	-	-	-	-	-	-	Unknown
Fluvalinate	Insecticide	W, S	69409-94-5	$C_{26}H_{22}ClF_3N_2O_3$	502.91	0.002 (low)	3.85 (high)	-	-	-	-	-	7*	Unknown
Hexythiazox	acaricide	W, S	78587-05-0	$C_{17}H_{21}ClN_2O_2S$	352.88	0.1 (low)	2.67 (low)	9455 (non mobile)	n/a	0.03	1100	11.5	37	Unknown
Imazalil	fungicide	W, S	35554-44-0	$C_{14}H_{14}Cl_2N_2O$	297.18	184 (moderate)	2.56 (low)	4753 (Non mobile)	6.5	0.26	56.3	7.8	**117**	Sterol biosynthesis inhibition
Imazamox	herbicide	W	114311-32-9	$C_{15}H_{19}N_3O_4$	305.34	626000 (high)	5.36 (high)	11.6 (Very mobile)	2.3	3.59	0.1	132	233	Protein biosynthesis inhibition
Imidacloprid	Insecticide	W, S	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	610 (high)	0.57 (low)	225 (mobile moderate)	n/a	3.69	0.61	30	129	Neuroactive
Isoproturon	herbicide	W, S	34123-59-6	$C_{12}H_{18}N_2O$	206.3	70.2 (moderate)	2.5 (low)	251[β]	n/a	2.61	177	40	149	Photosynthesis inhibition
Malathion	Insecticide	W, S	121-75-5	$C_{10}H_{19}O_6PS_2$	330.4	148 (moderate)	2.75 (moderate)	1800 (Slightly mobile)	n/a	0.00	103	0.4	0.4	Neuroactive
MCPA	herbicide	-	94-74-6	$C_9H_9ClO_3$	200.62	29390 (very high)	-0.81 (low)	74 (mobile)	3.7	2.98	1	13.5	17	Synthetic Auxin
Methiocarb	Insecticide	S	2032-65-7	$C_{11}H_{15}NO_2S$	225.3	27 (low)	3.18 (high)	660 (slightly mobile)	n/a	1.82	75	1.6	4.0	Neuroactive
Metolachlor	herbicide	W, S	51218-45-2	$C_{15}H_{22}ClNO_2$	283.8	530 (high)	3.4 (high)	120 (moderately mobile)	n/a	2.36	68.8	88	365	Mitosis, Cell cycle
Molinate	herbicide	W, S	2212-67-1	$C_9H_{17}NOS$	187.3	1100 (high)	2.86 (moderate)	190 (moderately mobile)	n/a	1.89	72	4	61	Lipid metabolism
Omethoate	Insecticide	W, S	1113-02-6	$C_5H_{12}NO_4PS$	213.2	500000 (high)	-0.9 (low)	41.3 (mobile)	-	2.73	75	-	4.5*	Neuroactive
Parathion-ethyl	Insecticide	S	56-38-2	$C_{10}H_{14}NO_5PS$	291.27	12.4 (low)	3.83 (high)	7660 (non mobile)	-	1.52	40	3.5	4.3	Unknown
Parathion-methyl	Insecticide	S	298-00-0	$C_8H_{10}NO_5PS$	263.21	55 (moderate)	3 (moderate)	240 (moderately mobile)	-	1.35	71	15	5	Neuroactive
Prochloraz	fungicide	W, S	67747-09-5	$C_{15}H_{16}Cl_3N_3O_2$	376.7	26.5 (low)	3.5 (high)	500 (bit mobile)	3.8	1.55	371	2.0	**359**	Sterol biosynthesis inhibition
Propanil	herbicide	W, S	709-98-8	$C_9H_9Cl_2NOT$	218.08	95 (moderate)	2.29 (low)	152 (mobile moderate)	19.1	-0.51	111	1.2	1.25	Photosynthesis inhibition
Propazine/Terbutylazine	herbicide	W, S	139-40-2	$C_9H_{16}ClN_5$	229.71	8.6 (low)	3.95 (high)	154 (moderately mobile)	1.7	3.86	62	77	77	Photosynthesis inhibition

Compounds	Pesticide type	Samples[a]	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
												W	S	
Propiconazole	fungicide	S	60207-90-1	$C_{15}H_{17}Cl_2N_3O_2$	342.22	150 (moderate)	3.72 (high)	1086 (bit mobile)	1.1	1.58	116	6	561	Sterol biosynthesis inhibition
Pyriproxyfen	Insecticide	W, S	95737-68-1	$C_{20}H_{19}NO_3$	321.37	0.37 (low)	5.37 (high)	21175 (non mobile)	6.9	-0.20	1379	1.6	6.5	Endocrine
Simazine/tebutylazine	herbicide	W, S	122-34-9	$C_7H_{12}ClN_5$	201.7	5 (low)	2.30 (low)	130 (moderately mobile)	1.6	2.20	221	46	33	Photosynthesis inhibition
Spinetoram	Insecticide	-	935545-74-7	$C_{42}H_{69}NO_{10}$	748.0	29.0 (low)	4.2 (high)	22836 (non mobile)	7.7	0.27	114	5.1	273	Unknown
Spinosyn A	Insecticide	-	131929-60-7	$C_{41}H_{65}NO_{10}$	731,46	-	-	-	-	-	-	16	126	Unknown
Spinosyn D	Insecticide	-	131929-63-0	$C_{42}H_{67}NO_{10}$	745.47	-	-	-	-	-	-	11	126	Unknown
Tebuconazole	fungicide	W, S	107534-96-3	$C_{16}H_{22}ClN_3O$	307.82	36 (low)	3.7 (high)	769 (bit mobile)	5.0	1.86	78	42.6	365	Sterol biosynthesis inhibition
Terbumeton	herbicide	W, S	33693-04-8	$C_{10}H1_9N_5O$	225.29	130 (moderate)	3.04 (high)	295 (mobile moderate)	-	3.79	-	-	-	Photosynthesis inhibition
Terbumeton-desethyl	herbicide	W, S	30125-64-5	$C_8H_{15}N_5O$	197.24	-	-	-	-	-	-	-	-	Unknown
Terbuthylazine	herbicide	W, S	5915-41-3	$C_9H_{16}ClN_5$	229.71	5 (low)	3.4 (high)		2.0	2.19	25	6	70	Photosynthesis inhibition
Terbuthylazine-2-hydroxy	herbicide	W, S	66753-07-9	$C_9H_{17}N_5O$	211.33	7.19 (low)	-	187 (moderate mobile)	-	4.75	-	-	559*	Unknown
Terbuthylazine desethyl	herbicide	W, S	30125-63-4	$C_7H_{12}ClN_5$	201.66					3.07			54*	Unknown
Terbutryn	herbicide	W, S	886-50-0	$C_{10}H_{19}N_5S$	241.36	25 (low)	3.66 (high)	2432 (bit mobile)	4.3	2.21	72.4	27	60	Photosynthesis inhibition
Thiabendazole	fungicide	W, S	148-79-8	$C_{10}H_7N_3S$	201.25		2.39 (low)	3983 (bit mobile)	4.7	1.94	96.5	1.6	4	Respiration inhibition
Thiamethoxam	Insecticide	W, S	153719-23-4	$C_8H_{10}ClN_5O_3S$	291.7	4100 (high)	-0.13 (low)	30 (low)	n/a	3.58	3[5]	30.6	40	Neuroactive
Tolclofos-methyl	fungicide	S	57018-04-9	$C_9H_{11}Cl_2O_3PS$	301.13	0.708 (low)	3.8 (high)	3028 (slightly mobile)	n/a	0.77	670	1.25	15	Unknown
Tricyclazole	fungicide	W	41814-78-2	$C_9H_7N_3S$	189.24	596 (high)	1.4 (low)	169 (moderate mobile)	n/a	3.89	3.1	92	453	Unknown

[a](W: Water; S: Sediment); MW: Molecular Weight (g mol^{-1}), K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, ka: Acidity Constant, GUS: Groundwater Ubiquity Score, BCF: Bioconcentration Factor, DT_{50}: Dissipation Half-Life, MoA: Mode of Action. The internal standards included in the method were chlorfenvinphos d_{10} and chlorpyriphos d10. It´s were purchased from Sigma Aldrich. The mechanisms of action (MoA) were derived in accordance with the methodology outlined by [1], [2]. The characteristics of the pesticides analyzed were obtained from the PubChem database, except for the GUS index and DT_{50} (days). The GUS index and DT_{50} (days) were sourced from the University of Hertfordshire's Pesticide Properties Database, accessible at https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/11.htm. Instances where physicochemical properties deviate from expected behavior are highlighted in red and bold. DT_{50} (W: Water phase only DT_{50} (days). S: Water-sediment DT_{50} (days). DT_{50} in water-sediment marked with an asterisk (*) indicates that the data pertain to soil degradation (days) under aerobic conditions).

Table S2. Chacteristics of the compounds qualitatively identified through non-target screening in this study

Compounds	Samples[a]	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
										W	S	
DEET	S	C12 H17 N O	191.2	0.019	2.02	43.3	-	-	-	-	-	Biocide
Caffeine	W	C8 H10 N4 O2	194.19	21600 (25º)	-0.07	1.85	14	-	-	-	-	Food constituent
Cotinine	W	C10 H12 N2 O	176.21	-	0.07	-	-	-	-	-	-	Food constituent
Citral	S	C10 H16 O	152.23	1340	2.76	-	-	-	-	-	-	Fragance
Methadone	W	C21 H27 N O	309.2	769	3.93	-	9.2	-	-	-	-	Illicit drug
Benzoylecgonine	W	C16 H19 N O4	289.33	-	-	-	11.8	-	-	-	-	Illicit drug
N,N'-Dicyclohexylurea	W	C13 H24 N2 O	224.34	-	-	-	13.89	-	-	-	-	Industrial
4-(Diethylamino)benzaldehyde	W	C11 H15 N O	177.24	-	-	-	3.48	-	-	-	-	Industrial
3-Methylbenzophenone	W	C14 H12 O	196.24	-	-	-		-	-	-	-	Industrial
4-Ethoxy ethylbenzoate	S	C11 H14 O3	194.23	210	-	-	-4.9	-	-	-	-	Industrial
N-Butylbenzenesulfonamide	S	C10 H15 N O2 S	213.30	460	-	-	10.19	-	-	-	-	Industrial
Tris(2-chloroethyl) phosphate	S	C6 H12 Cl3 O4 P	285.5	7820	1.78	-	-	-	-	-	-	Industrial
PEG n6	S	C12 H26 O7	-	-		-	-	-	-	-	-	Industrial
Benzenesulfonamide	S	C6 H7 N O2 S	157.19	-	-	-	10	-	-	-	-	Industrial
PEG n10	S	C20 H42 O11	-	-	-	-	-	-	-	-	-	Industrial
PEG n5	S	C10 H22 O6	-	-	-	-	-	-	-	-	-	Industrial
PEG n11	S	C22 H46 O12	-	-	-	-	-	-	-	-	-	Industrial
PPG n4	S	C12 H26 O5	-	-	-	-	-	-	-	-	-	Industrial
PEG n12	S	C24 H50 O13	-	-	-	-	-	-	-	-	-	Industrial
PEG n13	S	C26 H54 O14	-	-	-	-	-	-	-	-	-	Industrial
PEG n14	S	C28 H58 O15	-	-	-	-	-	-	-	-	-	Industrial
Diethyl phthalate	S	C12 H14 O4	222.24	1.08 (25ºC)	2.47	-	-	-	-	-	-	Industrial
Laurolactam	S	C12 H23 N O	197.32	-	-	-	-	-	-	-	-	Industrial

Compounds	Samples[a]	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
										W	S	
Hexadecanamide	S	C16 H33 N O	255.44	-	-	-	-	-	-	-	-	Industrial
Bisphenol A	S	C15 H16 O2	228.29	300 (25ºC)	3.32	636-931	9.6	-	-	-	-	Industrial
4-Methylbenzophenone	W	C14 H12 O	196.24	-	-	-	-	-	-	-	-	Industrial
PPG n5	W, S	C15 H32 O6	-	-	-	-	-	-	-	-	-	Industrial
Benzothiazole	W	C7 H5 N S	135.19	-	2.01	295	-	-	-	-	-	Industrial
N-Octyl-2-pyrrolidone	W	C12 H23 N O	197.32	-	-	-	-	-	-	-	-	Industrial
Pinocembrin	S	C15 H12 O4	256.25	-	-	-	-	-	-	-	-	Natural compound
Arachidonic acid	S	C20 H32 O2	304.5	-	-	-	-	-	-	-	-	Natural compound
Lauric acid	S	C12 H24 O2	200.32	4.81	4.6	7.6	5.3	-	-	-	-	Natural compound
Daidzein	S	C15 H10 O4	254.24	-	-	-	-	-	-	-	-	Natural compound
Palmitoleic Acid	S	C16 H30 O2	254.41	-	-	-	-	-	-	-	-	Natural compound
Carboxin	W	C12 H13 N O2 S	235.30	147	2.3	71	0.5	2.01	-	13.6	17.3	Pesticide
Pencycuron	W	C19 H21 Cl N2 O	328.8	0.3	-	-	-	0.49	-	5.3	113.5	Pesticide
Tebuthiuron	W	C9 H16 N4 O S	228.32	2.500 (25ºC)	1.79	130	1.2	5.36	-	-	360*	Pesticide
Monuron	W	C9 H11 Cl N2 O	362.0	-		150	-	-	-	-		Pesticide
Metalaxyl	W	C15 H21 N O4	279.33	8400 (22ºC)	1.65	30 to 284	-		-	56	56	Pesticide
Pyraclostrobin	W	C19 H18 Cl N3 O4	387.8	1.9	3.99	6000-16000	-	0.05	-	2	28	Pesticide
Pyrimethanil	W	C12 H13 N3	199.25	121 (25ºC)	2.84	835	3.52	2.17		6.7	81	Pesticide
Sebuthylazine-desethyl	W	C7 H12 Cl N5	201.66	-	-	-	-	-	-	-	-	Pesticide
Monodesmethylisoproturon	W	C11 H16 N2 O	192.26	-	-	-	-	-	-	-	-	Pesticide
Imazalil	S	C14 H14 Cl2 N2 O	297.18	184	2.56	4754	6.5	0.26	56.3	7.8	117	Pesticide
Propiconazole	S	C15 H17 Cl2 N3 O2	342.22	150	3.72	1086	1.1	1.58	116	6	561	Pesticide
Coumatetralyl	S	C19 H16 O3	292.3	425	3.46	3900	4.5-5.0	2.62	-	-	89*	Pesticide
Pendimethalin	S	C13 H19 N3 O4	281.31	0.33	5.2	10241-36604	2.8	-0.28	-	4	16	Pesticide

Compounds	Samples[a]	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
										W	S	
Difenoconazole	S	C19 H17 Cl2 N3 O3	406.26	15.0	4.36	3760	1.1	0.83	330	2.8	133*	Pesticide
Tricyclazole	S	C9 H7 N3 S	189.24	596	1.4	169	-	3.89	3.1	92	453	Pesticide
Clomazone	S	C12 H14 Cl N O2	239.7	1212	-	300	-	2.72	-	-	54	Pesticide
Azoxystrobin	S	C22 H17 N3 O5	403.4	6.7	2.5	207 to 594	-	3.1	Low risk	6.1	205	Pesticide
Ancymidol	S	C15 H16 N2 O2	256.30	650	-	83	-	2.45	-	-	120*	Pesticide
Tridemorph	S	C19 H39 N O	297.52	1.1	-	6250	6.5	0.28	-	26	60	Pesticide
Benthiocarb	S	C12 H16 Cl N O S	257.8	28.0 (25ºC)	3.40	-	-	0.59	-	4.4	94.9	Pesticide
Bentazone	S	C10 H12 N2 O3 S	240.3	7112	-0.46	55.3	3.5	1.95	21	80	716	Pesticide
Fludioxonil	S	C12 H6 F2 N2 O2	248.19	1.8	4.12	145600	-	-1.35	-	2	575	Pesticide
4-Acetamidoantipyrine	W	C13 H15 N3 O2	245.28	-	-	-	-	-	-	-	-	Pharmaceutical
Venlafaxine	W	C17 H27 N O2	277.4	572 mg/mL	3.20	190	10.09	-	-	-	-	Pharmaceutical
Fluconazole	W	C13 H12 F2 N6 O	306.27	1390	0.25	53000	2.27	-	-	-	-	Pharmaceutical
Propranolol	W	C16 H21 N O2	259.34	61.7 (25ºC)			9.42	-	-	-	-	Pharmaceutical
Amitriptyline	W	C20 H23 N	277.4	9.71 (24ºC)	4.92	3530	9.49	-	-	-	-	Pharmaceutical
4-Formylaminoantipyrine	W	C12 H13 N3 O2	203.24	-	-	-	-	-	-	-	-	Pharmaceutical
Flecainide	W, S	C17 H20 F6 N2 O3	414.34	32.4	-	-	9.3	-	-	-	-	Pharmaceutical
Monensin	W	C36 H62 O1	670.9	6.33	5.43	125-5700	4.2	-	-	-	-	Pharmaceutical
Oleandrin	W	C32 H48 O9	576.7	Practically insoluble	2.53	730	-	-	-	-	-	Pharmaceutical
Azithromycin	W	C38 H72 N2 O12	749.0	minimally soluble	4.02	3100	8.74	-	-	-	-	Pharmaceutical
Candesartan	W	C24 H20 N6 O3	440.5	7.71	-	-	-	-	-	-	-	Pharmaceutical
Sitagliptin	W	C16 H15 F6 N5 O	407.31	34	1.39	3400	-	-	-	-	-	Pharmaceutical
Benzydamine	W, S	C19 H23 N3 O	309.4	49.1	-	-	9.27	-	-	-	-	Pharmaceutical
Tapentadol	W, S	C14 H23 N O	221.34	780	-	-	9.34-10.45	-	-	-	-	Pharmaceutical

Compounds	Samples[a]	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
										W	S	
Valsartan	W	C24 H29 N5 O3	435.5	23.4	4	2.3X10+4	4	-	-	-	-	Pharmaceutical
Losartan	W	C22 H23 Cl N6 O	422.9	4.70	4.01	1.4X10+6	5.50	-	-	-	-	Pharmaceutical
Fenofibric acid	W	C17 H15 Cl O4	318.7	5.1	-	-	3.1	-	-	-	-	Pharmaceutical
10-Hydroxycarbazepine	W	C15 H14 N2 O2	254.28	-	-	-	-	-	-	-	-	Pharmaceutical
Clopidogrel carboxylic acid	W	C15 H14 Cl N O2 S	307.8	-	-	-	-	-	-	-	-	Pharmaceutical
Rosuvastatin	W	C22 H28 F N3 O6 S	481.5	Sparingly soluble	0.13	48	4.0	-	-	-	-	Pharmaceutical
Phenazone	W	C11 H12 N2 O	188.23	51900 (25ºC)	-	-	1.4	-	-	-	-	Pharmaceutical
Lamotrigine	W	C9 H7 Cl2 N5	256.09	170 (25ºC)	2.57	1900	8.53	-	-	-	-	Pharmaceutical
Irbesartan	W	C25 H28 N6 O	428.5	Practically insoluble in water	5.31	1.3X10+6	4.08 and 4.29	-	-	-	-	Pharmaceutical
Olmesartan	W	C24 H26 N6 O3	446.5	Insoluble	3.63	1.2X10+4	4.96 and 5.57	-	-	-	-	Pharmaceutical
Diclofenac	W	C14 H11 Cl2 N O2	296.1	2.37 (25ºC)	4.51	245	4.15	-	-	-	-	Pharmaceutical
Quinine	W	C20 H24 N2 O2	324.4	500 (15ºC)	3.44	-	8.56	-	-	-	-	Pharmaceutical
Dextrorphan	W	C17 H23 N O	257.37	173	-	-	10.46	-	-	-	-	Pharmaceutical
Levamisole hydrochloride	W	C11 H12 N2 S	240.75	1440	-	-	6.98	-	-	-	-	Pharmaceutical
Carbamazepine	W	C15 H12 N2 O	236.27	152	2.45	510	13.9	-	-	-	-	Pharmaceutical
Ricinine	W	C8 H8 N2 O2	164.16	-	-	-	-	-	-	-	-	Pharmaceutical
Sulpiride	W	C15 H23 N3 O4 S	341.4	537	-	-	9.12	-	-	-	-	Pharmaceutical
Doxylamine	W	C17 H22 N2 O	270.37	541	-	-	8.87	-	-	-	-	Pharmaceutical
Temazepam	W	C16 H13 Cl N2 O2	300.74	53.4	-	-	10.68	-	-	-	-	Pharmaceutical
Flufenamic acid	W	C14 H10 F3 N O2	281.23	9.09 (25ºC)	-	-	4.09	-	-	-	-	Pharmaceutical
Diazepam	W	C16 H13 Cl N2 O	284.74	50 (25ºC)	2.82	192 to 630	3.4	-	-	-	-	Pharmaceutical
Oxazepam	W	C15 H11 Cl N2 O2	286.71	20 (22ºC)	2.24	390	1.55	-	-	-	-	Pharmaceutical
Niflumic acid	W	C13 H9 F3 N2 O2	282.22	19 (25ºC)	-	-	1.88	-	-	-	-	Pharmaceutical

Compounds	Samples[a]	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)		MoA
										W	S	
Paclobutrazol	W	C15 H20 Cl N3 O	293.79	22,9	-	-	-	-	-	-	-	Pharmaceutical
Telmisartan	W	C33 H30 N4 O2	514.6	Practically insoluble	-	-	3.62	-	-	-	-	Pharmaceutical
Rhodamine 6G	W	C28 H30 N2 O3	479.0	0.496	-	-	5.58	-	-	-	-	Pharmaceutical
Palmitoyl ethanolamide	W	C18 H37 N O2	299.5	1.36	-	-	15.46	-	-	-	-	Pharmaceutical
Lorazepam	W	C15 H10 Cl2 N2 O2	321.2	17.6	-	-	13	-	-	-	-	Pharmaceutical
Neostigmine	W	C12 H18 N2 O2	223.29	67.7	-	-	5	-	-	-	-	Pharmaceutical
Simvastatin	S	C25 H38 O5	418.6	12.2	4.68	940	14.91	-	-	-	-	Pharmaceutical
Codeine	S	C18 H21 N O3	299.4	577	1.19	700.	8.21	-	-	-	-	Pharmaceutical
Etoricoxib	S	C18 H15 Cl N2 O2 S	358.8	3.28	-	-	16.19	-	-	-	-	Pharmaceutical
Fenofibrate	S	C20 H21 Cl O4	360.8	Practically insoluble	5.2	3800	-4.9	-	-	-	-	Pharmaceutical
Triclocarban	S	C13 H9 Cl3 N2 O	315.6	0.11	4.342	12.000 to 71.687	12.7	-	-	-	-	Pharmaceutical
Dicyclohexylamine	W	C12 H23 N	181.32	800 (25ºC)	4.37	260	10.4	-	-	-	-	Tire compound

[a](W: Water; S: Sediment); MW: Molecular Weight (g mol^{-1}), K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, k_a: Acidity Constant, GUS: Groundwater Ubiquity Score, BCF: Bioconcentration Factor, DT_{50}: Dissipation Half-Life, MoA: Mode of Action. The mechanisms of action (MoA) were derived in accordance with the methodology outlined by [1], [2]. The characteristics of the compounds identified were obtained from the PubChem database and DrugBank Online, except for the GUS index and DT_{50} (days). The GUS index and DT_{50} (days) were sourced from the University of Hertfordshire's Pesticide Properties Database, accessible at https://sitem.herts.ac.uk/aeru/ppdb/en/Reports/11.htm. Instances where physicochemical properties deviate from expected behavior are highlighted in red and bold. DT_{50} (W: Water phase only DT_{50} (days). S: Water-sediment DT_{50} (days). DT50 in water-sediment marked with an asterisk (*) indicates that the data pertain to soil degradation (days) under aerobic conditions).

Text S1. Reagents and chemicals

Solvents used included HPLC grade methanol (LC grade, 99.8% purity) were purchased from VWR Chemicals® (Radnor, PA, USA) and ammonium formate (NH_4HCO_2), formic acid (CH_2O_2), ammonium fluoride (NH_4F) and acetone (CH_3COCH_3) were purchased from Alfa Aesar (Karlsruhe, Germany). Acetonitrile (ACN) ≥ 99.9% purity was from Merck (Darmstadt, Germany). High purity water was obtained using a Milli-Q water purification system (Millipore, Milford, MA, USA).

Primary-secondaryamine (PSA) and C_{18} were from Análisis Vínicos (Tomelloso, Spain), magnesium sulfate ($MgSO_4$) and sodium sesquihydrate citrate [$HOC(COOH)$ $(CH_2COONa)_2$ 1.5 H_2O] from Alfa Aesar (Karlsruhe, Germany) and sodium chloride (NaCl) and trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$) from Prolabovwr (Leuven, Belgium).

The 15 mL and 50 mL polypropylene centrifuge Falcon tubes were from VWR International Eurolab (Barcelona, Spain). Strata-X-33 µm polymeric reversed phase (200 mg/6 mL) were from Phenomenex (Torrance, CA, USA). The 1.5 mL amber glass vials with stoppers 99 mm + Septum Sil /PTFE used to inject the samples were from Análisis Vínicos S.L. (Tomelloso, Spain) and the 250 µL polypropylene inserts were from Agilent Technologies (Santa Clara, CA, United States). Nylon 0.22 µm filters were purchased from Membrane Solutions (Plano, TX, USA). Polypropylene/polyethylene syringes were manufactured by BRAUN and distributed by Scharlab S.L. (Barcelona, Spain). For the solid phase extraction (SPE) Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL) cartridges and a vacuum manifold Supelco Visiprep 57030- U (Sigma-Aldrich, St. Louis, Missouri, USA) were used.

Text S2. Instrumental characteristics used for pesticides (target) determination and Non-Target Analysis (NTA)

For the analysis of pesticides via targeted analysis, the flow rate was maintained at 0.4 mL min^{-1}. In contrast, for NTA in both positive and negative ionization modes, the flow rate was set at 0.2 mL min^{-1}, and the injection volume was set at 5 µL. The column temperature was held at 30 ºC. The mobile phases for pesticides consisted of 0.1% formic acid and 5 mM ammonium formate in Milli-Q water (A) and 0.1% formic acid and 5 mM ammonium formate in methanol (MeOH) (B). For NTA under positive ionization, the mobile phases comprised 0.1% formic acid in Milli-Q water (A) and 0.1% formic acid in methanol (MeOH) (B). For NTA under negative ionization, the mobile phases comprised 2.5 mM ammonium fluoride in Milli-Q water (A) and 2.5 mM ammonium fluoride in methanol (MeOH) (B). The column utilized for pesticide analysis was a Luna C18 (15.0 cm × 0.21 cm) with a 3 µm particle size (Phenomenex, USA). For non-targeted analysis (NTA), a Kinetex Biphenyl column with a 1.7 µm particle size, measuring 50 × 2.1 mm, was employed (Phenomenex, USA). The linear gradient for pesticide analysis was as follows: 0 min (50% B), 10 min (83% B), 12 min (83% B), 12.5 min (98% B), 15.5 min (98% B), 16 min (50% B), followed by a return to the initial conditions with an equilibration time of 10 minutes. For NTA in both positive and negative ionization modes, the gradient was as follows: 0 min (30% B), 12 min (95% B), 20 min (95% B), followed by a return to the initial conditions with an equilibration time of 12 minutes. The survey scan type employed was a comprehensive scan mass spectrum ranging between m/z 100-1000. The ion source properties included a spray voltage of 3500 V for positive ions and 2500 V for negative ions. The ion transfer tube temperature was maintained at 320ºC, while the vaporizer temperature was set at 350ºC.

Text S3. Statistical analysis

TARGET COMPOUNDS

ANOVA

ANOVA analysis has been applied to the concentration of each target pesticide and the values of water physicochemical characteristics to determine if there are statistically significant differences between water sources, land uses, and sampling seasons. No statistical differences were observed between sampling seasons for any studied compound. Regarding water sources, differences were observed for Bensulfuron methyl, Tebuconazole, and Terbumeton-desethyl. In the first case, the concentration of bensulfuron methyl is significantly different in the Albufera Lake from the other water sources. Tebuconazole showed different behavior in the water at the floodgate that in the river water and the channels for citric irrigation. Similarly, Terbumeton-desethyl had a different statistical performance in the water at the floodgates than in river waters.

Different land uses showed statistically significant differences for Bensulfuron methyl, Diuron, Isoproturon, and Tricyclazole. Clear differences were observed again for Bensulfuron methyl comparing water from irrigation channels with different land uses and the water from the lake. Diuron and Isoproturon showed statistically significant differences between the water used to irrigate citrus orchards and those that surround riparian vegetation. Tricyclazole exhibited significant differences between concentrations in water from rice fields and in water from citrus orchards. The other compounds did not show significant differences across water types or land uses.

CORRELATIONS

The intrinsic water characteristics more correlated with the detected compounds were temperature, TDS, electric conductivity, NaCl, dissolved oxygen, and mV. This indicates the strong influence of salinity-related parameters (electric conductivity, NaCl, and mV) in the dynamics of these compounds.

This fact is reflected by the multiple stepwise linear regression models obtained for the following compounds:

[Bensulfuron methyl] = -19.130 + 1.025 [T]	R^2= 0.073	Sig.= 0.007
[Buprofezin] = 2.092 – 0.085 [T]	R^2= 0.048	Sig.= 0.029
[Carbendazim] = 3.721 + 0.002 [Res]	R^2= 0.065	Sig.= 0.011
[Chlotianidin]= 46.596 – 1.934 [T]	R^2= 0.044	Sig.= 0.036
[Diuron]= 9.715 - 0.092 [mV]	R^2= 0.100	Sig.= 0.001

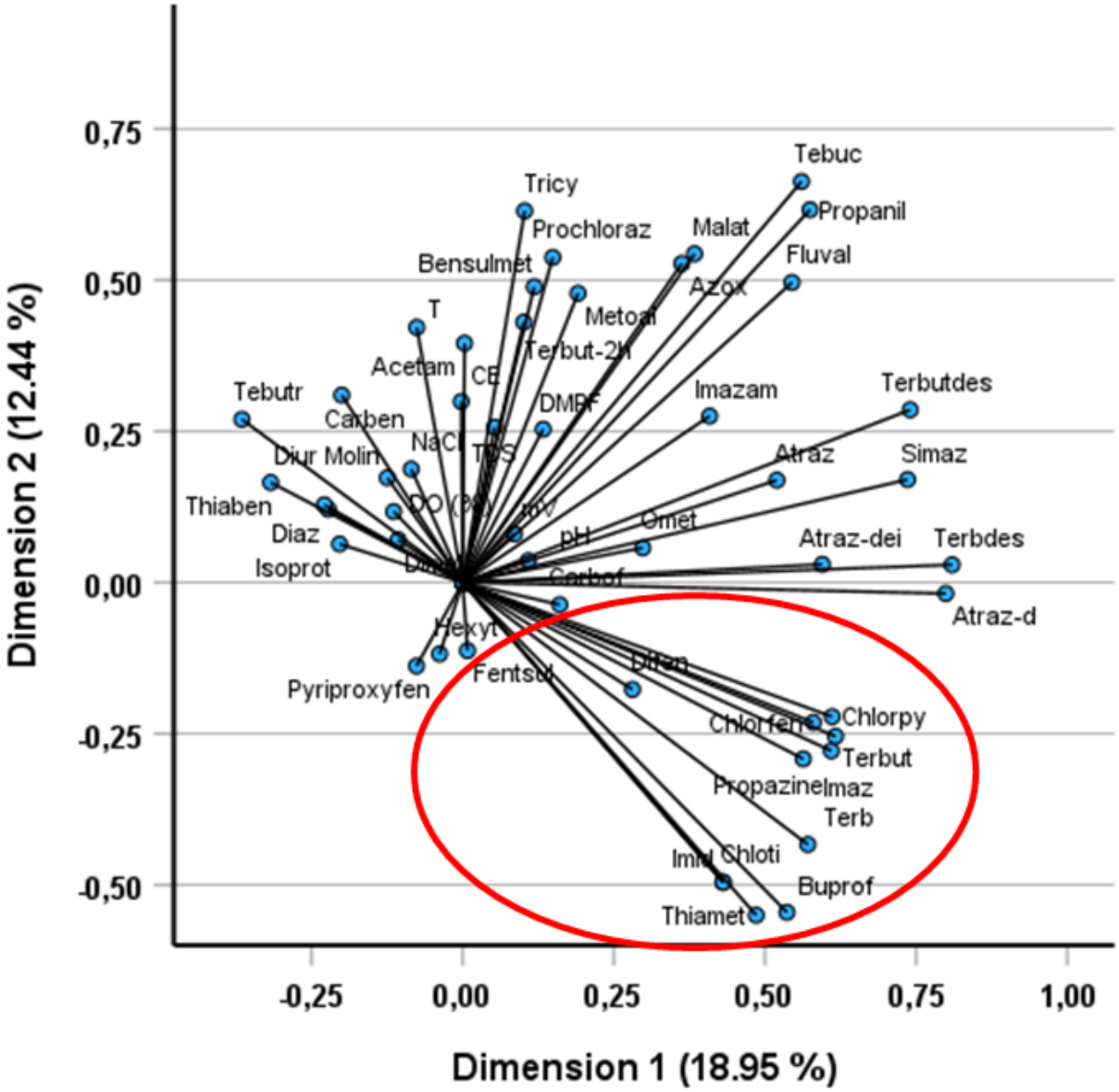
[DMPF] = 2300 + [NaCl] – 0.287 [pH]	R^2= 0.102	Sig.= 0.005
[Fenthion sulfoxide] = - 0.625 + 0.119 [DO]	R^2= 0.060	Sig.= 0.014
[Imazamox] = - 0.706 + 0.137 [DO]	R^2= 0.065	Sig.= 0.011
[Imidacloprid] = 3254.090 – 136.312 [T]	R^2= 0.044	Sig.= 0.036
[Isoproturon] = 0.753 - 0.008 [mV]	R^2= 0.00.055	Sig.= 0.019
[Malathion] = - 1.216 +0.003 [NaCl]	R^2= 0.095	Sig.= 0.002
[Molinate] = - 0.498 + 0.002 [TDS]	R^2= 0.212	Sig.= 0.001
[Prochloraz] = - 31.536 + 2.937 [T] – 3.912 [DO]	R^2= 0.263	Sig.= 0.001
[Terbuthylazine] = 329.808 – 10.475 [T]	R^2= 0.042	Sig.= 0.041
[Terbuthylazine-2-hydroxy] = -18.288 + 19.861 [EC]	R^2= 0.327	Sig.= 0.001
[Thiamethoxan] = 1149.577 – 48.403 [T]	R^2= 0.044	Sig.= 0.035
[Tricyclazol] = -100.491 + 0.022 [TDS] + 4.854 [T] – 0.068 [NaCl] + 31.593 [EC]	R^2= 0.442	Sig.= 0.001

T: Temperature. Res: Resistivity. mV: Millivolts. TDS: Total dissolved solids. EC: Electric conductivity. DP: Dissolved oxygen. NaCl: Sodium chloride.

PRINCIPAL COMPONENT ANALYSIS (PCA)

The PCA performed is not highly reliable, explaining only 31.39% of the variance. Anyway, it is reflected in a group of compounds not affected by the studied water characteristics while the other compounds are.

This mentioned group includes: Buprofezin, Thiametoxan, Chlotianidin, Imidacloprid, Terbumeton, Imazalil, Propazine, Terbuthylazine, Chlorfenvinphos, Chlorpyrifos and Difenoconazole.



NON TARGET COMPOUNDS

ANOVA

No statistically significant differences were seen between sampling seasons in all the compounds. In the case of water sources or uses, only were observed significant differences for Ricinine. This compound showed significant differences between waters from the inlet and the rice fields with the waters for citrus crops channels regarding source types. The differences between water uses for Ricinine appeared between citrus crops and rice fields.

CORRELATIONS

From the 72 compounds detected, 36 of them shown significant (P= 0.005) or highly significant (P= 0.001) correlations with the intrinsic water parameters, mainly temperature, millivolts (electrical potential), TDS, electric conductivity and NaCl. Millivolts (mV) is the parameter most correlated with almost all the compounds (77.78%). In the same way that for target compounds, mainly the electric characteristics of waters or the salts content are driven the dynamics of these compounds, although accompanied in less extent but temperature and total dissolved solids (TDS). This fact is reflected also by the multiple stepwise linear regression models obtained for the following compounds:

[Pencycuron] = 18592330.371 - 2453847.867 [DO]	R^2= 0.083	Sig.= 0.031
[Dyciclohexylamine] = 33683385.488 – 1301353.080 [T]	R^2= 0.122	Sig.= 0.008
[Azithromycin] = 13854496.880 + 191702.926 [mV]	R^2= 0.079	Sig.= 0.036
[Valsartan] = -74081877.290 + 1258292.119 [mV] + 7954123.152 [T]	R^2= 0.153	Sig.= 0.012
[Fenofibric acid] = 8459908.058 + 114856.69 [mV]	R^2= 0.097	Sig.= 0.011
[Rosuvastatin] = 3877662.862 + 52172.977 [mV]	R^2= 0.102	Sig.= 0.017
[Cotinine] = 2160142.655 + 2228.781 [TDS]	R^2= 0.107	Sig.= 0.014
[Olmesartan] = 31407780.761 + 405559.284 [mV]	R^2= 0.094	Sig.= 0.021
[Rhodamine 6G] = -630679.103 + 7781.927 [TDS]	R^2= 0.138	Sig.= 0.005

T: Temperature. mV: Millivolts. TDS: Total dissolved solids. DO: Dissolved oxygen.

PRINCIPAL COMPONENT ANALYSIS (PCA)

From the correlations obtained and the variables refined by the models, the results gave a highly significant PCA, explaining the 84.90 % of the variance (dimension 1 explains the 71.70 % and dimension 2 the13.20 %). In the graphic, two groups are differentiated:

Grupe A with Carbamacepine, Cotinine, Dyciclohexylamine, Flecainide, Irbesartan, Metalaxil, Olmesartan, Tapentadol, Valsartan and Venlafaxine, all of them mostly related to TDS.

Grupe B with 10-Hydroxicarbazepine, Azithromycin, Benzydamine, Fenofibric acid, Lamotrigine, Methadone, Niflumic acid, Oxazepam, Rhodamine 6G, Rosuvastatin, Sulpiride and Temazepam, all of them mostly related to mV.

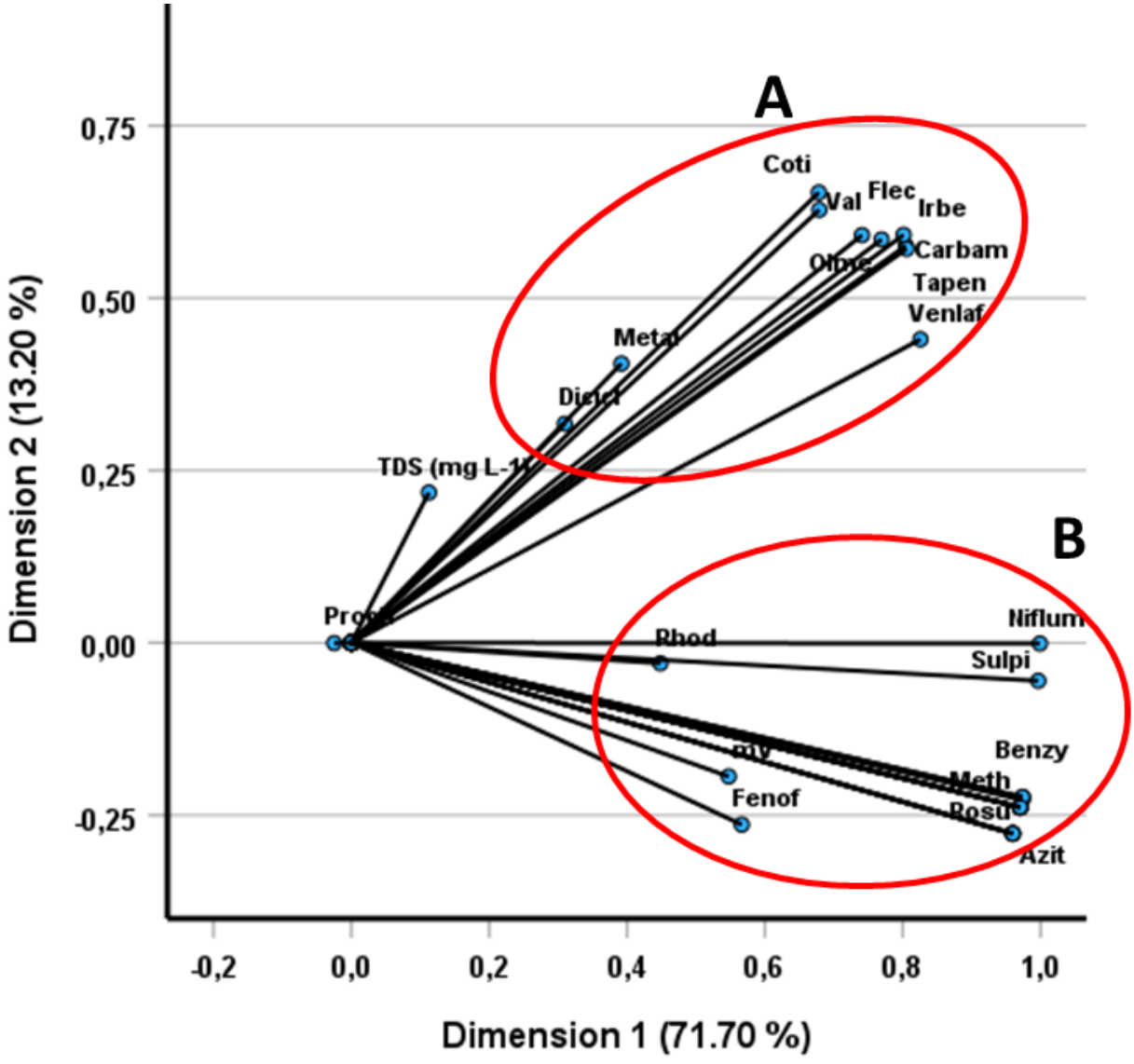


Figure S1. Cumulative concentrations (total sum of the measured concentrations) of fungicides, insecticides, herbicides and other in sediment samples.

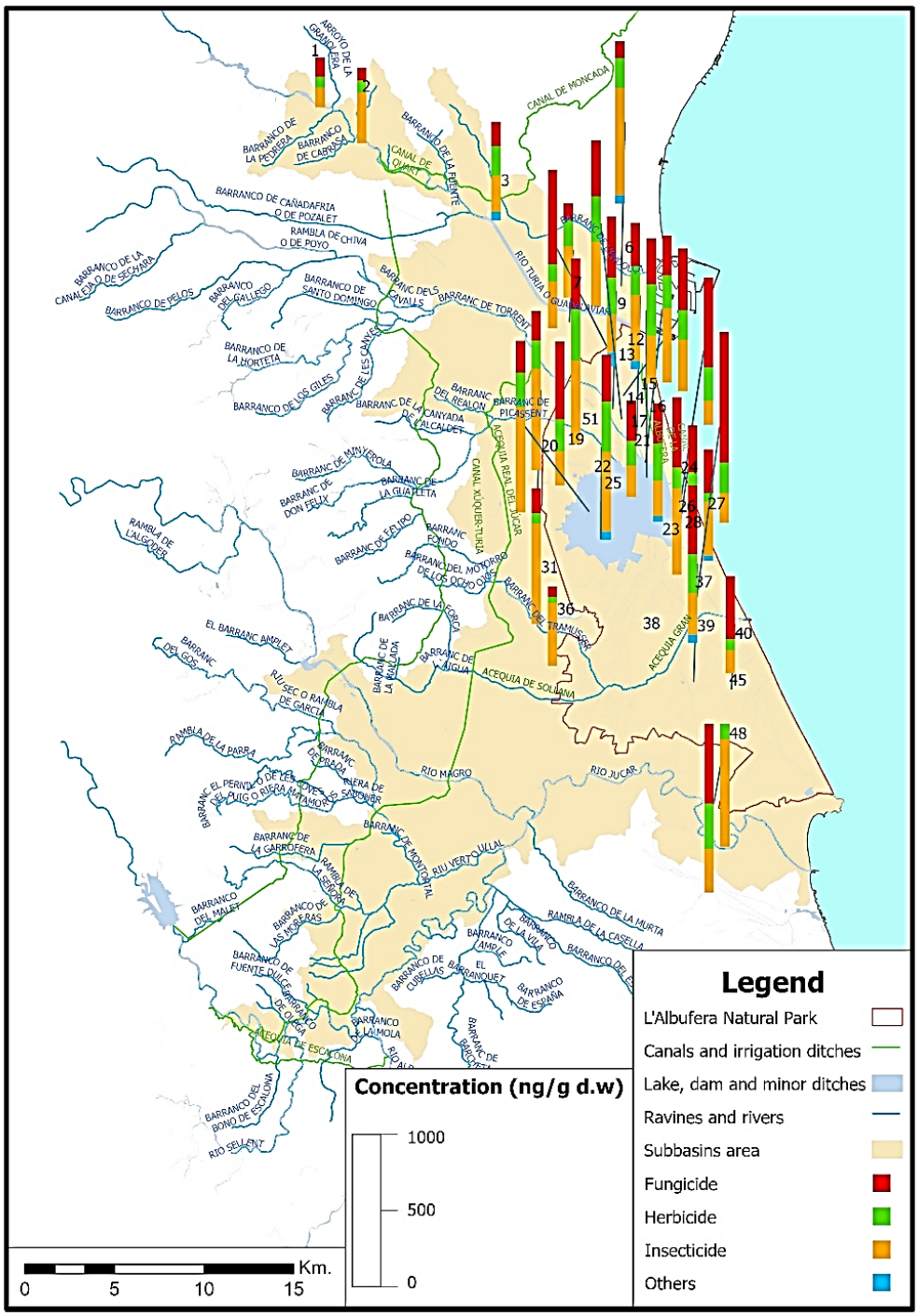
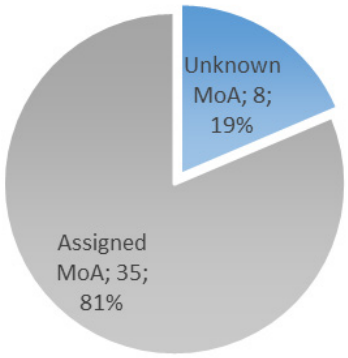
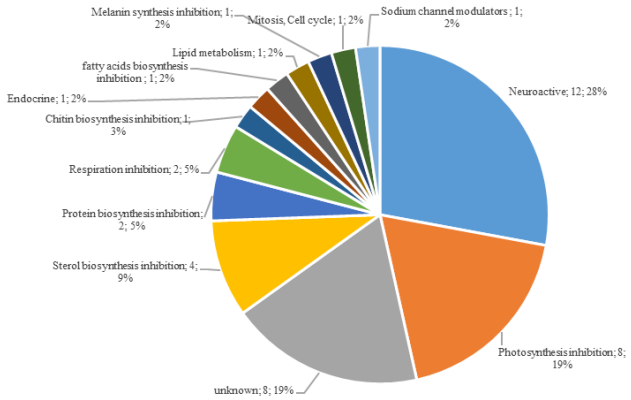


Figure S2. Mode of action information for target pesticides quantified. A: fraction of assigned and unknown MOAs. B: pie-chart of MOA information of target pesticides quantified (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A)



B)



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ARTICLE 02

Data on the profile of emerging contaminants in the L'albufera Natural Park (2019-2020). Target and non-target screening

Contents lists available at ScienceDirect

Data in Brief

journal homepage: www.elsevier.com/locate/dib

Data Article

Data on the profile of organic contaminants in the L'Albufera Natural Park (2019–2020). Target and non-target screening

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ARTICLE INFO

Article history:
Received 28 August 2024
Revised 17 September 2024
Accepted 24 September 2024
Available online 16 October 2024

Dataset link: Dataset of emerging contaminants in LÁlbufera Natural Park (2019–2020) by target and non-target screening using high resolution mass spectrometry (Original data)

Keywords:
Pesticides
Pharmaceuticals
Industrial compounds
Spatial distribution
Sediments
Surface waters

ABSTRACT

This article presents a dataset on 71 pesticide levels and the identification of additional synthetic organic chemicals, including pharmaceuticals and industrial compounds, in L'Albufera Natural Park (Valencia, Spain). Sampling was conducted during May–June (spring) and end of September–October (autumn) 2019, timed to the rice cultivation cycle, the region's main agricultural activity. A total of 130 samples (100 water and 30 sediments) were collected from 51 strategically selected sites, including rivers, irrigation channels, Albufera Lake, and Mediterranean outlets, utilizing a combination of targeted and non-targeted screening (NTS) methods. The dataset encompasses physical-chemical parameters for both spring and autumn seasons. Advanced analytical techniques, such as high-resolution mass spectrometry (HRMS), were employed to detect contaminants beyond traditional methods, providing critical insights for environmental management and policy development. The findings contribute to addressing gaps in knowledge regarding

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https://doi.org/10.1016/j.dib.2024.111021
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contaminants of emerging concern (CECs) and their distribution across different environmental compartments. These data supplement the findings of the research article "Fingerprinting of Emerging Contaminants in L'Albufera Natural Park (Valencia, Spain): Implications for Wetland Ecosystem Health".

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Specifications Table

Subject	Environmental Sciences – Pollution
Specific subject area	Detection and quantification of pesticides by target and non-target screening (NTS) and identification of other CECs by non-target analysis in LÁlbufera Natural Park in water and sediment samples.
Type of data	Raw, Analysed, Filtered Tables, Figures
Parameters for data collection	The mobile phase for pesticides was (A) Water and (B) methanol both with 0.1 % Formic Acid and 5 mM Ammonium formate. The mobile phase for polar compounds using NTS was (A) Water and (B) methanol both with 0.1 % formic acid for positive ionization and 2.5 mM NH_4F for negative ionization
Data collection	Data was generated from the analysis of samples of water and sediment obtained in fifty-one sampling points during spring and autumn of 2019. Target analysis and NTS was conducted using a reversed-phase liquid-chromatography (LC) separation employing a Vanquish Flex UHPLC consisted of a binary pump, a split sampler and a column compartment and HRMS using Thermo Scientific™ Orbitrap Exploris™ 120 high-resolution mass spectrometer equipped with a heated electrospray ionization (HESI) source. Targeted compounds were checked manually using the vendor software TraceFinder (version 4.1, Thermo Scientific). NTS results were analysed using Compound Discoverer 3.2 (Thermo Fisher Scientific, Software for HRMS data treatment) implementing the workflow for environmental samples and using mzCloud (On-line) as MS-library. Default workflow was named "Environmental w Stats Unknown ID w Online and Local Database Searches"
Data source location	Institution: *University of Valencia, Research Centre on Desertification (CIDE)* *City/Town/Region: Moncada, Community of Valencia* *Country: Spain*
Data accessibility	Repository name: Mendeley Direct URL to data: https://data.mendeley.com/datasets/n44rpfms7b/1
Related research article	[1] Fingerprinting of Emerging Contaminants in L'Albufera Natural Park (Valencia, Spain): Implications for Wetland Ecosystem Health Yolanda Soriano[1,*], Emilio Doñate[2], Sabina Asins[2], Vicente Andreu[1], Yolanda Picó[1]. Chemosphere

1. Value of the Data

- The dataset comprises the first detailed open access record of Non-Target Screening (NTS) in surface water and sediments samples in LÁlbufera Natural Park.
- Concentration values of pesticides and identification of anthropogenic chemicals such as industrial compounds and pharmaceuticals can be used by other researchers and local authorities.
- This data is useful for clearly understand the spatial distribution of contaminants and will help researchers on planning for further research studies within this area and for comparison studies (temporal and spatial ones).

- The datasets are relevant for performing a more appropriate environmental diagnostic. National and international authorities, wastewater treatment plant managers and researchers could estimate occurrence, transport and fate of emerging contaminants.

2. Background

This dataset supports a related research article that examines the occurrence of pesticides and other compounds in surface water and sediments from L'Albufera Lake (Valencia, Spain). The assessment encompasses several innovative aspects of environmental significance: it establishes the pathways through which emerging pollutants enter the natural wetland using both target and non-target screening (NTS) methods for management purposes, and it identifies specific contamination hotspots through Geographic Information Systems (GIS).

3. Data Description

Samples were collected from fifty-one sampling sites along LÁlbufera Natural Park, Valencia, in two sampling campaigns conducted during spring (May-June) and Autumn (September-October), tailored to the rice cultivation season, which is the primary activity in the region. Sampling sites were selected based on the type of land use in the surrounding area. This allowed us to characterize sites with different levels of anthropogenic impact. Fig. 1 shows the location of LÁlbufera Natural Park, as well as the location of the fifty-one sampling points.

The data were saved and stored in Mendeley Data. There are three excel raw data files. A complete folders structure can be seen in Table 1.

Furthermore, within the main text the following Figures and Tables summarizing most important information are provided:

- Fig. 2 illustrates the grab water samples extraction.
- Fig. 3 illustrates the sediment extraction for moderately polar compounds.
- Fig. 4 illustrates the sediment extraction for polar compounds.
- Table 2 provides information on the instrumentals characteristics used for pesticides (target) determination and Non-Target Screening (NTS).
- Fig. 5 show the workflow "Environmental w Stats Unknown ID w Online and Local Database Searches" in Compound Discoverer software.
- Fig. 6 exemplifies the total concentrations of fungicides, herbicides, insecticides, and other compounds by target analysis in water samples in spring (left), autumn (middle) and sediment samples (right).
- Fig. 7 show the highest median concentrations of quantified pesticides in at least one sampling site in surface water samples.
- Fig. 8 show the highest median concentrations of quantified pesticides in at least one sampling site in sediment samples.

Table 1
Folder structure from Mendeley data link.

File path	File description
Data of the physical-chemical parameters	Excel file that contains raw data on physical-chemical parameters, such as T: temperature, mV: oxidation–reduction potential, CE: conductivity, TDS: Total Dissolved Solids, DO: dissolved oxygen
Result Target and Non-Target WATER	Excel files that contain raw data on pesticides quantified in surface water samples, compounds identified using NTS, Risk Assessment, Modes of Action (MoA)
Result Target and Non-Target SEDIMENT	Excel files that contain raw data on pesticides quantified in sediment samples, compounds identified using NTS, and MoA

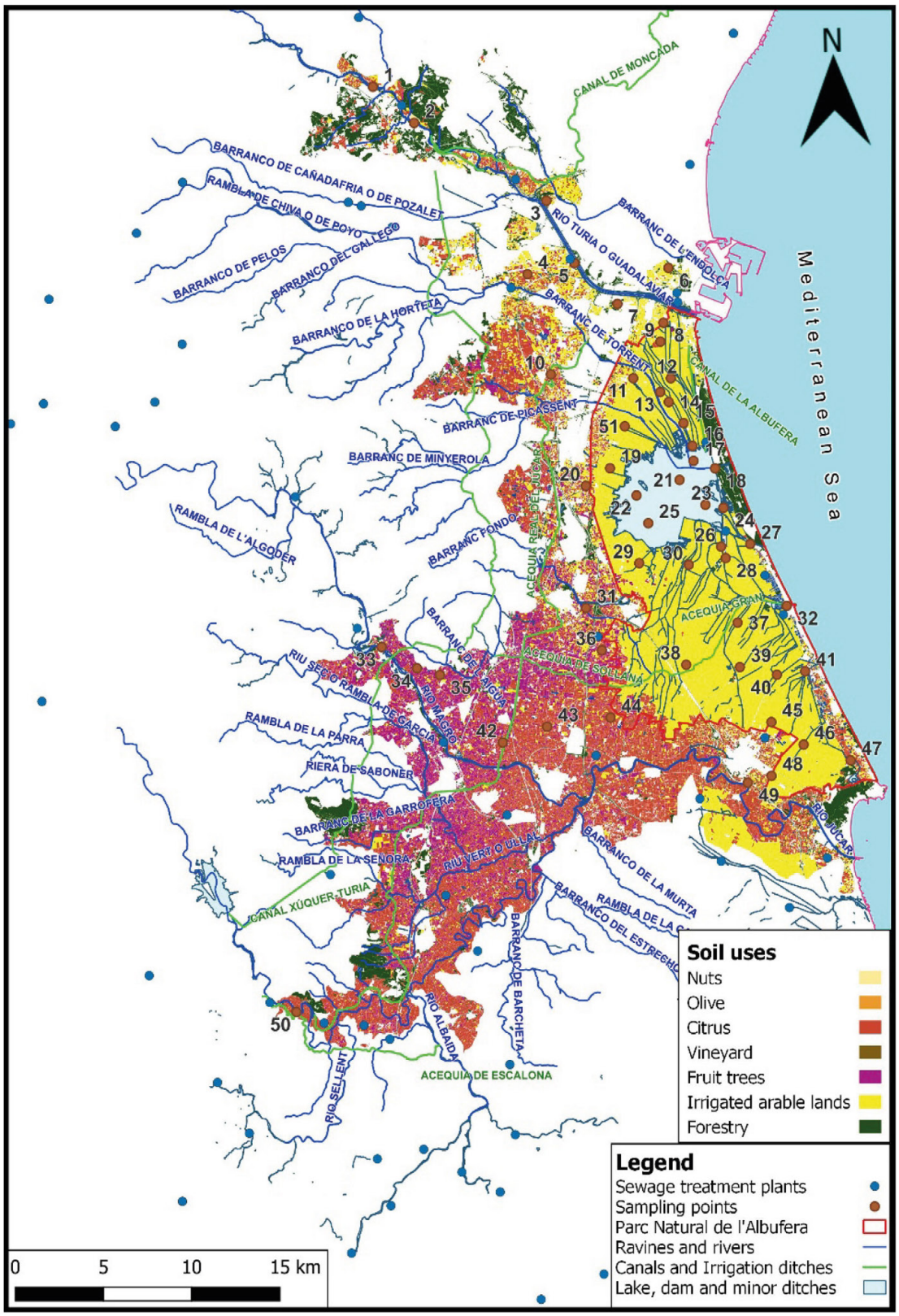


Fig. 1. Location of LÁlbufera Natural Park, as well as the location of the sampling points and agricultural land use.

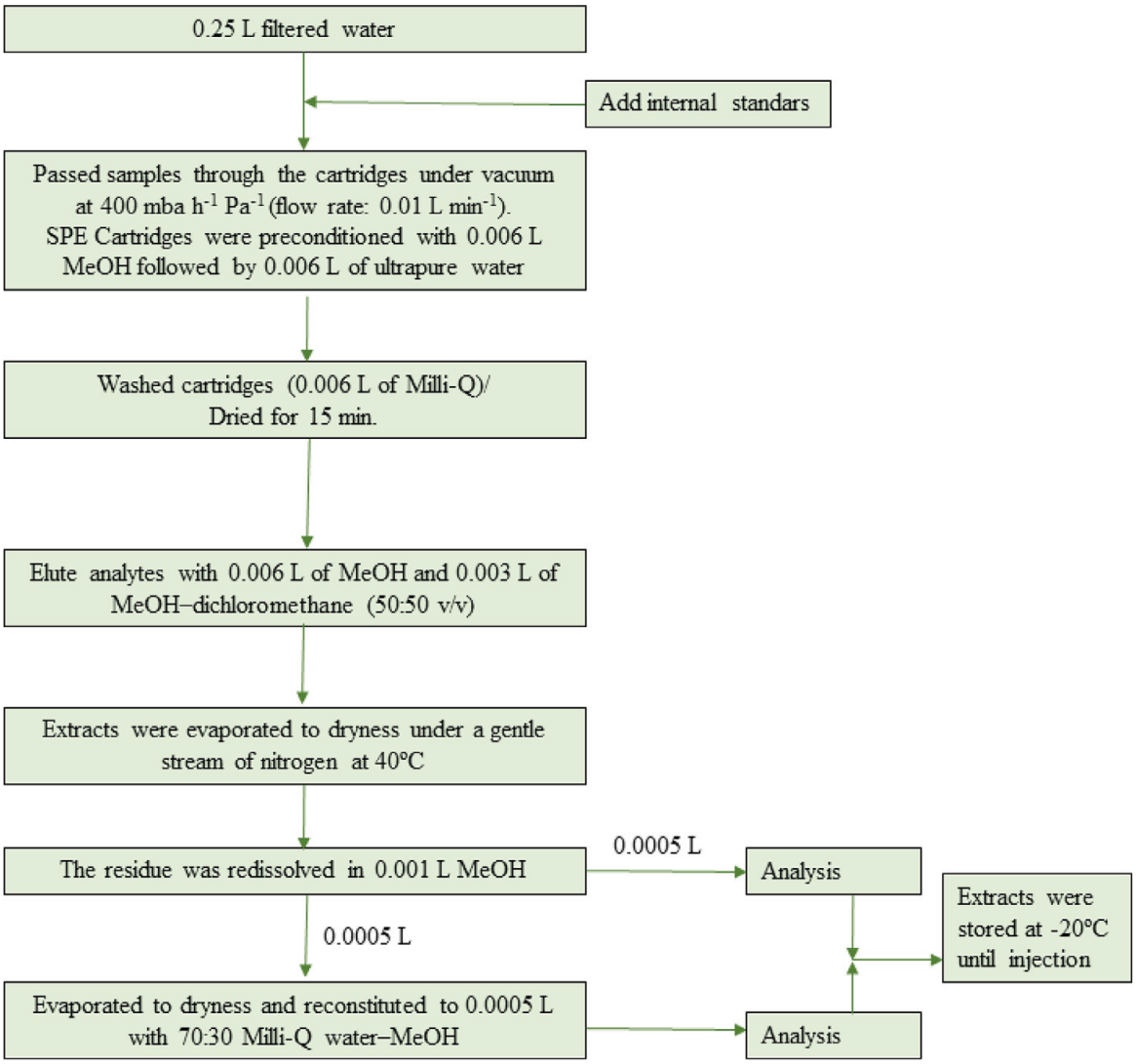


Fig. 2. Grab water samples extraction.

Table 2
Instrumental characteristics used for pesticides (target) determination and Non-Target Screening (NTS).

LC Conditions	
Analytical column	*Pesticides:* Luna C18 (15.0 cm × 0.21 cm) with a 3 µm particle size (Phenomenex, USA) *NTA (for positive and negative mode):* Kinetex 1.7 µm Biphenyl, 1.7 µm. 50 × 2.1 mm, (Phenomenex, USA)
Column temperature	30 °C
Volume injected	5 µL
Mobile phase	*Pesticides:* (A) Water – (B) methanol both with 0.1 % Formic Acid and 5 mM Ammonium formate *NTS (for positive mode):* (A) Water – (B) methanol both with 0.1 % Formic Acid *NTS (for negative mode):* (A) Water – (B) methanol both with 2.4 mM Ammonium fluoride
Flow rate	*Pesticides:* 0.4 mL min^{-1} *NTS (for positive and negative mode):* 0.2 mL min^{-1}
Linear gradient	*Pesticides:* 0 min (50 % B), 10 min (83 % B), 12 min (83 % B), 12.5 min (98 % B), 15.5 min (98 % B), 16 min (50 % B), and return to the initial conditions (equilibration time 10 min). *NTS (for positive and negative mode):* 0 min (30 % B), 12 min (95 % B), 20 min (95 % B), and return to the initial conditions (equilibration time 12 min).

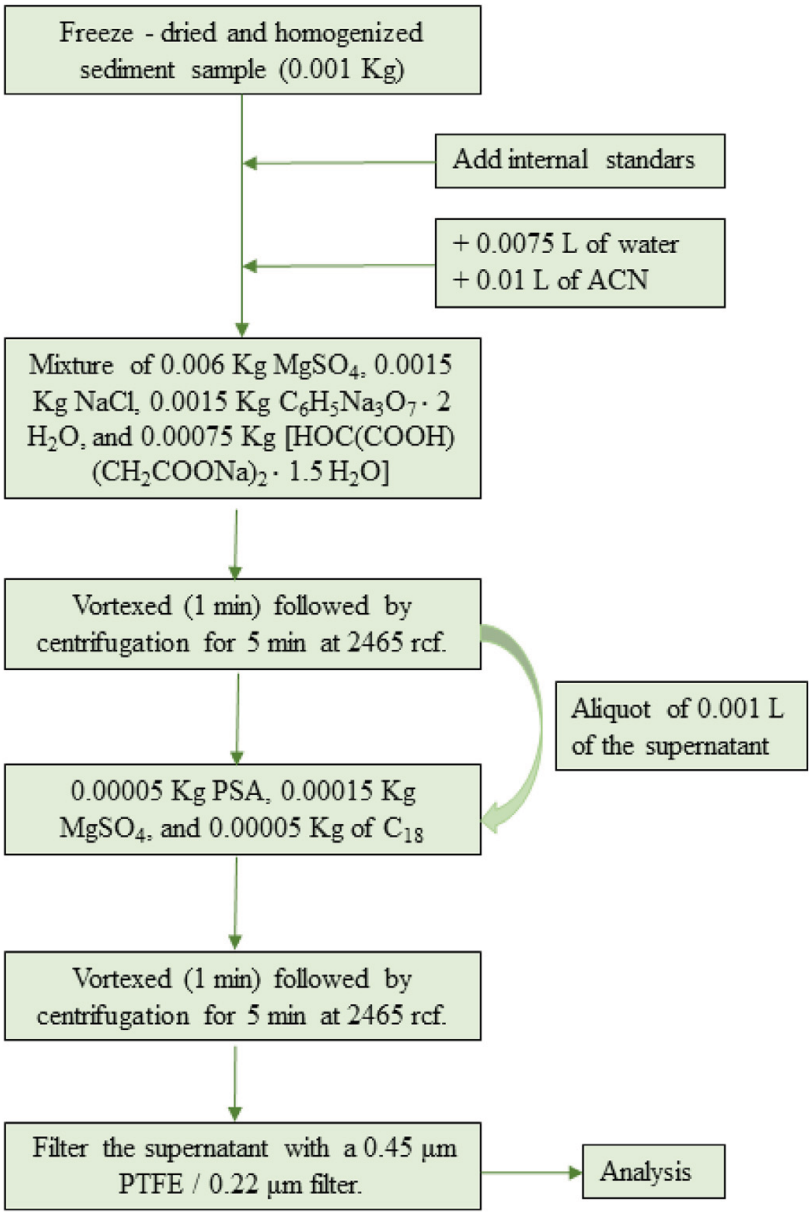


Fig. 3. Sediment extraction for moderately polar compounds.

- Figs. 9–11 illustrates the spatial distribution of quantified pesticides in two seasons for water samples and in sediment samples for spring based on compound concentrations (ng L^{-1} or ng g^{-1}) detected in the study sites.

4. Experimental Design, Materials and Methods

4.1. Reagents and chemicals

Solvents used included HPLC grade methanol (LC grade, 99.8 % purity) were purchased from VWR Chemicals® (Radnor, PA, USA) and ammonium formate (NH_4HCO_2), formic acid (CH_2O_2), ammonium fluoride (NH_4F) and acetone (CH_3COCH_3) were purchased from Alfa Aesar (Karlsruhe, Germany). Acetonitrile (ACN) ≥ 99.9 % purity was from Merck (Darmstadt, Germany). High purity water was obtained using a Milli-Q water purification system (Millipore, Milford, MA, USA).

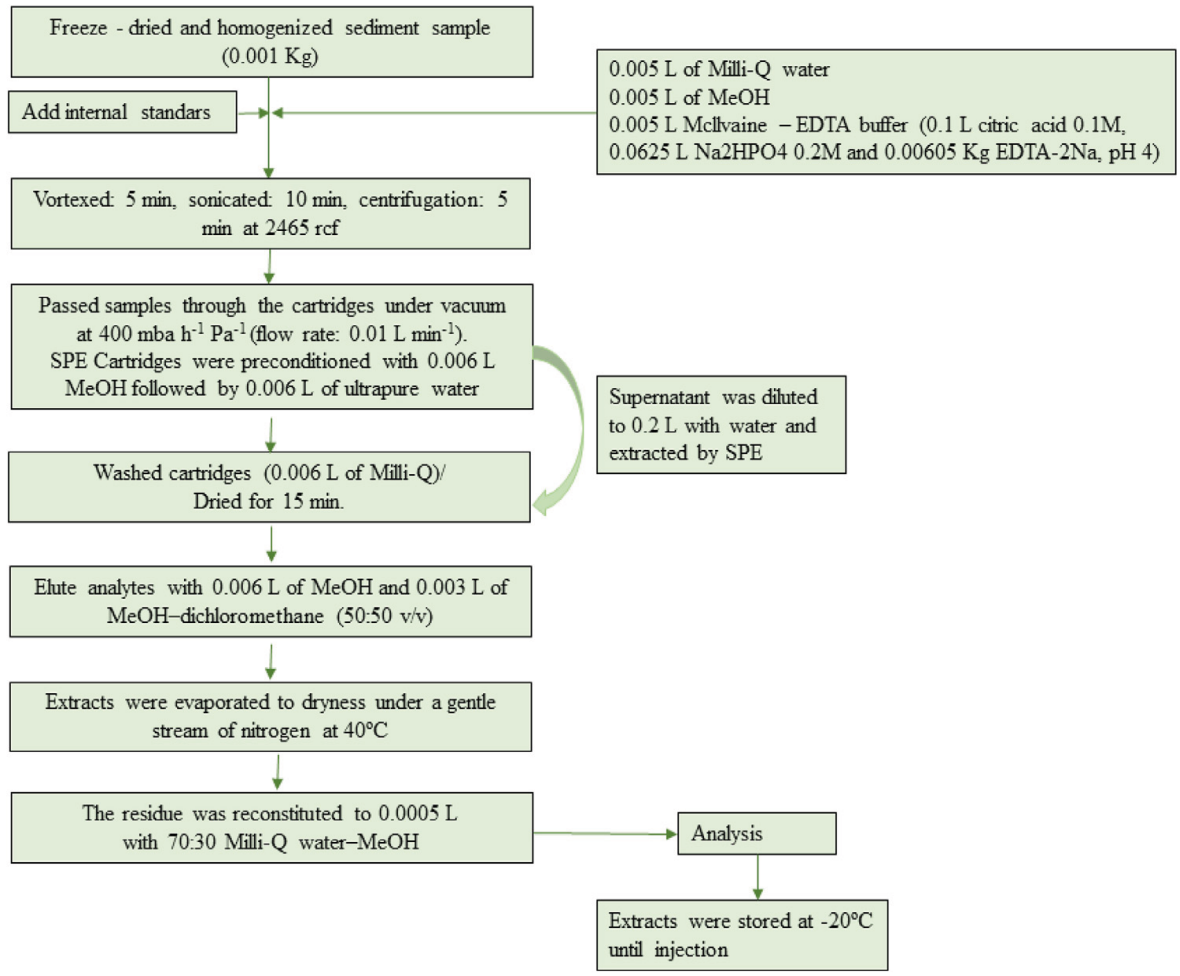


Fig. 4. Sediment extraction for polar compounds.

Primary-secondary amine (PSA) and C_{18} were from Análisis Vínicos (Tomelloso, Spain), magnesium sulfate ($MgSO_4$) and sodium sesquihydrate citrate [$HOC(COOH)\ (CH_2COONa)_2\ 1.5\ H_2O$] from Alfa Aesar (Karlsruhe, Germany) and sodium chloride (NaCl) and trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$) from Prolabovwr (Leuven, Belgium).

The 15 mL and 50 mL polypropylene centrifuge Falcon tubes were from VWR International Eurolab (Barcelona, Spain). Strata-X-33 µm polymeric reversed phase (200 mg/6 mL) were from Phenomenex (Torrance, CA, USA). The 1.5 mL amber glass vials with stoppers 99 mm + Septum Sil /PTFE used to inject the samples were from Análisis Vínicos S.L. (Tomelloso, Spain) and the 250 µL polypropylene inserts were from Agilent Technologies (Santa Clara, CA, United States). Nylon 0.22 µm filters were purchased from Membrane Solutions (Plano, TX, USA). Polypropylene/polyethylene syringes were manufactured by BRAUN and distributed by Scharlab S.L. (Barcelona, Spain). For the solid phase extraction (SPE) Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL) cartridges and a vacuum manifold Supelco Visiprep 57,030-U (Sigma-Aldrich, St. Louis, Missouri, USA) were used.

4.2. Samples extraction

The extraction procedures used for the water and sediment samples are shown in Figs. 2–4.

The surface waters (250 mL) were vacuum filtered by a 0.6-µm glass fiber filter (GA-55, 90 mm - Advantec MFS, Dublin, CA, USA) and stored at –20 °C until the analysis. Water samples

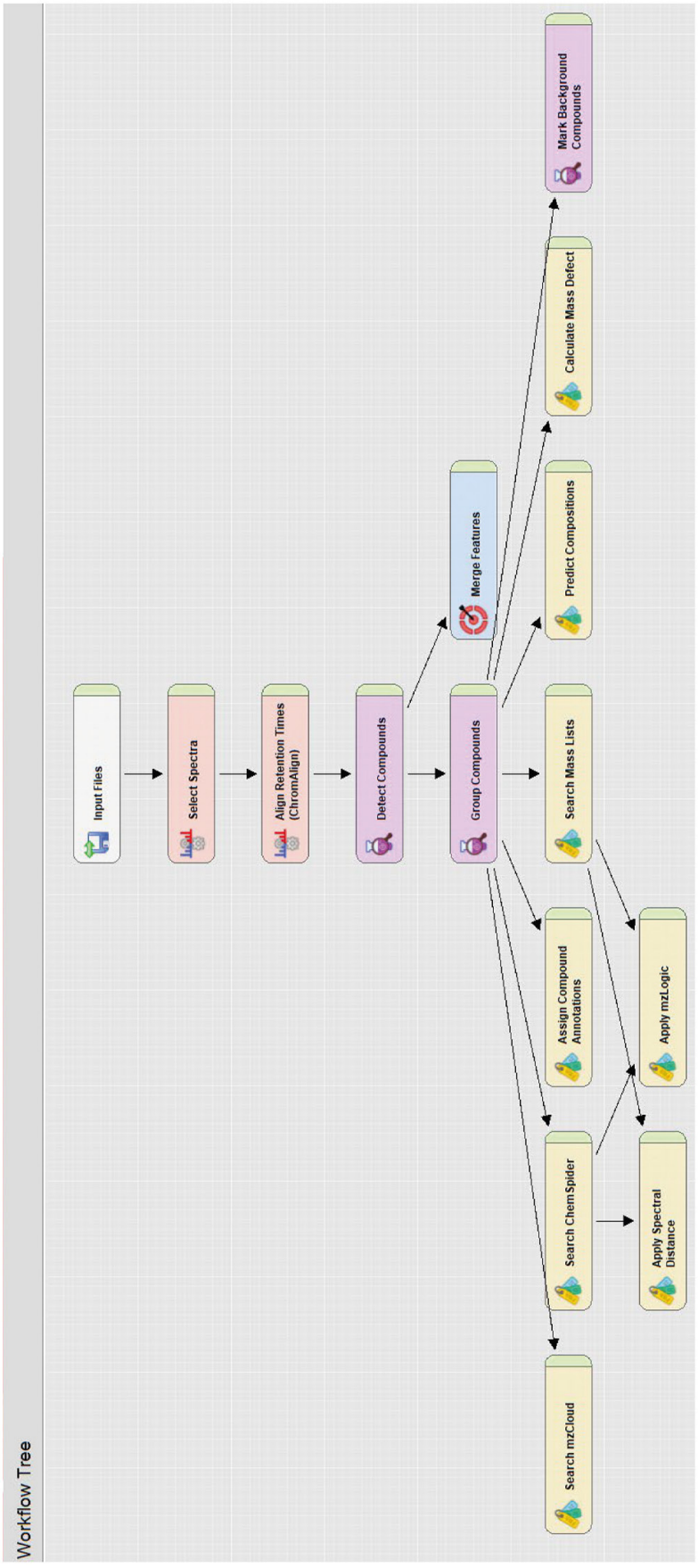


Fig. 5. Workflow "Environmental w Stats Unknown ID w Online and Local Database Searches" in Compound Discoverer software.

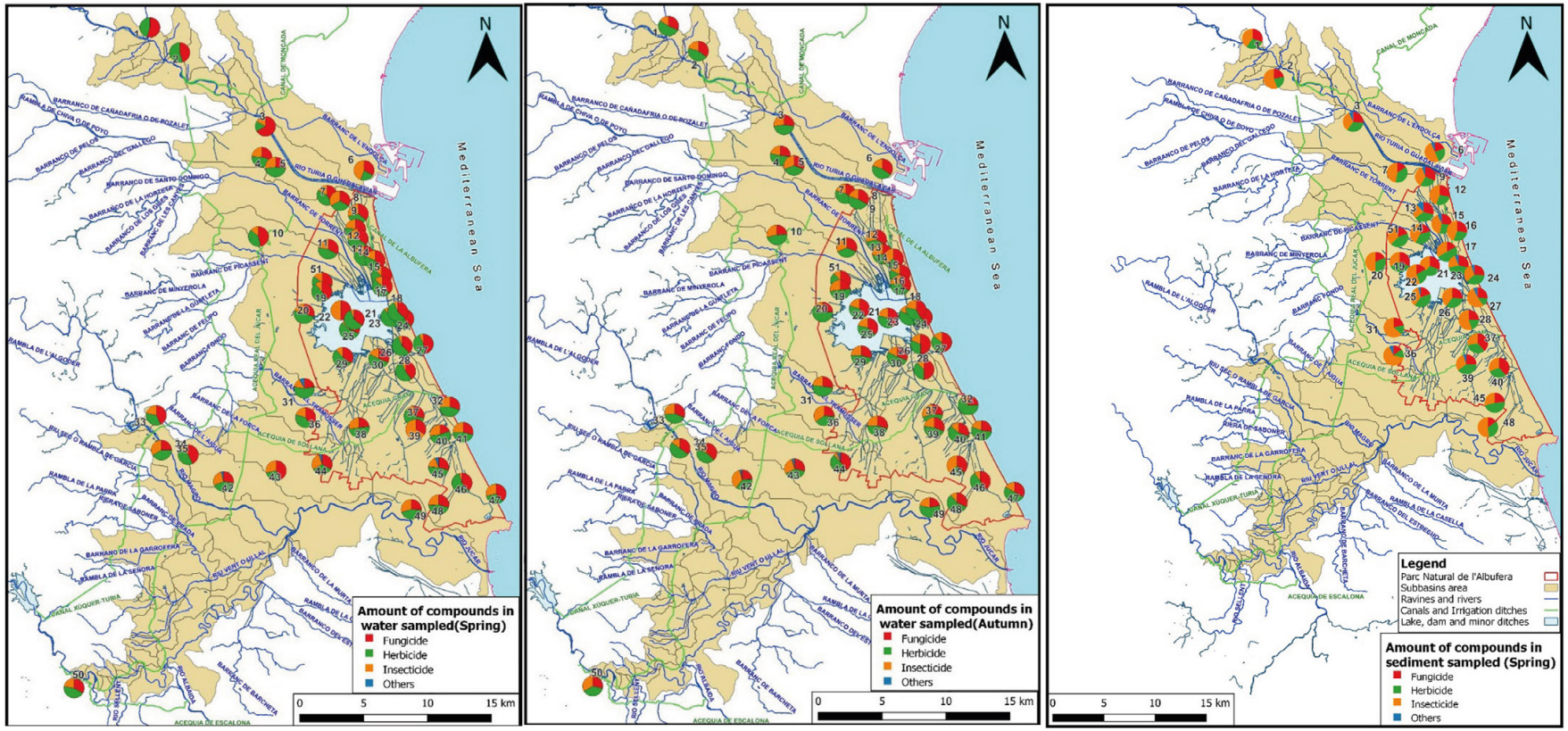


Fig. 6. Distribution of the total concentrations of fungicides, herbicides, insecticides, and other compounds by target analysis in water samples in spring (left), autumn (middle) and sediment samples (right).

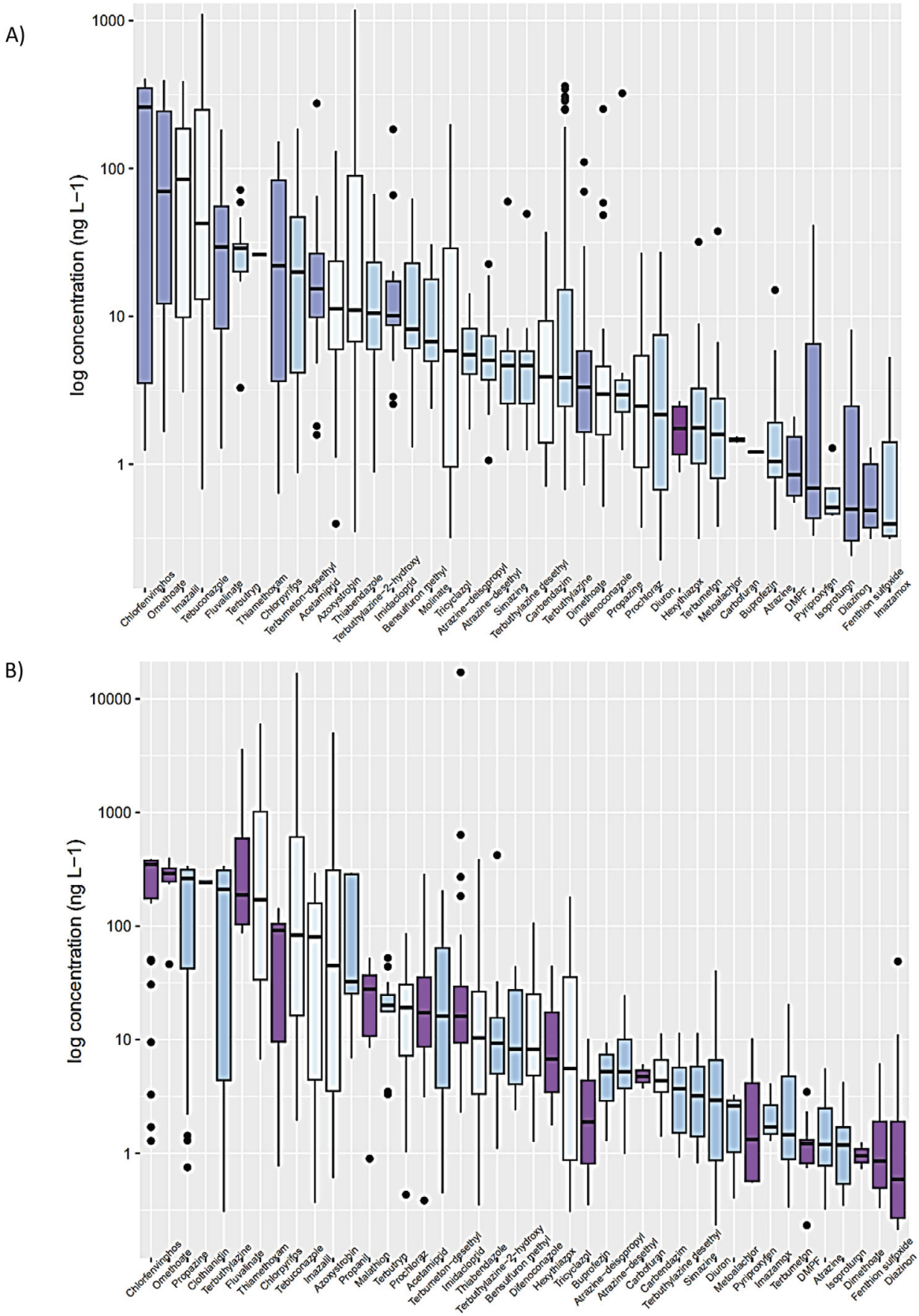


Fig. 7. Median concentrations (ng L^{-1}) of quantified pesticides in at least one sampling site in surface water in spring (A) and autumn (B). The color white represents fungicides, blue denotes herbicides, and purple signifies insecticides. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

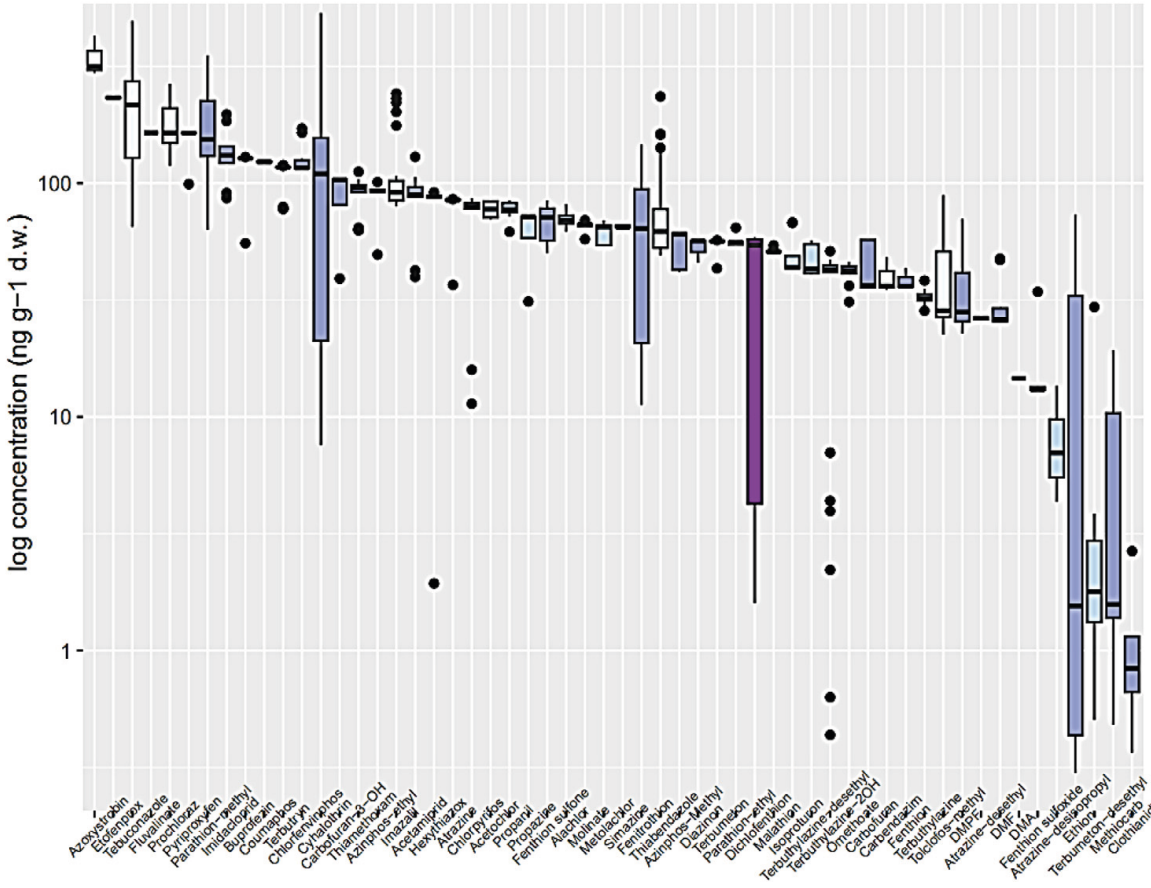


Fig. 8. Median concentrations (ng g^{-1}) of quantified pesticides in at least one sampling site in sediment samples. The color white represents fungicides, blue denotes herbicides, and purple signifies insecticides. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were extracted using the method previously reported by [2]. The sediments were lyophilized with a Virtis lyophilizer (SP Scientific, Gardiner, NY, USA) and the sediment samples were sieved, and air-dried in the dark at 20 °C to reduce the moisture content. Sediment samples were extracted using the method previously reported by [2,3].

The water quality parameters were measured in situ using a portable multiparametric meter (model HI9829, HANNA Instruments): pH, temperature (T, °C), oxidation–reduction potential (ORP, mV), conductivity (CE, in dS m^{-1}), Total Disolved Solids (TDS, mg L^{-1}), NaCl (mg L^{-1}), Resistivity (Ω) and dissolved oxygen (DO, % and mg L^{-1}) (These parameters for each sampling points in spring and in autumn are listed in "Data of the physical-chemical parameters").

Target screening and non-target screening was conducted using a Thermo Scientific™ Orbitrap Exploris™ 120 high-resolution mass spectrometer equipped with a heated electrospray ionization (HESI) source [4]. More information about the instrumental characteristics used for pesticides (target) determination and NTS as well as in the workflow used in NTS in Table 2 and Fig. 5.

5. Results

Out of the 71 compounds included in the target analysis, 43 and 59 pesticides were quantified at least once in water and sediment samples respectively. Herbicides and fungicides represented up to 50 % of the quantified chemicals. The number of quantified pesticides varied across sampling sites with an increase of herbicides from spring to autumn. However, the num-

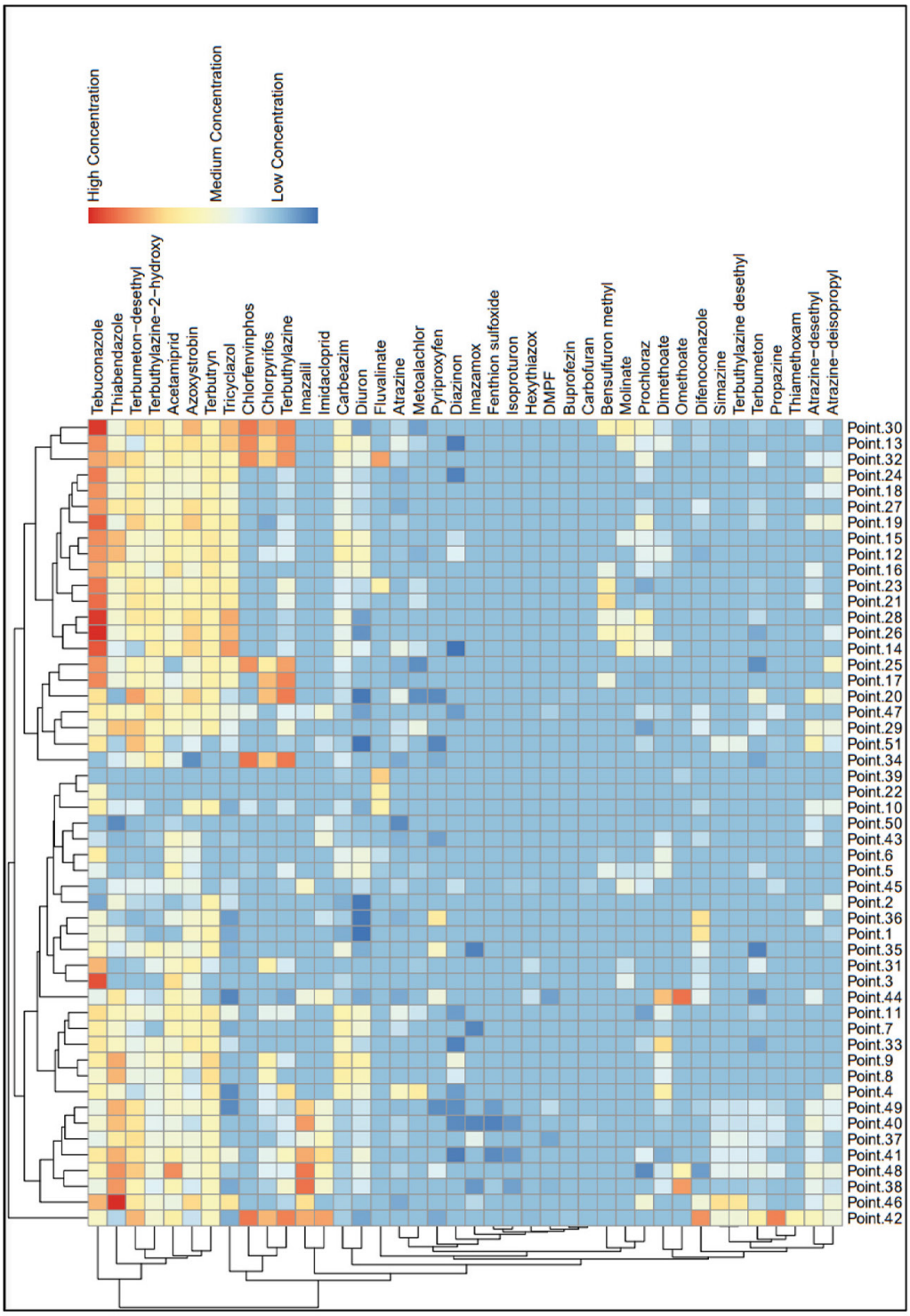


Fig. 9. Spatial pollution patterns of quantified pesticides in water samples in spring based on compound concentrations (ng L^{-1}) detected in the study sites (data log-transformed, scaled and centered). The color of each cell indicates scaled intensity level increasing from blue to red. Heatmaps were created in R (version 4.3.1) (R package 'gplots', function heatmap.2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

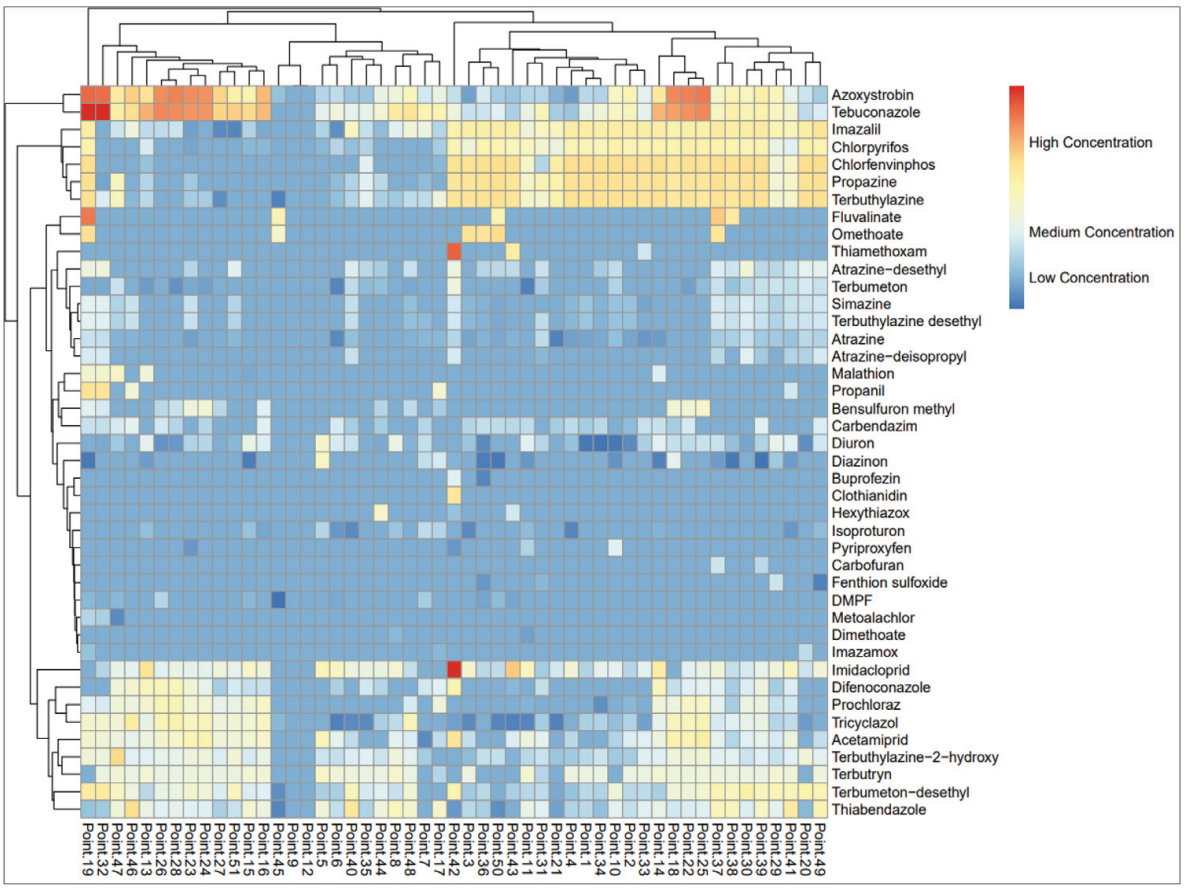


Fig. 10. Spatial pollution patterns of quantified pesticides in water samples in autumn based on compound concentrations (ng L^{-1}) detected in the study sites (data log-transformed, scaled and centered). The color of each cell indicates scaled intensity level increasing from blue to red. Heatmaps were created in R (version 4.3.1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ber of insecticides was higher in the sediment samples than in the water samples (Fig. 6). From a basin-specific perspective, sampling points 38, 40, 42, 48 and 29 exhibited the highest number of quantified pesticides with 26, 26, 26, 27 and 27 quantified pesticides in spring, respectively. While sampling points 42, 44 and 46 exhibited the highest number of quantified pesticides with 27, 26 and 26 quantified pesticides in autumn, respectively. Conversely, sampling points 22 and 39 exhibited the lower number of quantified pesticides (2 and 3 quantified pesticides respectively, in spring). While sampling point 41 exhibited the lower (8 quantified pesticides in autumn).

The highest measured environmental median concentrations of pesticides quantified for the spring are plotted in Fig. 7(A), with the insecticide chlorpyrifos reaching highest concentrations followed by fungicide omethoate and insecticide imazalil as the second and third TOP concentrations, respectively. However, the highest measured environmental median concentrations of pesticides quantified for autumn are plotted in Fig. 7(B), with the insecticide chlorpyrifos reaching highest concentrations followed by fungicide omethoate and herbicide propazine as the second and third TOP concentrations, respectively. The boxplot representation reveals a comparable pattern between the spring and autumn datasets. Instead, the highest measured environmental median concentrations of pesticides quantified in sediment samples are plotted in Fig. 8, with

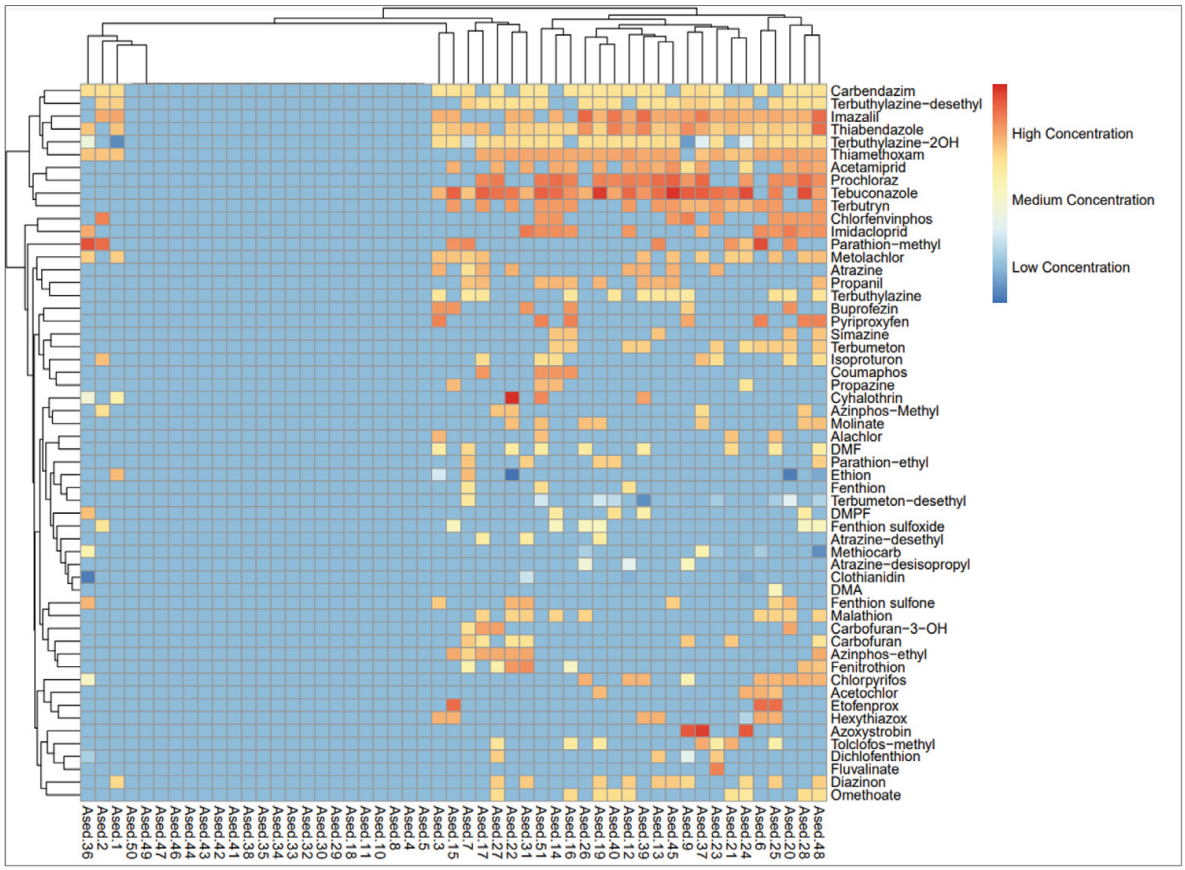


Fig. 11. Spatial pollution patterns of quantified pesticides in sediment samples based on compound concentrations (ng g^{-1}) detected in the study sites (data log-transformed, scaled and centered). The color of each cell indicates scaled intensity level increasing from blue to red. Heatmaps were created in R (version 4.3.1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the fungicide azoxystrobin reaching highest concentrations followed by insecticide etofenprox and fungicide tebuconazole as the second and third TOP concentrations, respectively.

Limitations

The list of target chemicals for pesticide analysis in this study was primarily derived from compounds frequently detected in rice fields and citrus crops, as well as those commonly observed within L'Albufera Natural Park.

Ethics Statement

The authors have read and follow the ethical requirements for publication in Data in Brief and confirming that the current work does not involve human subjects, animal experiments, or any data collected from social media platforms.

Credit Author Statement

Yolanda Soriano: Conceptualization, Methodology, Data curation, writing – original draft preparation, Writing – review & editing, Visualization. **Emilio Doñate:** Writing – review & editing, Visualization. **Sabina Asins:** Writing – review & editing, Visualization. **Vicente Andreu:**

Methodology, Resources, Writing – review & editing. **Yolanda Picó:** Conceptualization, Methodology, Reviewing and Editing, Supervision, Project Administration; Funding acquisition.

Data Availability

Dataset of emerging contaminants in LÁlbufera Natural Park (2019–2020) by target and non-target screening using high resolution mass spectrometry (Original data) (Mendeley Data).

Acknowledgements

This study was supported by the Prometeo program for research groups of excellence (CIPROM/2021/032) of the Conselleria d'Educació, Universitats i Ocupació (Valèncian Generalitat). Y. Soriano acknowledges her pre-doctoral contract by the grant PRE2019-089042 funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". Also supported by the project SERENA (Soil ecosystem services and soil threats modelling and mapping) – EJP-SOIL (Horizon 2020-European Union- grant agreement 862695). We also thank the director and the staff of the Office of the Natural Park of L'Albufera for their continuous advice and support.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SECCIÓN 3

Evaluación de la contaminación del Parque Natural de L'Albufera utilizando muestreadores pasivos

ARTICLE 03

Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: an environmental risk assessment

Science of the Total Environment 903 (2023) 166594

Contents lists available at ScienceDirect

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Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: An environmental risk assessment

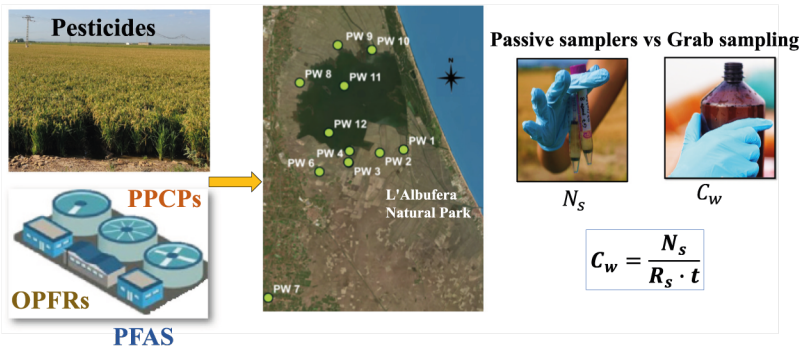
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HIGHLIGHTS

- 45 pesticides, 30 PPCPs, 22 PFAS and 7 OPFRs detected in L'Albufera Natural Park
- Pesticides were the dominant contaminants in the area.
- Spatial distribution showed more contaminants at higher concentrations in the North of the Lake.
- Risk Quotient factors showed that contamination is of concern within the Natural Park.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Dimitra A Lambropoulou

Keywords:
Organic contaminants
Passive samplers
Surface water
Coastal Mediterranean Wetlands

ABSTRACT

L'Albufera Natural Park (Valencia, Spain) is a protected wetland of international significance that provides critical habitats to endemic and threatened bird and plant species. This study aims to use multiple cross-validation techniques to generate an accurate estimation of the environmental risk of organic contaminants (OCs) in an internationally important coastal wetland, to identify compounds of concern and their potential sources and risk factors. Microporous polyethylene tube (MPT) passive samplers were deployed at 12 locations across L'Albufera Natural Park with concurrent grab samples collected. A subset of MPT samplers were also analysed by an additional laboratory in Australia to widen the range of contaminants and assess interlaboratory reproducibility of results. Forty-three pesticides, 20 pharmaceuticals and personal care products (PPCPs), 20 *per*- and polyfluoroalkyl substances (PFAS) and 4 organophosphorus flame retardants (OPFRs) were detected in the MPT samplers. The fungicides tebuconazole and difenoconazole were detected at the highest concentrations in passive samplers (maximum concentrations, 153 ng sampler^{-1} and 106 ng sampler^{-1}, respectively). Several other pesticides were detected in all locations (mean concentrations >1 ng sampler^{-1}). The compounds fenamiphos, propyzamide, difenoconazole, propiconazole, metsulfuron methyl, sodium bis (perfluorohexyl) phosphinate (6:6 PFPiA), 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), 6:2 fluorotelomersulfonate (6:2

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https://doi.org/10.1016/j.scitotenv.2023.166594
Received 31 January 2023; Received in revised form 24 August 2023; Accepted 24 August 2023
Available online 26 August 2023
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FTS), citalopram desmethyl and citalopram were reported in the wetland for the first time. Spatial distribution analysis revealed higher pesticide concentrations in the North of L'Albufera. A risk quotient (RQ) analysis showed that ibuprofen is of concern in the area. Overall, the MPT sampling approach is promising as a risk assessment tool for better understanding the transport and fate of OCs in protected areas.

1. Introduction

L'Albufera, a Mediterranean coastal wetland, was declared a Natural Park in 1986 for its ecological value, providing a critical habitat to endemic and migratory endangered species. Only three years later, in 1989, it was recognized as Wetland of International Importance especially as a Waterfowl Habitat (Ramsar, 1971). It is also an integral part of the Natura 2000 Network - having been designated as a Special Protection Area for Birds (Directive 2009/147/EC), and as a Site of Community Importance by the Habitat Directive (Council Directive 92/43/EEC).

Mediterranean coastal wetlands play an additional, important ecological role, acting as natural filters that retain and/or eliminate pollution, such as, metals (Li et al., 2022), runoff sediments and nitrogen (Gargallo et al., 2017). However, these systems can also experience deleterious effects from organic contaminants (OCs) pollution. The increasing scarcity of water in these areas has led to the utilization of non-conventional water resources that are typically discharged into the water system in large quantities and intermittently, mostly through irrigation channels to maintain the ecological flow (Martín et al., 2020). The presence of OCs in recycled or reclaimed water from industry or agriculture and wastewater could negatively impact the environment, biota or human health (Pascual-Aguilar et al., 2015).

The occurrence of several OCs within the sub-ecosystems of L'Albufera have previously been reported, including pesticides such as terbumeton, terbuthylazine and their metabolites (Calvo et al., 2021; Lorenzo et al., 2019; Sadutto et al., 2021; Andreu Sánchez, 2008). Land-use surrounding the ecosystem consists of various urban, agricultural and industrial activities, contributing to non-conventional waste release to the wetland. A wide range of OCs belonging mainly to four relevant use classes were identified as important for investigation in this study (pesticides, pharmaceuticals and personal care products (PPCPs), perfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs)). The high scientific and ecological value of this ecosystem coupled with the potential threat of OCs from surrounding land uses justify an in-depth assessment of the types and concentrations of OCs for a comprehensive risk assessment.

Sensitive monitoring tools that can detect a broad range of OCs are crucial to ensure risk assessment and adequately preserve threatened ecosystems such as L'Albufera. So far, water quality monitoring has been performed mainly by analyzing grab (spot) samples that provide information on a singular moment within the system. Consequently, this method may fail to capture the presence of certain substances or variations in their concentrations over time (Brack et al., 2017). The occurrence of events such as contamination plumes, accidental spills or deliberate industrial releases can also be missed (Vrana et al., 2005). Representative sampling is an essential requirement for accurately estimating the concentration of OCs and to evaluate risks they may pose to ecosystems.

Passive sampling can overcome many of the limitations of grab sampling by accumulating chemicals in situ over an extended time-period. These samplers can also provide additional information through time-weighted average or equilibrium concentrations of the freely dissolved contaminant fraction (Booij et al., 2007; Liu et al., 2011; Vrana et al., 2005). Different passive sampler configurations (e.g. Polar Organic Chemical Integrative Sampler (POCIS), Chemcatcher®, Microporous Polyethylene Tubes (MPT), organic-diffusive gradients in thin films (o-DGT), etc.) have been used in wastewater influent, wastewater effluent, surface waters, seawaters, and urban waterways to establish the occurrence of contaminants such as PFAS, pesticides, PPCPs, and so on (Benedetti et al., 2022; MacKeown et al., 2022; Alvarez et al., 2021; Hageman et al., 2019; MacKeown et al., 2022; Martínez Bueno et al., 2016; Menger et al., 2021; Niemi et al., 2022; Novic et al., 2017; Overdahl et al., 2021; Quintana et al., 2021; Rico et al., 2019).

MPT passive samplers have demonstrated high versatility for a range of contaminants owing to interchangeable sorbents and reduced flow-dependence. This is achieved due to the thicker diffusive layer used (Fauvelle et al., 2017; Brack et al., 2017), i.e. the thicker diffusive membrane dictates the majority of the diffusion rate thus limiting the water boundary layer's influence. MPT samplers have been applied for sampling of pesticides, illicit drugs, PPCPs, PFAS and glyphosate, by adapting a variety of sorbent phases to target compounds (Hageman et al., 2019; McKay et al., 2020; Verhagen et al., 2021; Kaserzon et al., 2019; Clokey et al., 2023; Fauvelle et al., 2017). Due to the MPT's versatility and its cost-effectiveness in monitoring projects, these passive samplers were selected for deployment in this study to investigate contaminants in L'Albufera Natural Park.

The aim of this study was to use multiple complementary sampling methods to increase understanding of the presence and concentrations of OCs in L'Albufera Natural Park. In order to achieve this aim, four specific objectives were formulated (i) to determine the presence and concentration of a wide range of OCs at multiple sites within L'Albufera Natural Park using grab sampling and two configurations of MPT passive samplers (ii) to compare the analytes detected and their concentrations in grab samples and MPT passive samplers to establish the degree of complementarity between these two sampling approach in monitoring OCs in the Natural Park (iii) to map the spatial variability of OCs in the Natural Park to assess the effects of different OC inputs (iv) to assess combined risk posed to the Natural Park by detected OCs considering their presence, concentrations, and spatial distribution.

2. Materials and methods

2.1. Reagents and chemicals

A total of 229 contaminants were analysed, including 57 PFAS, 11 OPFRs (7 non-halogenated and 4 halogenated), 50 PPCPs and 111 pesticides (refer to Supplementary Information (SI) Text S1 and Tables S1-S4 for a detailed list of compounds and the laboratory where they were analysed). Other reagents and chemicals are also detailed in the SI (Text S2).

2.2. Passive sampler assembly

Two configurations of the MPT passive sampler were used in this study; one for sampling glyphosate and its metabolite aminomethylphosphonic acid (AMPA) (filled with agarose gel and titanium (IV) oxide (TiO_2) powder, Sigma-Aldrich, China) and another for the sampling of pesticides, PPCPs, OPFRs and PFAS (filled with hydrophilic lipophilic sorbent phase – Strata-X, a reversed phase surface modified polymer of styrene and divinylbenzene functionalized with N-vinyl-2-pyrrolidone) (Phenomenex, Melbourne, Australia). The assembly of the MPT sampler for glyphosate and AMPA has been described in Fauvelle et al. (2017) and the MPT configuration for PPCPs, OPFRs and PFAS is described in McKay et al. (2020). Microporous polyethylene tubes were purchased from Pall Corp. Crailsheim, Germany (Filterplast®, 8 mm ID, 35 % porosity, 2.5 μm in size, 12 mm OD, and 0.6 gcm^{-3} density) (Hageman et al., 2019; Kaserzon et al., 2019). Exposed tube length was

4 cm with a sorbent mass 400 ± 10 mg.

2.3. Description of the sampling area

L'Albufera Natural Park (Valencia, Spain) is one of the most representative and valuable coastal wetlands in the Valencian Community and the Mediterranean basin covering over 21 thousand hectares. It is located 10 km from Valencia City and extends between the mouth of the rivers Turia and Júcar (Fig. 1).

L'Albufera Natural Park comprises: a lake separated from the sea by a sand bar, rice paddies that now occupy the primitive marshy lands (a potential source of contaminants), and a smaller area dedicated to citrus orchards. The main crop bounding the Natural Park is citrus. The area has an important network of irrigation channels and canals that supply water to the fields (especially rice fields that are flooded most of the time) and collect excess water after irrigation or when rice paddies are emptying. Near the lake, some rice paddies have been repurposed into artificial wetlands to recover the primitive habitats of the marshland. The lake has a maximum diameter of ~8 km, an estimated surface area of 2.3 ha and its average depth is approximately 1.2 m.

2.4. Sampling

Twelve sampling points were selected as representative sites within L'Albufera Natural Park (Fig. 1). These cover three different habitats: lake (sites 11, 12), artificial wetland (sites 3, 4, 5) and channels (sites 2, 6, 8, 9, 10). Sites with different contaminant sources were also investigated: PPCPs through wastewater treatment plants (WWTPs) effluent (sites 3, 10) and pesticides from agricultural runoff reaching the wetlands and channels. Two points were selected as a control (i) the fish farm for autochthonous species preservation belonging to the local government (site 1) and (ii) the Royal Jucar channel that transports freshwater from the Jucar River to the orchards and rice paddies (site 7); its average flow during irrigation periods is 15 m^3/s. Further details can be found in Table S5.

Sampling was conducted between September 21, 2020, and October 15, 2020. At each site two configurations of MPTs were deployed in triplicate: for polar and moderately polar compounds (PPCPs, pesticides and PFAS) and for glyphosate and AMPA. One sampler of each configuration was collected after 14 days and the other two were collected after 28 days of deployment. The MPT samplers were submerged in the middle of the water column (between 0.3 and 0.7 m deep depending on the depth of the sampling point) so that the passive samplers were completely submerged but did not touch the sediment. Upon retrieval the MPTs were removed from the water, rinsed with deionised water and transferred to separately labelled, single-use 15 mL centrifuge tubes. Samples were transported to the laboratory in a cooler with ice bricks. Once in the laboratory, the MPTs were frozen at −20 °C until extraction. One 28-day sample from each site was sent to the University of Queensland (UQ) in Australia for analysis. The two remaining samplers

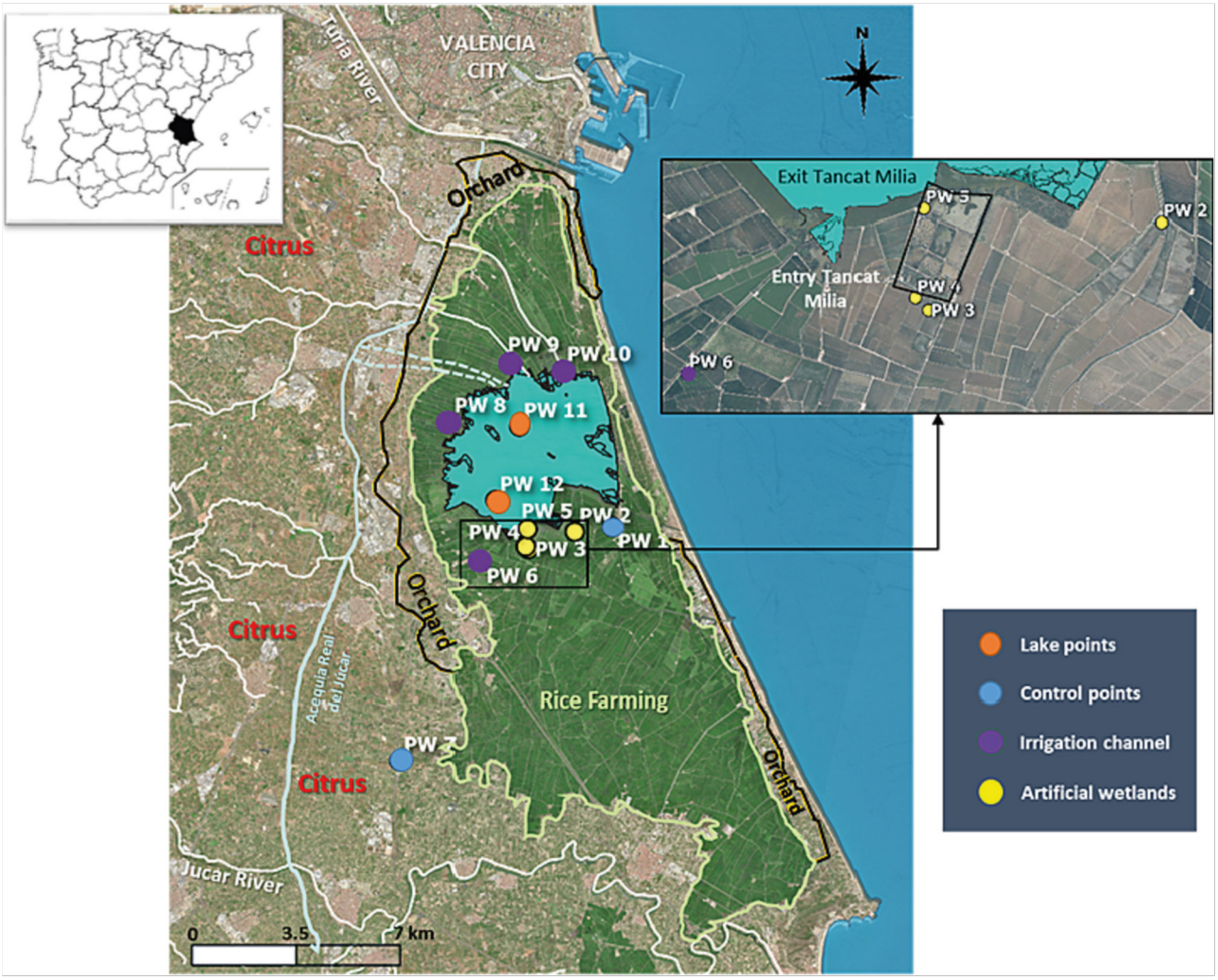


Fig. 1. Map of L'Albufera Natural Park. Location of the sampling sites are highlighted in orange, blue, yellow and violet. Three closely clustered sites are shown zoomed in in the top left. Satellite image by Orthopnea 2018 CC-BY 4.0 scne.es (National Cartographic System).

(collected at 14 and 28 days, respectively) were analysed at the University of Valencia (UV). Images showing the sampling process are available in Fig. S1 of the supplementary material. At each sampling point, 1 L of surface water was collected in clean polyethylene terephthalate amber bottles from the middle of the water column. Grab samples were collected during deployment of the passive samplers (day zero) and at days 14 and 28.

The following water quality parameters were measured in situ: dissolved oxygen (DO) (15.0–153 % or 1.30–12.5 mg L^{-1}), pH (7.30–8.50), temperature (15.6–26.6 °C), salinity (0.53–1.63 PSU), conductivity (1.06×10^3 - 3.13×10^3 µS cm^{-1}), chlorophyll A (0.07–37.5 µg L^{-1}), phycoerythrin (0.38–77.2 µg L^{-1}) (Table S6 lists these parameters for each sampling points at days 0, 14 and 28 days). These values were obtained using a portable multiparametric meter (model HI9829, HANNA Instruments).

2.5. Sample treatment and extraction

2.5.1. Grab water

Grab samples were analysed at UV. Grab water samples were defrosted for 24 h at room temperature in darkness, followed by filtration of 250 mL using a 0.45-µm glass fiber filter under vacuum (Advantec MFS, Dublin, CA, USA). Then, 50 µL of mixed isotopically labelled internal standards at a concentration of 1 µg mL^{-1} was spiked into each sample (Text S1 and Text S3). The samples were extracted by solid phase extraction (SPE) using Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL) SPE cartridges according to the method previously reported by Carmona et al. (2017).

2.5.2. Passive sampler extraction

Passive samplers were extracted at UV and UQ following the methods described by Fauvelle et al. (2017) and McKay et al. (2020) (Text S4). Briefly, sorbent in the tube was spiked with a mix of isotopically labelled internal standards (50 µL of internal standards mix at a concentration of 1 µg mL^{-1}) prior to extraction (See Text S1). Samples were then extracted using methanol (MeOH).

Extracts were concentrated to 1 mL in different solvents (MeOH/water:MeOH) as reported in the supplementary information (Text S4) prior to analysis via liquid chromatography-mass spectrometry (LC-MS/MS).

2.6. LC-MS/MS analysis

Analysis was performed by liquid chromatography-mass spectrometry in both laboratories. The instruments used were an Agilent 6410 (Santa Clara, CA, USA) at UV and the API5500 and API6500 QTRAP (Sciex, Melbourne, Australia) at UQ. The compounds analysed as well as the specific conditions of each determination are detailed in the SI (Text S1, S5 and Table S7).

2.7. Calculation of analyte concentrations in water from passive samplers

If chemical uptake into the sampler is linear with time over the deployment period, accumulation can be reduced to a linear approximation model. Time-weighted average concentrations in water (C_w) over the deployment periods were calculated using Eq. (1) (Alvarez, 2010).

$$C_w = \frac{N_s}{R_s \bullet t} \quad (1)$$

where N_s is the mass of the compound in the sampler receiving phase or sorbent (ng $sampler^{-1}$), C_w is the concentration of the compound in the water (ng mL^{-1}), R_s is the sampling rate (mL d^{-1} $sampler^{-1}$) at the time of deployment (t, days). R_s values were compiled from literature and are shown in Table S8 for the detected analytes.

2.8. Calculation of risk quotient (RQ) and predicted no effect concentrations (PNEC)

Risk Quotients (RQ) were calculated for OCs of concern in this study according to Eq. (2) (Anagnostopoulpou et al., 2022; Picó et al., 2021).

$$RQ = \frac{C_w}{PNEC} \quad (2)$$

where C_w is water concentration (ng L^{-1}) and PNEC is the Lowest Predicted No Effect Concentrations (ng L^{-1}). PNEC values were extracted from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php) (Table S9). RQ > 1 suggests high ecological risk. For $0.1 \leq RQ \leq 1$ suggests medium ecological risk and RQ < 0.1 suggests low ecological risk.

2.9. Quality assurance/quality control

Procedural blanks were prepared to check for possible contamination from reagents, MPT tubes or equipment. Results showed that no relevant OCs were detected.

The quality control followed with grab samples involved the processing of laboratory blanks and field blanks collected alongside the samples. The field blank samples consisted of MilliQ water that was taken to the field. Only negligible amounts of PFOS (up to 0.05 ng L^{-1}) were detected in the blanks and these were subtracted from the signals observed in the samples to eliminate any background noise or contamination effects. The analytical validation of the methods for analysis of grab water samples for pesticides, PPCPs, PFAS and OPFRs was previously reported (Picó et al., 2021; Sadutto et al., 2020; Lorenzo et al., 2016a; Picó et al., 2020; Lorenzo et al., 2016b). Average recovery percentage of the internal standards obtained in grab water samples of these studies for pesticides, PFAS, PPCPs and OPFRS ranged from 57 % -107 %, 85–102 %, 57 %–104 % and 70–112 %, respectively. The limits of detections (LODs) and quantification (LOQs) were calculated using spiked matrix samples and ranged from 1 to 5 ng L^{-1} for water. These limits were calculated as the concentration that provides a response 3 and 10 times higher, respectively, than the standard deviation of the average field blank concentration. To validate the quality of the chemical analysis of these samplers, the recoveries of the isotopically labelled internal standard spiked into passive samplers prior to extraction were established. These recoveries ranged from 57 to 107 %. Laboratory blank MTP passive samplers were prepared alongside samplers and kept in the refrigerator until the processing and extraction of the MPT samplers. In the blanks no contamination was observed. The LODs and LOQs were estimated with the grab sample results. The MPT interlaboratory analysis (Text S6) provides an idea of the reproducibility within the deployment and reliability of the MPT across laboratories. Collected data shows compound percentage variations on a site-by-site basis from −200 % to 198 % (Fig. S2A). The average ratio was between 0.5 (terbuthylazine) and 15 (desethyl atrazine) (Fig. S2B).

2.10. Statistical analysis

Concentrations are expressed as ng L^{-1} or in ng $sampler^{-1}$. Concentrations below the LOQ were considered as the average between LOQ and LOD while n.d. were consider as half of the LOD for statistical treatment. In the case of UQ laboratory, LORs, represent three times the LODs. In the case of blank detection LOR were calculated as the average blank plus three times the standard deviation of the blanks. LODs are calculated using three times the standard deviation from a repeated injections ($n = 7$) of a low analytical standard.

Statistical analysis was conducted using IBM SPSS version 26.0. The differences between the results obtained from both laboratories (UQ and UV), as well as between grab and passive sampling, were assessed using a paired t-test. Furthermore, to compare the spatial differences in

concentrations of OCs, analysis of variance (ANOVA) and Tukey's multiple range test at $\alpha = 0.05$ were performed. To assess the positive relationships between water quality and OC levels, bivariate correlation analysis was conducted at both 95 % and 99 % significance levels. Pearson's correlation analysis was used for variables with normal distribution, while Spearman Rho correlation analysis was used for variables without normal distribution. The R2 and standard deviation of residuals (Sy.x) were calculated as well.

To establish the weight and dependence among variables and recognize possible behavioral patterns, multiple stepwise linear correlation analysis, discriminant analysis, and categorical principal component analysis (PCA) were used.

3. Results and discussion

3.1. Presence of OCs in L'Albufera Natural Park

One hundred and four OCs (45 pesticides, 30 PPCPs, 22 PFAS and 7 OPFRs) were detected between grab and passive samplers in L'Albufera Natural Park (detailed in Table S10–18). Also, results for the inter-laboratory comparison study are provided in the Text S6, Tables S19-S20 and Fig. S2. Frequency and concentration showed similar patterns with pesticides >PPCPs > PFAS> OPFRs. Results showed that 87 compounds (43 pesticides, 20 PFAS, 20 PPCPs, 4 OPFRs) were detected in MPT passive samplers. Mass accumulated in the MPTs ranged from 0.10 ng sampler^{-1} for atrazine desisopropyl, 1-(3,4-Dichlorophenyl)-3-methylurea (DCPMU), PFBS, PFHpS, PFUnDA, sulfadiazine, atenolol and temazepam to 153 ng sampler^{-1} for tebuconazole (Table S10–12). In grab samples, 61 compounds were detected (24 pesticides, 14 PFAS, 16 PPCPs, 7 OPFRs). Concentration in grab samples ranged from 0.11 ng L^{-1} for TnBP to 1470 ng L^{-1} for ibuprofen (Table S13). Of these compounds, 44 were detected in both grab and MPT samplers.

In passive samplers 43 pesticides were detected after 28 days deployment with compound mass accumulated ranging from LOQ to 153 ng sampler^{-1} (tebuconazole) (see Tables S10 and S12). Globally, samples contained highest concentrations of conazoles fungicides (tebuconazole, difenoconazole and propiconazole). 3,4-Dichloroaniline, DEET, propiconazole, difenoconazole, MCPA, chlorpyrifos, acetamiprid, tebumeton desethyl, terbuthylazine-2OH, tebuconazole, dichlofenthion and prochloraz were detected at a frequency ≥ 50 % of samples and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. Herbicides and their metabolites (3,4-dichloraniline, MCPA, terbumeton desethyl and AMPA), insecticides (DEET, chlorpyriphos and dichlofenthion) and one fungicide (propiconazole) were also frequently detected in passive samplers (frequency of detection of >70 % in the samples and median ≥ 1 ng sampler^{-1}). Herbicides were previously reported in L'Albufera Natural Park as being widely used in rice cultivation, especially at the beginning of cultivation cycle (end of May/beginning of June) (Calvo et al., 2021). In addition to the herbicides used for the rice, glyphosate was used on field margins, which are planted with lilies and other ornamentals, to eliminate weeds.

In grab samples, 24 pesticides were detected ranging from <LOQ to 71.0 ng L^{-1}. Imidacloprid, acetamiprid, atrazine-desethyl, carbendazim, thiabendazole, terbumeton desethyl, terbuthylazine-2OH, terbuthylazine desethyl, tebuconazole and prochloraz presented the highest value measured ≥10 ng L^{-1} and detected at a frequency ≥ 50 % (see Tables S13 and S15-S17). Bromacil, metalaxyl, fenamiphos, propyzamide, metsulfuron methyl were reported here for the first time in the Natural Park.

Twenty PFAS were detected in passive samplers ranging from 0.10 (PFHpS) to 10.2 (PFOPA) ng sampler^{-1}. PFOS, PFOPA, 6:2 FTAB were at a frequency of ≥50 % and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. PFOS (median 2.07 ng sampler^{-1}, Table S10) was present in 100 % of the sites investigated.

Long-chain PFAS (i.e., PFNA, PFDA, PFUndA) were only detected at levels of <0.85 ng sampler^{-1} in some MPTs. It has been reported that long-chain PFAS were less common in water than short-chain (C ≤ 8) (Onghena et al., 2012). 6:2 FTAB, 6:6 PFPiA and 6:2 FTS were detected here for the first time in the Natural Park. PFTeDA, FBSA, PFTeDA, PFHxDA, and PFHxA were only detected in the passive samplers. Again, the pattern in passive samplers is different to that of grab samples where 14 PFAS were detected ranging from 0.13 (PFHxS) to 10.2 (PFOS) ng L^{-1}. PFTrDA and PFDS were only detected in grab samples. Results obtained in grab water samples showed the high occurrence of PFHxS and PFOA (100 % of the samples). However, PFOA (maximum concentration 4.51 ng L^{-1}) was at concentrations lower than PFOS (maximum concentration 10.2 ng L^{-1}). PFPeA was detected in ≥50 % of the samples and the highest concentration was ≥3 ng L^{-1}. This pattern was similar to that already reported in other Spanish rivers and in L'Albufera Natural Park using grab sampling with PFOA generally showing higher frequency than PFOS (Pico et al., 2012).

Twenty PPCPs were detected in the MPTs, ranging from 0.10 (Sulfadiazine, atenolol, temazepam) to 13.5 ng sampler^{-1} (salicylic acid). Caffeine, temazepam, acesulfame, gabapentin and tramadol were detected at frequency ≥ 50 % and the highest value measured for all of these compounds was ≥3.0 ng sampler^{-1}. Iopromide, oxazepam, and triclosan were detected in MPTs with a frequency of detection of 25, 42 and 33 %, respectively at the sampling points (Table S10). The results indicate that acidic OCs are less efficiently extracted than neutral or basic OCs with this passive sampler configuration. In grab water samples, 16 PPCPs were detected ranging from 1.34 ng L^{-1} (caffeine) to 1470 ng L^{-1} (ibuprofen). Salicylic acid, naproxen, diclofenac and ibuprofen were detected at frequency ≥ 50 % in the samples and the highest value measured for all these compounds was ≥100 ng L^{-1}.

Four OPFRs were detected in passive samplers deployed for 28 days with mass accumulated in samplers ranging from 0.28 to 1.48 ng sampler^{-1}. TDCIPP and TPhP were detected at a frequency of ≥50 % in samples and an amount ≥ 1.0 ng sampler^{-1}. In the grab water samples, 7 OPFRs were detected ranging from 0.11 to 816 ng L^{-1} for TnBP and TClPP, respectively. The OPFR detected at the highest concentration was TCIPP with a frequency of detection of 42 % in passive samplers. TCIPP, TDCIPP, TnBP and TPhP were detected in grab water samples and in passive samplers. In grab water samples TnBP (median 1.45 ng L^{-1}) was present in at least 75 % of the samples. TCEP, TPP and TBEP were only detected in grab water samples. TnBP and TBEP were detected at a frequency of detection of ≥50 % in the samples and the highest value measured for all these compounds was ≥10 ng L^{-1}.

3.2. Comparison of the performance of MPT passive samplers and grab samples

Fig. 2 compares the individual OCs detected in grab samples and passive samplers. It highlights the OCs that were exclusively identified in the passive samplers, namely buprofezin, chlorpyrifos, clothianidin, dichlofenthion, hexythiazox, fluvalinate, and flumethrin. Additionally, it also indicates the OCs that were only detected in the grab samples, including propanil, spinosad A, PFDS, PFTrDA, methylparaben, ethylparaben, naproxen, bezafibrate, propylparaben, ibuprofen, flufenamic acid, paracetamol, ofloxacin, lorazepam, TCEP, TPP, and TBEP. Two possible explanations could be considered as to why some OCs were detected in grab sampling and not in passive sampling even through the same sorbent was used to concentrate analytes. The first is that certain OCs may have higher interactions with the microporous polyethylene material and are therefore hindered in accumulating onto the sorbent material. The second, more straightforward explanation may be that the concentration factors between MPT and grab samples are different. With grab samples 250 mL of water is extracted providing a x250 concentration factor. MPT samplers can accumulate contaminants with sampling rates of 10's of milliliters per day. Considering the reported R_s range of 3 to 30 mL d^{-1}, this yields 84 to 840 mL for 28-day deployments. Although the value of 84 mL is only three times lower than that of 250 mL, it cannot be ruled out that it has some influence on the

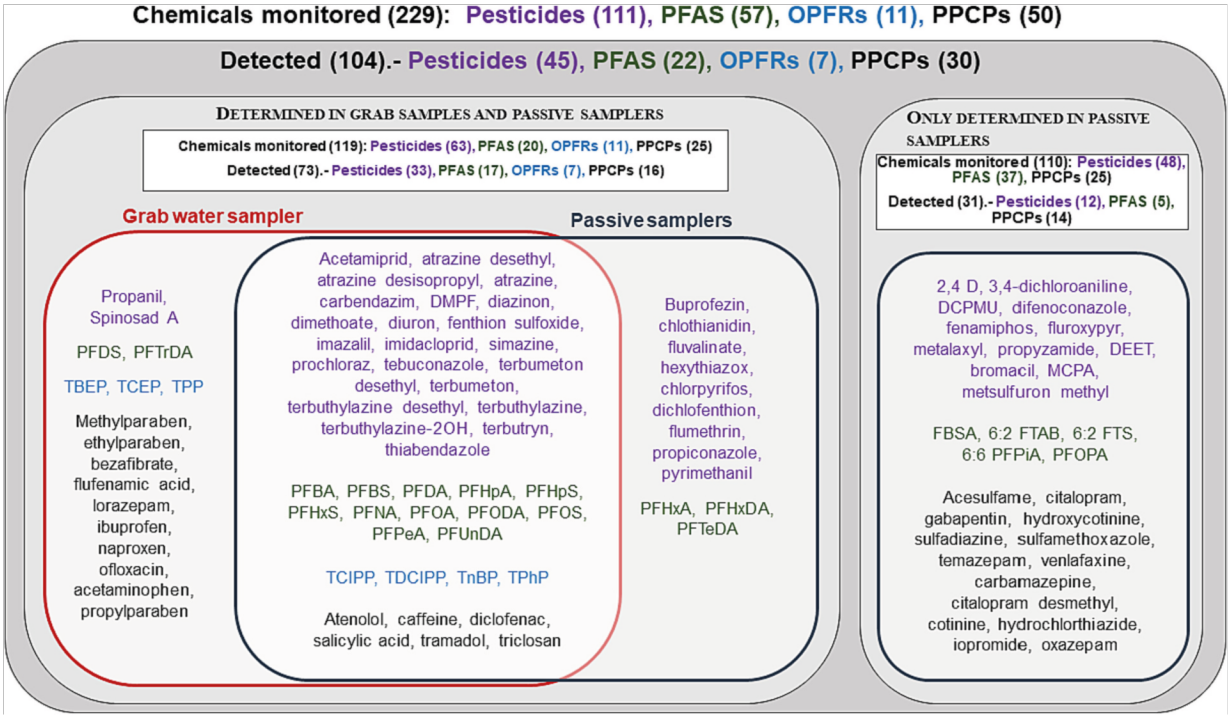


Fig. 2. Diagram of organic contaminants (OCs) [Pesticides, pharmaceutical care products (PPCPs), perfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs)] detected in grab water samples and microporous polyethylene tubes (MPT) passive samplers. The compounds only analysed and detected in passive samplers are not used for comparison purposes between the sampling methods.

missing of some compounds from the passive samplers. Therefore, MPT samplers may be less sensitive in comparison depending on the R_s of the compounds and the deployment duration.

The pesticides pattern in L'Albufera differs between passive samplers and grab samples. While neonicotinoid insecticides and herbicides are primarily detected in grab samples, passive samplers also identify these compounds, along with additional ones such as chlorpyrifos, dichlofenthion, and flumethrin. These latter pesticides, characterized by being nonpolar, water insoluble, and having a log $P > 4$, were consistently found in passive samplers throughout our study. This displays the benefit of simultaneous passive deployment, allowing the detection of chemicals which may otherwise not be detected. The chlorpyrifos results contradict those reported for Hageman et al. (2019) who detected chlorpyrifos mostly in grab samples and not in POCIS. Other studies have demonstrated adequate quantification of chlorpyrifos using several types of passive samplers (Quintana et al., 2021; Rico et al., 2019). The pattern of OPFRs is similar in grab samples and passive samplers with TClPP and TDClPP as predominant compounds as also pointed out a previous study. This study also indicated that most relevant compounds in water were TCIPP and TDCIPP (Lorenzo et al., 2018). Overall, the disparity between different sampling types reinforces the benefits of simultaneous deployment of MPTs with grab samples.

Therefore, water concentration estimates (C_w) were calculated for 16 compounds detected in MPTs for which previously calibrated sampling rates were available (Cárdenas-Soracá et al., 2020; Clokey et al., 2023; Hageman et al., 2019; McKay et al., 2020). Table S14 reports the values of C_w (ng L^{-1}) at 14 and 28 days of pesticides, PPCPs and PFAS in water obtained from passive samplers using Eq. (1), and sampling rates are reported in Table S8. The C_w calculated during both periods varies depending on the compound and the sampling point. At some sites certain compounds C_w decrease with time by more than a factor of 2 (e.g., atrazine desethyl in sampling points 4 and 5). Contrasting significant increases were observed at other sites from 14 to 28 days (e.g., tebuconazole at sites 11 and 12). Differences in C_w estimates between days 14 and 28 would indicate that compounds could have dissipated from passive samplers. This may be due to a decrease in chemical concentrations in the water of the Natural Park over time. It is possible there could have been a dilution event, or that concentrations of some compounds dissipated from water. C_w is an average of the previous 14 days and day 28 is the same (i.e. average of the previous 28 days), therefore reductions could be due to a lack of further input of a compound. Without costly and time-demanding high resolution grab sampling we can only hypothesize this was the case. The MPTs only sample tens of mL of water per day, so the samplers would be nowhere near their capacity to sorb compounds (i.e., using 400 mg of sorbent phase provides significant further sorption capacity). Changes in C_w observed are likely reflecting changes in the system over time.

Grab samples were collected at 0, 14 and 28 days (detailed concentration of the three sampling days are outlined in Tables S15-S17). The concentrations obtained also showed fluctuations dependent on the compound and site. Grab samples displayed a general decrease in concentrations from 14 to 28 days. Furthermore, the grab samples represent a point in time concentration estimate and therefore it is not possible to evaluate intermittent dilution or concentration of the compounds that instead may influence the concentrations in passive samplers.

The MPT C_w at 28 days were compared to those from grab samples (mean concentration of samples taken at 0, 14 and 28 days). The comparison of each detected compound site by site revealed variations in percentage ranging from −198 % to 195 % (refer to Table S21 for the paired *t*-test results and Table S22 for the specific percentage differences). The results showed variations for individual OCs when comparing the ratio of water concentrations (Cw) in grab samples and passive samplers to the concentrations in grab samples (see Figs. S3-S5). Similarly, differences were observed for each OC when comparing water concentrations (Cw) in grab samples to those in passive samplers (see Figs. S6-S8). Additionally, differences can be also observed in the site-by-site comparison of the concentrations in grab samples and passive samplers (see Figs. S9-S11). It is worth mentioning that the largest mismatch between grab and passive sampling occurs for PFOA, PFDA, and PFOS (see Fig. S10). However, when considering the average

concentrations of the different compounds over all sites, better results were observed for most compounds with normalized differences >33 % except for diuron, atenolol, tramadol and PFHxS (Fig. S12 for the average value of 12 points).

3.3. Spatial assessment of organic contaminants in the wetland

To better understand occurrences and concentrations, spatial distribution of the concentrations of pesticides, PFAS, PPCPs and OPFRs in twelve sites of the wetland was examined. Fig. 3 and Fig. S13 show the spatial distribution of contaminants in the Natural Park (Fig. S13 is

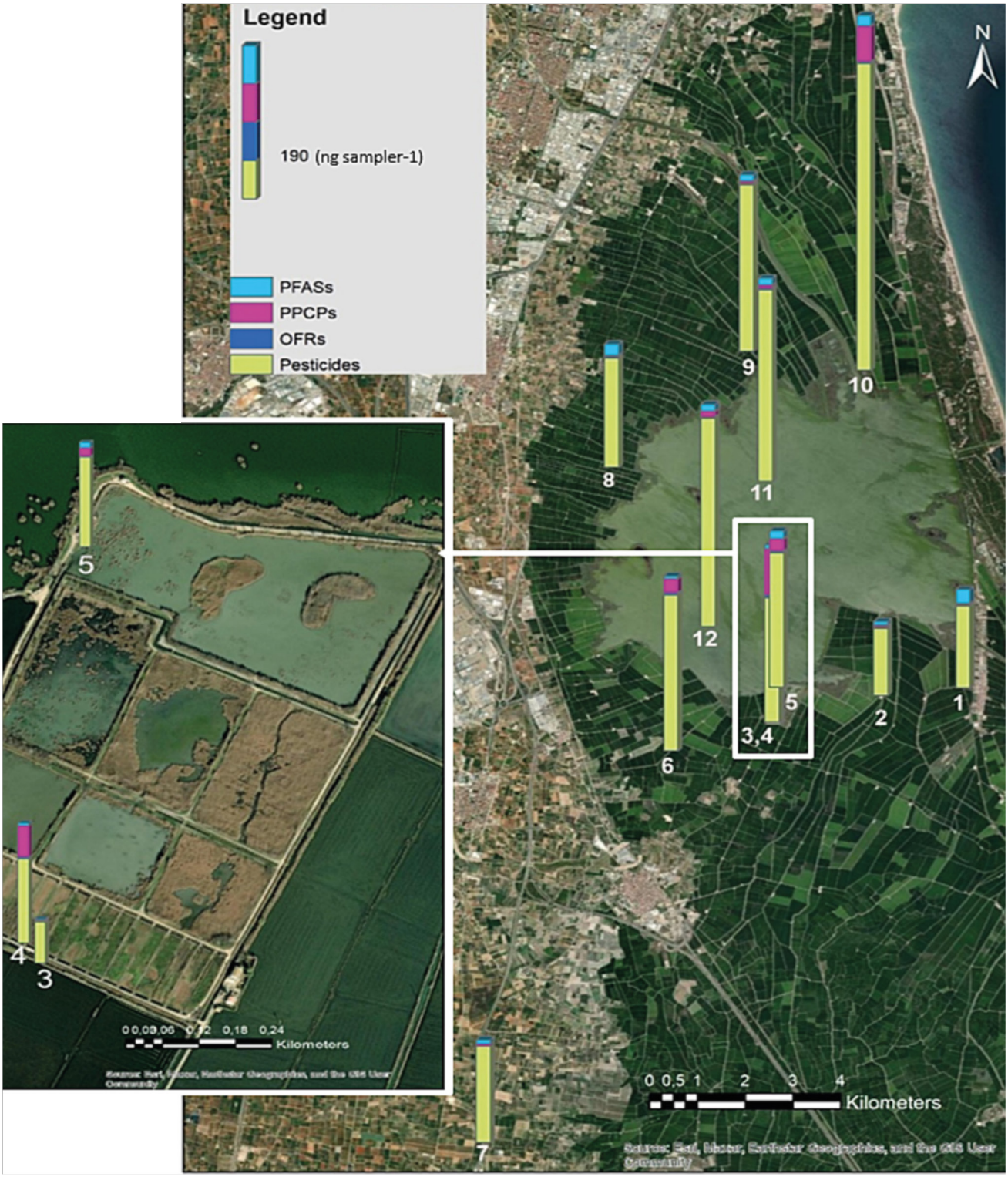


Fig. 3. Sum of the mass per sampler (ng sampler^{-1}) accumulated in microporous polyethylene tube (MPT) passive samplers of target pesticides, pharmaceuticals (PPCPs), *per*-and polyfluoroalkyl substances (PFAS) and organophosphorus flame retardants (OPFRs) across twelve sampling sites of L'Albufera Natural Park, Valencia, Spain.

equal to Fig. 3 but without the pesticides). The statistical analysis applied to these spatial assessment is also shown in the Supplementary Material (see Annex 1).

Pesticides were the most notable contaminants in L'Albufera. This is in line with nearby agricultural land-use devoted to rice and citrus cultivation. Pesticide treatment is matched to the plant, differing with each cultivar grown. Pesticides were detected at every site tested. It should be taken into account that aerial treatments on rice cause diffuse contamination throughout the area. Prochloraz, propiconazole and tebuconazole are post emergence fungicides usually sprayed from the mid-term of July until the harvest of the rice depending on the strength of the Pyricularia infection in the year of the cultivation (they had low or moderate solubility and are bioaccumulative). Carbendazim, imazalil, and thiabendazole were detected in the samples, despite not being used in rice cultivation. These compounds are typically employed in pest management for other crops such as citrus, specifically oranges and tangerines, which also aligns with the crop profile of L'Albufera.

Fewer pesticides were detected in control sites (sites 1, 7) but typically, these pesticides had higher concentrations compared to Obera (Site 2) and Els campets (Site 3). One potential explanation for these results is that grab water samples were taken in September when harvesting had not been completed in the north; the fields in the Obera and Els campets channels had already been harvested (in the south of the Natural Park).

Sites 4 and 5 correspond to the entrance and exit of the Milia artificial wetland. This is an old rice field bordering L'Albufera, which has been transformed into an artificial wetland or green filter for purification of the water that reaches the lagoon. This artificial wetland (Site 4) is fed by treated water from the L'Albufera Sur treatment plant (located 10 km from the artificial wetland). Pesticide levels were lower at the inlet and highest at the outlet. The treated water from the WWTP may have been contaminated by pesticides due to drift from overhead spraying, or upstream application. This shows a limited capacity for the artificial wetland to remove certain pesticides. The other irrigation channels corresponding to Sites 6, 7, 8 and 9, present comparable levels of pesticides in the east of the Natural Park. The levels increase slightly within the lake (Sites 11 in the north and 12 in the south) and in the points located in the irrigation channel of Tancaeta (Site 10, the most northerly point,), which carries treated water from the city of Valencia via the Pinedo II treatment plant in addition to that from rice cultivation. The differences were only significant for tebuconazole that showed higher levels in the channels and lake than in the controls. In the case of grab samples there were also statistically significant differences for atrazine and diazinon.

Figs. 3 and S13 provide at-a-glance fingerprints of contaminant groups at each site derived from the MPTs. The difference in the concentration of PPCPs between Site 3 (an irrigation channel that collects the outflows of the rice field) and Site 4 (the irrigation channel that transport the treated wastewater) is notable considering their proximity. Site 4 corresponds to the channel that carries the tertiary treatment water from the L'Albufera Sur treatment plant (urban treatment plant) to the Tancat de Milia (artificial wetland) for its final treatment before being discharged into the lake, likely leading to Site 4's elevated levels. The reduction in concentration at Site 5 (90 % lower), which corresponds to the outlet of the artificial wetland, gives credence to the efficacy of the wetland's purification capabilities. Sites 6 and 10 showed relatively high levels of PPCPs, likely attributable to wastewater discharges. The level of PPCPs was higher in the South part of the lake than in the North. This may indicate that the hydrology of the lake attenuates contaminants in the south. However, differences are not statistically significant for passive samplers or grab samples. This division has already been noted in other studies for PPCPs (Sadutto et al., 2021) and PFAS (Pico et al., 2012; Lorenzo et al., 2019). Levels of PFAS and OPFRs are much lower and less variable in L'Albufera. However, it is noteworthy that the highest levels of PFAS were observed in Sites 1 and 8. The observed higher levels present in Site 1 may indicate that the materials used in the construction, maintenance and operation of the fish farm (aquaria, tanks, etc.) may contain PFAS. Site 8's contamination might be linked to its location within Valencia city's industrial belt. Differences were only significant for 6:2 FTS that was at lower concentrations in the lake. The completed results of the special analysis including grab samples and passive samplers are presented in the Annex 1 of the supplementary material. Please see Figs. S14-S21). The PCA differentiate two groups for passive samplers in the case of PPCPs and pesticides (see Figs. S18 and S19) noting the influence of phycoerythrin and chlorophyll A in some OCs and the influence of conductivity and salinity in others. In the case of PPCPs these explain variance at 99.8 % and in the pesticides 80.8 %. PFAS variance is explained at 76.26 % by two groups of parameters (one group include salinity, conductivity, phycoerythrin and chlorophyll A and the other pH and DO) (see Fig. S20). Instead, salinity, conductivity and temperature are driven variables that influence the behavior of OPFRs (see Fig. S21). This study demonstrates the significant variability within the Park, elucidating the variety of OCs sources. In addition, it demonstrates the north/south division and the importance of broad understanding of contamination across the entire Natural Park.

3.4. Risk assessment for the wetland

For individual contaminants, RQs were calculated by dividing the C_w (mean or maximum concentration of OC detected in the grab water samples) by the corresponding predicted no-effect concentration (PNEC), as shown in Eq. (2). The results of the ecotoxicological risk assessment derived from the presence of the different OCs in grab water samples with the RQ method are outlined in Table 1.

For average C_w (grab samples) in the park, PFOS, diclofenac and ibuprofen showed RQ >1 indicating that these are OCs of concern for aquatic biota. Demonstrated toxicological effects of these OCs in fish comprise developmental malformations, oxidative stress, cellular damage, behavioral alterations and alterations of biochemical, immunological and hematological parameters among others (Abdel Rahman et al., 2023; Jo et al., 2014; Mathias et al., 2018; Muñoz-Peñuela et al., 2022).

Ibuprofen (RQ >15 at the average concentration and RQ > 100 at maximum concentration) as well as diclofenac (RQ >10 at maximum concentrations) could be of particular concern to aquatic biota. These PPCPs have recently also been described as of high concern in two other Spanish hydrological systems — the Guadiana River Basin (Palma et al., 2020) and the Ebro delta (Barbieri et al., 2021). Worldwide studies on risk assessment performed on these contaminants showed risk to a variety of aquatic biota (Lin et al., 2022; Naumann et al., 2022; Stehle et al., 2023).

Acetamiprid, and terbumeton desethyl exhibited mean concentrations within the range of $0.1 \leq RQ < 1$ while flufenamic acid, triclosan, dimethoate and terbutryn displayed their maximum concentrations within the same range in L'Albufera Natural Park. This indicates a moderate risk to the Natural Park's ecosystem. The other compounds detected have RQ <0.1 and are thus considered to be of negligible risk.

This risk assessment is limited and low RQ may be the result of low concentrations and/or too high a PNEC in the absence of experimental values. Some experimental PNEC data were not available, so it was not possible to calculate the RQ of some OCs. The RQ does not consider certain phenomena that affect higher trophic levels such as bioaccumulation and biomagnification of OCs along the food chain. In addition, the OCs were considered individually, however in the environment, a mixture of compounds is present that can add up or even potentiate their effects. Several studies that conducted a cumulative risk assessment of OCs that by themselves did not represent any hazard to biota concluded that instead the mixtures are of concern (Barbieri et al., 2021; Nantaba et al., 2020; Sadutto et al., 2021; Wang et al., 2021; Yu et al., 2023). Therefore, additive, antagonistic and synergistic effects may need to be considered to better assess if there is additional risk posed to aquatic biota by OCs.

Table 1
Risk quotient (RQ) values for individual organic contaminants (OCs) detected in grab samples at mean and maximum concentrations found in L'Albufera Natural Park. Results are categorized by high, medium and low risk.

Contaminant	RQ (mean environmental concentrations)	RQ (max environmental concentrations)
At mean concentration. $1 \leq RQ$		
PFAS		
PFOS	1.1	5.1
PPCPS		
Diclofenac	2.5	14
Ibuprofen	16	103
At maximum concentration. $1 \leq RQ$		
Pesticides		
Imidacloprid	0.63	3.5
At mean concentration. $0.1 \leq RQ < 1$		
Pesticides		
Acetamiprid	0.68	3.0
Terbumeton desethyl	0.31	0.94
At maximum concentration. $0.1 \leq RQ < 1$		
Pesticides		
Diazinon	$4.4 \cdot 10^{-2}$	0.35
Diuron	$6.0 \cdot 10^{-2}$	0.41
Dimethoate	$1.0 \cdot 10^{-2}$	0.13
Terbutryn	$2.0 \cdot 10^{-2}$	0.13
PPCPs		
Flufenamic acid	$5.0 \cdot 10^{-2}$	0.23
Triclosan	$7.5 \cdot 10^{-2}$	0.21
At any concentration. $RQ < 0.1$		
OPFRs		
TCEP	$3.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
TPhP	$5.0 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$
TnBP	$3.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$
Pesticides		
Atrazine	$1.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Atrazine-Desethyl	$1.6 \cdot 10^{-2}$	$5.9 \cdot 10^{-2}$
Atrazine-Desisopropyl	$7.0 \cdot 10^{-3}$	$2.3 \cdot 10^{-2}$
Carbendazim	$7.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$
Imazalil	$6.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$
Prochloraz	$3.9 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
Propanil	$1.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$
Simazine	$1.0 \cdot 10^{-3}$	$4.0 \cdot 10^{-3}$
Tebuconazole	$2.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$
Terbumeton	$4.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$
Thiabendazole	$7.0 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$
PFAS		
PFBA	$3.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$
PFBS	$1.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$
PFDA	$4.7 \cdot 10^{-3}$	$3.0 \cdot 10^{-2}$
PFDS	$4.1 \cdot 10^{-3}$	$7.5 \cdot 10^{-3}$
PFHpA	$1.2 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$
PFHpS	$1.4 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$
PFHxS	$8.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$
PFNA	$4.0 \cdot 10^{-3}$	$3.4 \cdot 10^{-2}$
PFOA	$9.1 \cdot 10^{-3}$	$1.6 \cdot 10^{-2}$
PFODA	$4.4 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$
PFTrDA	$7.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-2}$
PFUnDA	$1.1 \cdot 10^{-2}$	$3.3 \cdot 10^{-2}$
PPCPs		
Atenolol	$3.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-5}$
Bezafibrate	$3.4 \cdot 10^{-3}$	$3.6 \cdot 10^{-2}$
Caffeine	$7.0 \cdot 10^{-4}$	$4.8 \cdot 10^{-3}$
Ethylparaben	$1.0 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
Lorazepam	$1.4 \cdot 10^{-2}$	$5.8 \cdot 10^{-2}$
Methylparaben	$2.3 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$
Naproxen	$2.11 \cdot 10^{-2}$	$9.26 \cdot 10^{-2}$
Ofloxacin	$2.47 \cdot 10^{-3}$	$1.90 \cdot 10^{-2}$
Acetaminophen	$6.00 \cdot 10^{-5}$	$4.00 \cdot 10^{-4}$
Propylparaben	$4.70 \cdot 10^{-4}$	$1.50 \cdot 10^{-3}$
Salicylic acid	$1.60 \cdot 10^{-3}$	$2.70 \cdot 10^{-3}$
Tramadol	$2.66 \cdot 10^{-3}$	$9.50 \cdot 10^{-3}$

The sum of exposure to the detected OCs present at each sampling point may suggest environmental concern for some biota in the wetlands. Therefore, to overcome some of the previous drawbacks and to improve this risk assessment, the cumulative risk of the simultaneous presence of several OCs in the 12 grab water samples was spatially represented (Fig. 4).

The risk assessment for the individual compounds showed that some compounds (ibuprofen, imidacloprid, acetamiprid, PFOS and diclofenc) might be of environmental concern. Concentration and number of contaminants that were present in each sample are of environmental concern. These results highlight the importance of examining the whole mixture of organic contaminants to assess the environmental risk. If all the compounds are considered, the RQ for all sampling points would be >1 for all sites. In this calculation, RQ were highest for sites 3 and 10 (Fig. 4). The lack of information on the effects of this mixed contamination makes this an appropriate area for future studies.

4. Conclusions

The determination of a wide range of contaminants in L'Albufera Natural Park revealed that pesticides are the most abundant OCs with the highest observed masses followed by PPCPs>PFAS>OPFRs. MPT passive samplers showed themselves to be comparable and complementary tool for the assessment of medium-term pollution status within coastal wetlands. The passive samplers provide good agreement with information from the grab samples and in some cases additional information on compounds that were not successfully sampled via grab sampling. The passive samplers integrate water concentrations only during the sampling period and can help reflect the pollution situation in a water body. The need to apply compound specific sampling rates means that some OCs detected at elevated concentrations in passive samplers could not be quantified because sampling rates have not yet been calibrated for certain compounds. Future work will include measurement of sampling rates for additional analytes with MPT samplers.

The spatial variability of many of the OCs in the studied region was relatively small, indicating greater contributions from diffusive sources than point sources in most locations. Agricultural contaminants were the exception to this, with greater prevalence in the open lake and the north of the Natural Park.

The risk assessment of individual compounds to aquatic biota showed that imidacloprid, acetamiprid, PFOS, PFDA, diclofenac and ibuprofen pose the highest individual risk quotients. However, when calculating RQ based on the sum of exposure to all the OCs detected in the sampling sites, all samples were of environmental concern.

CRediT authorship contribution statement

Yolanda Soriano: Data curation, Writing- Original draft preparation.

Rodrigo Alvarez-Ruiz: Writing- Reviewing and Editing, Visualization.

Joseph Clokey: Writing- Reviewing and Editing, Investigation.

Sara Ghorbani Gorji: Writing- Reviewing and Editing.

Sarit Kaserzon: Conceptualization, Methodology, Visualization.

Yolanda Picó: Conceptualization, Methodology, Reviewing and Editing, Supervision, Project Administration; Funding acquisition,



Fig. 4. ΣRisk Quotients (RQs) at each sampling point showing the differences between the sampling points.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work has been supported by Grant RTI2018-097158-B-C31 funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe" and by the Grant CIPROM/2021/032 funded by the Generalitat Valenciana. Y. Soriano acknowledges her pre-doctoral contract by the grant PRE2019-089042 funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in your future". This project was supported by an Australian Research Council (ARC) Linkage grant (LP180101128). We also thank direction and the staff of the Office of the Natural Park of L'Albufera for their continuous advice and support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.166594.

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ARTICLE 03

SUPPLEMENTARY MATERIAL:

Determination of organic contaminants in L'Albufera Natural Park using microporous polyethylene tube passive samplers: an environmental risk assessment

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Text S1. Standards.

- Organophosphorus flame retardants (OPFRs) (11 compounds):

Tris(2-chloroethyl) phosphate (TCEP), tri-n-propylphosphate (TPP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), triphenyl phosphate (TPhP), tris(2,3-dibromopropyl) phosphate (TDBPP), cresyl diphenyl phosphate (CDP), tributyl phosphate (TnBP), tris(2-Butoxyethyl) phosphate (TBEP), tris(methylphenyl) phosphate (TMPP), tris-(2-ethylhexyl) phosphate (TEHP) were purchased from Sigma-Aldrich (St, Louis, MO, USA). Acronym, CAS number, empirical formula and molecular weight are listed in Table S3. The deuterium-labeled d_{15}-TDCIPP, d_{15}-TPhP, d_{12}-TCEP, and d_{18}-TCIPP were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). This group of pollutants was only analyzed at the University of Valencia.

- Per-and polyfluoroalkyl substances (PFAS) (18 in common + 2 University of Valencia (UV) + 37 compounds at The University of Queensland (UQ)):

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluoro-7-methyloctanoic acid (ipPFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA), perfluorooctadecanoic acid (PFODA), potassium perfluorobutanesulfonate (PFBS), potassium perfluorohexanesulfonate (PFHxS), sodium perfluoroheptanesulfonate (PFHpS), sodium perfluorooctanesulfonate (PFOS), sodium perfluoro-7-methyloctanesulfonate (ipPFNS), sodium perfluorodecanesulfonate (PFDS) were purchased from Wellington Laboratories Inc, Canada. These compounds were analyzed at the University of Valencia and also at the University of Queensland, except for ipPFNA and ipPFNS.

Perfluoropentanesulfonic acid (PFPeS), 4:2 fluorotelomer sulfonic acid (4:2 FTS), perfluorohexanesulfonamide (FHxSA), perfluorooctane sulfonamide (PFOSA), N-methyl-perfluorooctane sulfonamide (N-MeFOSA), perfluorononanesulfonic acid (PFNS), perfluorooctane sulphonamide acetic acid (FOSAA), N-ethyl-perfluorooctane sulfonamide (N-EtFOSA), N- [3-(perfluoro-1-hexanesulfonamide) propan-1-yl]-N,N,N-trimethylammonium (N-TAmP-FHxSA), perfluorododecane sulfonic acid (PFDoDS), 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB), N-methylperfluorooctanesulfonamideacetic acid (N-MeFOSAA), N-methylperfluorooctanesulfonamideethanol (N-MeFOSE), N-ethyl perfluorooctane sulfonamide ethanol (N-EtFOSE), perfluorohexylphosphonic acid (PFHxPA), N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA), perfluorooctane sulfonamide ethanol-based phosphate (SAmPAP) diester, 10:2 sulfonate fluorotelomeric (10:2 FTS), 5:3 fluorotelomer carboxylic acid (5:3 FTCA), 6:2 fluorotelomer carboxylic acid (6:2 FTCA), 10:2 fluorotelomer carboxylic acid (10:2 FTCA), 8:2 fluorotelomer carboxylic acid (8:2 FTCA), perfluorobutane sulfonamide (H-FBSA), 6:2 fluorotelomersulfonate (6:2 FTS), 8:2 fluorotelomersulfonate (8:2 FTS), perfluoropropane sulfonic acid (PFPrS), 6:2 fluorotelomer phosphate monoester (6:2 monoPAP), 6:2 fluorotelomer phosphate diester (6:2 DiPAP), 6:2/8:2 fluorotelomer phosphate diester (6:2/8:2 DiPAP), 8:2 Fluorotelomer phosphate diester (8:2 DiPAP), 4,8-Dioxa-3H-perfluorononanoic acid (ADONA), sodium bis(perfluorohexyl) phosphinate (6:6 PFPiA) and perfluorooctyl phosphonic acid (PFOPA), 8-chloro-perfluoro-1-octane sulfonic acid (8Cl-PFOS), 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-F53B), 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-F53B) and

6:2 polyfluoroalkyl phosphoric acid monoesters (6:2 PAP) were purchased from Wellington Laboratories, Guelph, Canadá. The name of the compound, structure, acronym, CAS number, formula and molar mass of all PFAS detected by both universities are reflected in Table S4.

The deuterium-labeled sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octane sulfonate ($^{13}C_4$-PFOS), sodium perfluoro-1-hexane [$^{18}O_5$] sulfonate ($^{18}O_5$-PFHxS) and surrogates perfluoro-n- [1,2,3,4-$^{13}C_4$] butanoic acid ($^{13}C_4$-PFBA), perfluoro-n- [1,2-$^{13}C_2$] hexanoic acid ($^{13}C_2$-PFHxA), perfluoro-n-[1,2,3,4-$^{13}C_4$] octanoic acid ($^{13}C_4$-PFOA), perfluoro-n- [1,2,3,4,5 -$^{13}C_5$] nonanoic acid ($^{13}C_5$-PFNA), perfluoro-n- [1,2-$^{13}C_2$] decanoic acid ($^{13}C_2$-PFDA), perfluoro-n-[1,2-$^{13}C_2$] undecanoic acid ($^{13}C_2$-PFUdA) and perfluoro-n- [1,2-$^{13}C_2$] dodecanoic acid ($^{13}C_2$-PFDoA) were also purchased from Wellington Laboratories Inc, and were used at the University of Valencia.

The deuterium-labeled perfluoro-n- [1,2,3,4-$^{13}C_4$] butanoic acid ($^{13}C_4$-PFBA), $^{13}C_4$-perfluoropentanoic acid ($^{13}C_4$-PFPeA), sodium perfluoro-1-[2,3,4- $^{13}C_3$] butanesulfonate ($^{13}C_3$-PFBS), perfluoro-n- [1,2-$^{13}C_2$] hexanoic acid ($^{13}C_2$-PFHxA), sodium 1H,1H,2H,2H-perfluorohexane sulfonate $^{13}C_2$ ($^{13}C_2$ 4:2 FTS), perfluoro-1- [1,2,3,4-13C4] octanesulfonate (13C4-PFOS), 13C4- perfluoroheptanoic acid (13C4-PFHpA), perfluoro-1-[13C8] octanesulfonamide (M8FOSA), sodium perfluoro-1-hexane [$^{18}O_2$] sulfonate (MPFHxS), perfluoro-n- [1,2,3,4-$^{13}C_4$] octanoic acid ($^{13}C_4$-PFOA), sodium 1H, 1H, 2H, 2H-perfluoro (1,2-$^{13}C_2$) octane sulfonate (M2-6:2 FTS), sodium 1H, 1H, 2H, 2H-perfluoro (1,2-$^{13}C_2$) decane sulfonate (M_2 8:2 FTS), sodium 1H,1H,2H,2H-[1,2-$^{13}C_2$] perfluoro octyl phosphate (M_2-6:2 PAP), perfluoro-n- [1,2,3,4,5 -$^{13}C_5$] nonanoic acid ($^{13}C_5$-PFNA), N-methyl-d3-perfluoro-1-octanesulfonamide (d-N-MeFOSA), perfluoro-n- [1,2-$^{13}C_2$] decanoic acid ($^{13}C_2$-PFDA), N-ethyl-d5-perfluoro-1-octanesulfonamide (d-N-EtFOSA), Sodium 1H,1H,2H,2H- [1,2-$^{13}C_2$] perfluorodecylphosphate (M2-8:2 PAP), N-methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA), perfluoro-n- [1,2-$^{13}C_2$] undecanoic acid ($^{13}C_2$-PFUdA), N-ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA), perfluoro-n- [1,2-$^{13}C_2$] dodecanoic acid ($^{13}C_2$-PFDoA), 2- (N-ethyl-d5-perfluoro-1-octanesulfonamido) ethan-d4-ol (d9-N-EtFOSE), 2- (N-methyl-d3-perfluoro-1-octanesulfonamido) ethan-d4-ol (d7-N-MeFOSE), sodium bis (1H,1H,2H,2H-[1,2-$^{13}C_2$] perfluorooctyl) phosphate (M_4-6:2 diPAP), perfluoro-n-[1,2-$^{13}C_2$] tetradecanoic acid (M_2PFTeDA), sodium bis (1H,1H,2H,2H-[1,2-$^{13}C_2$] perfluorodecyl) phosphate (M_4-8:2diPAP), $^{13}C_2$-labeled FTCAs [$C_6F_{13}CH_2COOH$] ($^{13}C_2$-6:2 FTCA), perfluoro-n-[1,2- $^{13}C_2$] hexadecanoic acid ($^{13}C_2$-PFHxDA) were used at the University of Queesland, Australia and were purchased from Wellington Laboratories, Guelph, Canadá.

- Pesticides (23 in common + 40 University of Valencia (UV) + 48 compounds at The University of Queensland (UQ)):

Atrazine, atrazine-desethyl, atrazine-desisopropyl, azinphos-methyl, carbendazim, carbofuran, chlorpyrifos, diazinon, diuron, fenthion, fipronil, hexythiazox, imidacloprid, malathion, methiocarb, methoalachlor, propazine, simazine, tebuconazol, terbuthylazine, terbuthylazine-desethyl, terbutryn and thiabendazole were analyzed at both Universities.

Acetamiprid, acetochlor, acrinathrin, alachlor, azinphos-ethyl, bifentrhrin, buprofezin, carbofuran-3-OH, chlorfenvinphos, chlothianidin, coumaphos, cyhalothrin, dichlofenthion, dimethoate, DMA (2.4-dimethylaniline), DMF (N.N-Dimethylformamide), DMPF (N'-(2.4- Dimethylphenyl)-N-methylformamidine), ethion, etofenprox, fenitrothion, fenthion sulfone, fenthion sulfoxide, flumethrin, fluvalinate, imazalil, isoproturon, molinate, omethoate, parathion-ethyl, parathion-methyl, prochloraz, propanil, pyriproxifen,

spinosad A, spinosad D, terbumeton, terbumeton-desethyl, terbuthylazine-2-OH, thiamethoxam, tolclofos-methyl were analyzed only at the University of Valencia, Spain.

2,4,5-T (2,4, 5-Trichlorophenoxyacetic acid), 2,4-D (2, 4-dichlorophenoxyacetic acid), 3,4-Dichloroaniline, ametryn, bendiocarb, bifenthrin, bromacil, bromoxynil, carbaryl, clopyralid, cyanazine, cyproconazole, DCPMU (1-(3, 4-Dichlorophenyl)-3-methylurea), DEET (Diethyltoluamide), dichlorvos, difenoconazole, diketonitrile, fenamiphos, fluazifop, fluazinam, fluometuron, fluroxypyr, haloxyfop, hexazinone, hydroxysimazine, imazapic, imazapyr, imazethapyr, MCPA(4-Chloro-2-methylphenoxyacetic acid), metalaxyl, methidathion, methomyl, metribuzin, metsulfuron methyl, oryzalin, pencycuron, pendimethalin, picloram, prometryn, propachlor, propargite, propiconazole, propoxur, propyzamide, pyrimethanil, sulfoxaflor, tebuthiuron and tyclopyr were analyzed at the University of Queesland, Australia. See characteristics of the pesticides in Table S5 of the supplementary material. The internal standards included in the method by the University of Queesland, Australia were carbendazim d_4, atrazine desethyl $^{15}N_3$, DEET d_{10}, atrazine desisopropyl d_5, imidacloprid d_4, tebuthylazine desethyl d_9, MCPA d_3, atrazine d_5, terbuthylazine d_5, propiconazole d_5, simazine d_{10}, carbofuran d_3, methiocarb d_3, 2,4-D $^{13}C_6$, 2,4,5 - T-$^{13}C_6$, fipronil $^{13}C_4$ $^{15}N_2$, fenthion d_5, diazinon d_{10}, thiamethoxam d_4, tebuconazole d_6, chlorpyriphos d_{10}, diuron d_6, bromacil d_3, metsulfuron methyl d_3, methomyl-d_3, carbaryl d_7, propoxur d_3, metribuzin d_3, prometryn d_6, hexazinone d_6, pendimethalin d_5, metolachlor d_6, fluazifop d_4, haloxyfop d_4. All analytical standards were purchased from Sigma Aldrich.

- Pharmaceuticals and personal care products (PPCPs) (8 in common + 17 University of Valencia (UV) +25 compounds at The University of Queensland (UQ)):

Salicylic acid, thiamphenicol, furosemide, chloramphenicol, methylparaben, clofibric acid, ethylparaben, ofloxacin, lorazepam, naproxen, bezafibrate, acetaminophen, propylparaben, warfarin, bisphenol A, diclofenac, butylparaben, indomethacin, ibuprofen, flufenamic acid, triclosan, triclocarban, caffeine, atenolol and tramadol were purchased from Sigma Aldrich. These compounds were analyzed at the University of Valencia, Spain. Compounds highlighted in black were analysed at both laboratories
The internal standards included in the method by the University of Valencia were bisphenol A-d_{16}, diclofenac-d_4, ibuprofen-d_3, triclosan-d_3, were from Sigma-Aldrich (Steinheim, Germany).

Acetaminophen, gabapentin, paraxanthine, caffeine, naproxen, carbamazepine, sulfadiazine, sulfamethoxazole, atenolol, venlafaxine, oxazepam, trimethoprim, diclofenac, codeine, temazepam, tadalafil, verapamil, atorvastatin, iopromide, salicylic acid, acesulfame, hydrochlorthiazide, nicotine, cotinine, hydroxycotinine, tramadol, desmethyldiazepam, fluoxetine, citalopram desmethyl, citalopram, sildenafil, furosemide and triclosan were analyzed at the University of Queesland, Australia. The internal standards included in the method by the University of Queesland, Australia were gabapentin d_4, naproxen d_3, atorvastatin d_5, iopromide d_3, venlafaxine d_6, oxazepam d_4, diclofenac d_4, citalopram d_6, fluoxetine d_6. All analytical standards were purchased from Novachem (VIC, Australia). See characteristics of PPCPs in Table S6 of the supplementary material.

Text S2. Reagents and chemicals.

Solvents used included HPLC grade methanol (MeOH) ≥ 99.8% purity were purchased from VWR Chemicals® (Radnor, PA, USA) and ammonium formate (NH_4HCO_2), formic acid (CH_2O_2), ammonium fluoride (NH_4F) and acetone (CH_3COCH_3) were purchased from Alfa Aesar (Karlsruhe, Germany). Acetonitrile (ACN) ≥ 99.9% purity was from Merck (Darmstadt, Germany). High purity water was obtained using a Milli-Q water purification system (Millipore, Milford, MA, USA). The 15 mL and 50 mL polypropylene centrifuge Falcon tubes were from VWR International Eurolab (Barcelona, Spain).

Primary-secondaryamine (PSA) and C18 were from Análisis Vínicos (Tomelloso, Spain), magnesium sulfate ($MgSO_4$) and sodium sesquihydrate citrate [$HOC(COOH)(CH_2COONa)_2$ 1.5 H_2O] from Alfa Aesar (Karlsruhe, Germany) and sodium chloride (NaCl) and trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$) from Prolabovwr (Leuven, Belgium).

Strata-X-33 µm polymeric reversed phase (200 mg/6 mL) were from Phenomenex (Torrance, CA, USA). The 1.5 mL amber glass vials with stoppers 99 mm + Septum Sil /PTFE used to inject the samples were from Análisis Vínicos S.L. (Tomelloso, Spain) and the 250 µL polypropylene inserts were from Agilent Technologies (Santa Clara, CA, United States). Nylon 0.22 µm filters were purchased from Membrane Solutions (Plano, TX, USA). Polypropylene/polyethylene syringes were manufactured by BRAUN and distributed by Scharlab S.L. (Barcelona, Spain). For the solid phase extraction (SPE) Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL) cartridges and a vacuum manifold Supelco Visiprep 57030- U (Sigma-Aldrich, St. Louis, Missouri, USA) were used.

Sediment samples were lyophilized using a Sentry 2.0 lyophilizer from VirTis SP Scientific manufacturer (Gardiner, NY, USA). The sampler combined sample concentrator model SBHCONC/1 and heating plate model SBH130D/3 were provided by (Stuart®UK).

Text S3. Grab samples extraction.

SPE Cartridges (Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL)) were preconditioned with 6 mL MeOH followed by 6 mL of ultrapure water. A sample of 250 mL was passed through the cartridges under vacuum at 400 mba h^{-1} Pa^{-1} (flow rate: 10 mL min^{-1}). The cartridges were then washed with 6 mL of Milli-Q and dried for 15 min. The analytes were eluted with 6 mL of MeOH followed by 3 mL of MeOH–dichloromethane (50:50 v/v) and collected in a 15 mL plastic Falcon tube of polypropylene. Extracts were evaporated to dryness under a gentle stream of nitrogen at 40ºC. The residue was redissolved in 1 mL of MeOH, vortexed for 1 min and sonicated for 3 min. Then 500 µl of the extract was added to a 1.5 mL LC vial using a PTFE filter (0.22 µm pore size and 13 mm diameter) attached to a glass syringe and stored for pesticides analysis. The rest of the extract (500 µL) was evaporated to dryness, then reconstituted to 500 µL with 70:30 Milli-Q water–MeOH, vortex for 1 min and sonicated for 3 min. The extract was added to a 1.5 mL glass vial with a 250 µL polypropylene insert, using a Nylon filter (0.22 µm pore size and 4 mm diameter) coupled to a disposable polypropylene/polyethylene syringe and stored for PPCPs, PFAS and OPFRs analysis. Extracts were stored at -20ºC until injection.

Text S4. Passive samplers extraction.

Sorbent in the tube was spiked with a mix of internal standards (50 µL of internal standards mix at a concentration of 1 µg mL^{-1} by removing the cap of the MPT on one side, adding the solutions and then closing the cap. Then, 4 mL of MeOH were added into each Falcon tube and were centrifuged for 15 min at 2465 rcf and 22º C. The resulting extract was transferred into a clean Falcon tube. Then, the solid sorbent remaining in each Falcon tube was poured into empty SPE cartridge tubes, 12cc Polypropylene, with frits for 12cc SPE tubes, 20 µm, Polyethylene from Phenomenex® (Torrance, CA, USA) and eluted with acetone (4mL) and (2x2mL) acidified methanol 2% acidic MeOH (v/v). These extracts were mixed with those of the previous centrifugation, and then concentrated under a gentle stream of nitrogen to 1 mL. Then, 500 µL were transferred to a 1.5 mL vial ready for the analysis of pesticides. The remaining 500 µL were evaporated to 25 and the 475 µL of MilliQ water were added. The extract was transferred to a vial with polypropylen insert ready for the analysis of PPCPs, PFAS and OPFRs.

Text S5. LC-MS/MS Analysis.

The analysis at UV was performed with a 1260 Infinity Ultrahigh-Performance Liquid Chromatographer (UHPLC) system coupled to an Agilent 6410 triple quadrupole (QQQ) mass spectrometer (MS/MS) with electrospray ionization (ESI) interface from Agilent Technologies (Santa Clara, CA, USA). The operating conditions for the analysis of the different contaminants by LC-MS/MS are shown in Table S7.

At UQ, PFAS were analyzed with a high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) using a Nexera HPLC (Shimadzu Corp., Kyoto, Japan) coupled to API5500 QTRAP mass spectrometer (Sciex, Melbourne, Australia) with ESI interface operating in negative ion mode. Chromatographic separation of the analytes was achieved with a Gemini C18 column (50 × 2.0 mm, 4 µm; Phenomenex, Torrance, CA), maintained at 45 °C, with a flow rate of 0.3 mL min^{-1} and injection volume of 5 µL. Mobile phases consisted of MeOH: water (1:99 v/v) (A), and MeOH: water (95:5 v/v) (B), with 5 mM ammonium acetate in both phases. An isolator column (Phenomenex) was included inline directly after the mobile phase mixing chamber to delay the elution of any solvent-derived background PFAS contamination. Data acquisition and processing was carried out using Analyst® TF 1.6 and MultiQuant™ software (Sciex) (Kaserzon et al., 2019).

Pesticide extracts were quantified on an AB/SCIEX (Ontario, Canada) 6500 QTRAP system with electrospray ionization using positive and negative ionization based on a scheduled multiple reaction monitoring (MRM) switching process. Separation was achieved with a Shimadzu Nexera HPLC system (Kyoto, Japan) with a Phenomenex biphenyl column (50 mm × 2.1 mm × 2.6 µm particle size) with a Kinetex EVO C18 pre-injector column. And PPCP extracts were using LC (Shimadzu, Nexera HPLC system, Kyoto, Japan) coupled to ESI MS/MS (SCIEX API5500 and 6500+ QTRAP® Mass Spectrometers, Ontario, Canada).

Both, positive and negative ionization modes were operated based on scheduled MRM switching process (Further details in: (Hageman et al., 2019; McKay et al., 2020)). Glyphosate and AMPA were also analyzed using an AB/Sciex API6500+ Triple Quadrupole Mass Spectrometer equipped with an electrospray (Turbo V) interface coupled to an Exion HPLC system (AB/Sciex, Concord, Ontario, Canada). Separation was achieved using a Micro-Guard Cation H^+ cartridge guard column (30 x 4.6 mm; Bio-Rad Laboratories,

Gladesville, NSW) run at 40°C. A flow rate of 0.75 mL min^{-1} with linear gradient elution starting with 75% A: 25% B for 1 min, ramped to 100% A: 0% B in 3 min then back to 25% B and flow rate increased to 1 mL min^{-1} at 4 min. This flow rate was kept at these conditions for 3 min with flow rate reduced to 0.75 mL min^{-1} at 7 min. A = 1% v/v acetonitrile in HPLC grade water containing 0.1% v/v formic acid and 5 µM medronic acid (methanediylbis (phosphonic acid), B = 99% v/v acetonitrile in HPLC grade water containing 0.1% v/v formic acid and 5 µM medronic acid.

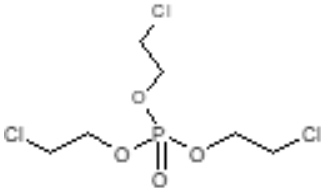
The mass spectrometer was operated in negative ion multiple reaction-monitoring mode using nitrogen as the collision gas with a dwell time of 50 milliseconds per MRM giving a scan time of 0.4 seconds. Positive detections were confirmed using isotope ratios with labelled internal standards ($^{13}C_2$ -glyphosate and ^{13}C-D_2-AMPA).

Text S6. Interlaboratory comparison.

Nineteen analytes (8 pesticides, 8 PFAS, and 3 PPCPs) were detected at the two laboratories. For each of the identified compounds, the collected data reveals variations in percentage on a site-by-site basis, spanning from -200% to 198% (refer to Table S19 for the paired t-test results, Table S20 for the specific percentage differences and Figure S2A for the representation of the mean differences and their standard deviation). The average ratio of mass per sampler (ng $sampler^{-1}$) is between 0.5 (for terbuthylazine) and 15 (atrazine desethyl). Results are presented in Figure S2B where the compounds are ordered in ascending order within their respective groups.

Five analytes (26%) were within 33% of between-lab measurements, while terbutylazine were within ~ 50%, and the other compounds fell outside these ranges. From the 18 common analysed PFAS, eight were detected in both Universities (Figure S2A). Seven (i.e. PFPeA, PFHpS, PFNA, PFDA, PFTeDA, PFHxDA and PFODA) were only detected at UQ because concentrations were below the LODs of UV. Diazinon (maximum concentration: 1.87 ng $sampler^{-1}$) was detected only at UQ and carbendazim (maximum concentration: 1.80 ng $sampler^{-1}$) was detected only at UV.

Table S1. Characteristics of the organophosphorus flame retardants (OPFRs) analysed in the present study.

Compound	Acronym		CAS Number	Formula	Molecular Weight
Tris(2-chloroethyl) phosphate	TCEP		115-96-8	$C_6H_{12}Cl_3O_4P$	285.49

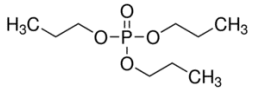
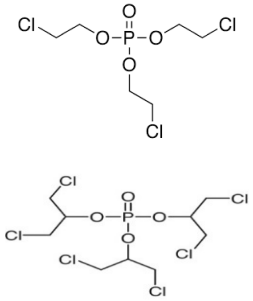
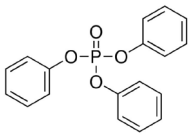
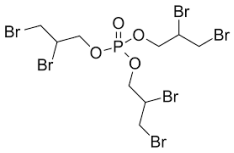
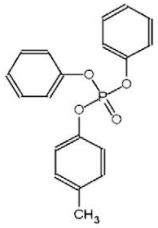
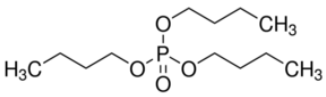
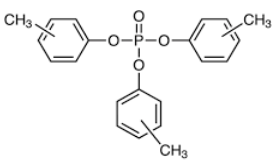
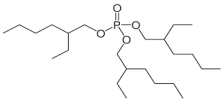
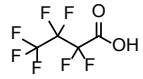
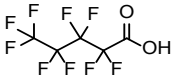
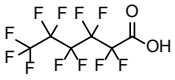
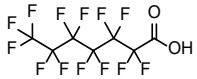
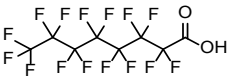
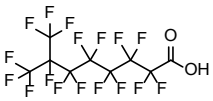
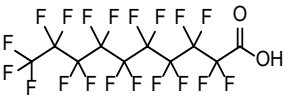
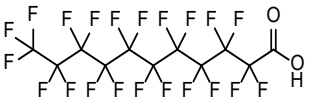
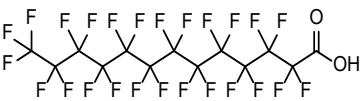
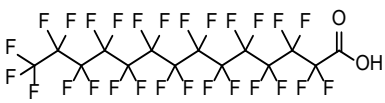
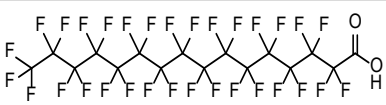
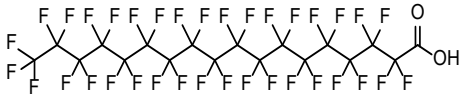
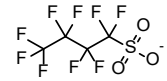
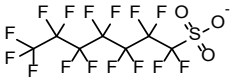
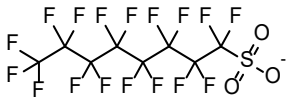
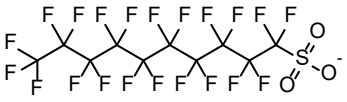
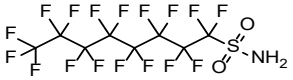
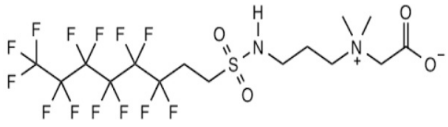
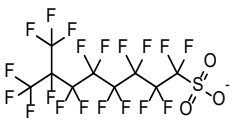
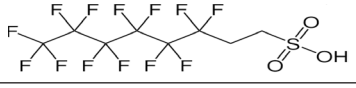
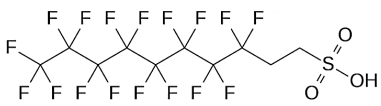
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Tris(2-chloroisopropyl) phosphate	TCIPP		13674-84-5	$C_9H_{18}Cl_3O_4P$	327.56
Tris(1.3-dichloro-2-propyl) phosphate	TDCIPP		13674-87-8	$C_9H_{15}Cl_6O_4P$	430.90
Triphenyl phosphate	TPhP		115-86-6	$C_{18}H_{15}O_4P$	326.29
Tris(2.3-dibromopropyl) phosphate	TDBPP		126-72-7	$C_9H_{15}Br_6O_4P$	697.61
Cresyl diphenyl phosphate	CDP		26444-49-5	$C_{19}H_{17}O_4P$	340.31
Tributyl phosphate	TnBP		126-73-8	$C_{12}H_{27}O_4P$	266.32
Tris(2-Butoxyethyl) phosphate	TBEP	-	78-51-3	$C_{18}H_{39}O_7P$	398.47
Tris(methylphenyl) phosphate	TMPP		1330-78-5	$C_{21}H_{21}O_4P$	368.37
Tris-(2-ethylhexyl) phosphate	TEHP		78-42-2	$C_{24}H_{51}O_4P$	434.64

Table S2. Characteristics of the per- and polyfluoroalkyl substanses (PFAS) analysed in the present study. Compounds were analyzed at the [1)] University of Valencia (UV) and/or [2)] The University of Queensland (UQ).

Family	Compound	Structure	Acronym	CAS number	Formula	Molecular Weight
Perfluoroalkyl carboxylic acids			**PFCAs**			
	Perfluorobutanoic acid		PFBA[1,2]	375-22-4	C_4F_7COOH	214.04
	Perfluoropentenoic acid		PFPeA[1,2]	2706-90-3	C_5F_9COOH	264.05
	Perflurohexanoic acid		PFHxA[1,2]	307-24-4	$C_6F_{11}COOH$	314.05
	Perfluroheptanoic acid		PFHpA[1,2]	375-85-9	$C_7F_{13}COOH$	364.06
	Perfluorooctanoic acid		PFOA[1,2]	335-67-1	$C_8F_{15}COOH$	414.07
	Perfluoro-ro-7-methyloctanoic acid		ipPFNA[1]	Not available	-	-
	Perfluorononanoic acid		PFNA[1,2]	375-95-1	$C_9F_{17}COOH$	464.08
	Perfluorodecanoic acid		PFDA[1,2]	335-76-2	$C_{10}F_{19}COOH$	514.08
	Perfluoroundecanoic acid		PFUnDA[1,2]	2058-94-8	$C_{11}F_{21}COOH$	564.09
	Perfluorododecanoic acid		PFDoDA[1,2]	307-55-1	$C_{12}F_{23}COOH$	614.10
	Perfluorotridecanoic acid		PFTrDA[1,2]	72629-94-8	$C_{13}F_{25}COOH$	664.11
	Perfluorotetradecanoic acid		PFTeDA[1,2]	376-06-7	C_4F_7COOH	714.11
	Perfluorohexadecanoic acid		PFHxDA[1,2]	67905-19-5	C_5F_9COOH	814.13

Family	Compound	Structure	Acronym	CAS number	Formula	Molecular Weight
	Perfluorooctadecanoic acid		PFODA[1,2]	16517-11-6	$C_6F_{11}COOH$	914.10
Perfluoroalkyl sulfonic acids			**PFSAs**			
	Perfluorobutane sulfonic acid		PFBS[1,2]	29420-49-3	$C_4HF_9SO_3$	300.10
	Perflurohexane sulfonic acid		PFHxS[1,2]	82382-12-5	$C_6HF_{13}SO_3$	400.12
	Perfluoroheptane sulfonic acid		PFHpS[1,2]	375-92-8	$C_7HF_{15}SO_3$	450.12
	Perfluorooctane sulfonic acid		PFOS[1,2]	4021-47-0	$C_8HF_{17}SO_3$	500.13
	Perfluorodecane sulfonic acid		PFDS[1,2]	335-77-3	$C_{10}HF_{21}SO_3$	600.15
	Perfluoropentane-sulfonic acid		PFPeS[2]	2706-91-4	$C_5HF_{11}O_3S$	350.11
Perfluoroalkane sulfonamides			**FASAs**			
	Perfluorooctane sulfonamide		PFOSA[2]	754-91-6	$C_8F_{17}SO_2NH_2$	499.15
	6:2 fluorotelomer sulfonamide alkylbetaine		6:2 FTAB[2]	Not available	-	-
Fluorotelomer sulfonic acid			**FTSA**			
	Perfluoro-7-methyloctane sulfonate		ipPFNS[1]	Not available	-	-
	6:2 fluorotelomer-sulfonate		6:2 FTS[2]	27619-97-2	$C_8F_{13}SO_3H_5$	428.17
	8:2 fluorotelomer-sulfonate		8:2 FTS[2]	39108-34-4	$C_{10}F_{17}SO_3H_5$	528.18
Polyfluoroalkyl-phosphatediesters			**diPAPs**			

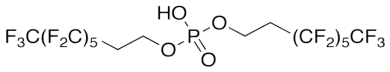
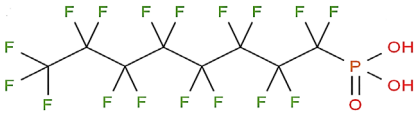
Family	Compound	Structure	Acronym	CAS number	Formula	Molecular Weight
	6:2 Fluorotelomer phosphate diester		6:2 DiPAP[2]	57677-95-9	$C_{16}H_9F_{26}O_4P$	790.17
	6:2/8:2 Fluorotelomer phosphate Diester		6:2/8:2 DiPAP[2]	943913-15-3	$C_{18}H_9F_{30}O_4P$	890.20
	8:2 Fluorotelomer phosphate diester		8:2 DiPAP[2]	678-41-1	$C_{20}H_9F_{34}O_4P$	990.20
Perfluoroalkyl phosphinic acids			**PFPAs**			
	Perfluorooctyl phosphonic acid		PFOPA[2]	40143-78-0	$C_8H_2F_{17}O_3P$	500.05

Table S3. Characteristics of the pesticides analysed in the present study. Compounds were analyzed at the [1)] University of Valencia (UV) and/or [2)] The University of Queensland (UQ).

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg L^{-1})	pKa	Log K_{ow} at 25 °C
Acetamiprid[1]	135410-20-7	$C_{10}H_{11}ClN_4$	222.67	4250	0.70	0.800
Acetochlor[1]	34256-82-1	$C_{14}H_{20}ClNO_2$	269.77	233	Not applicable	4.14
Acrinathrin[1]	-	-	-	$2.20x10^{-3}$ at 20 °C	Not applicable	6.30 at 20 °C
Alachlor[1]	15972-60-8	$C_{14}H_{20}ClNO_2$	269.77	240	0.62	3.52
Ametryn[2]	834-12-8	$C_9H_{17}N_5S$	227.33	209	4.10	2.98
Asulam[2]	3337-71-1	$C_8H_{10}N_2O_4S$	230.24	$5.00x10^3$ at 22 °C	4.82	-0.270
Atrazine[1,2]	1912-24-9	$C_8H_{14}ClN_5$	215.68	33.0	1.60	2.61
Atrazine-desethyl (Desethylatrazine)[1,2]	6190-65-4	$C_6H_{10}ClN_5$	187.63	$3.20x10^3$ at 22°C	-	1.51
Atrazine-desisopropyl (Deisopropylatrazine)[1,2]	1007-28-9	$C_5H_8ClN_5$	173.60	4.50 at 20 °C	-	3.18 at 20 °C
Azinphos-ethyl[1]	2642-71-9	$C_{12}H_{16}N_3O_3PS_2$	345.40	10.5 at 20 °C	-	3.40
Azinphos-methyl[1,2]	86-50-0	$C_{10}H_{12}N_3O_3PS_2$	317.30	20.9 at 20 °C	5.00	2.75
Azoxistrobina[1]	131860-33-8	$C_{22}H_{17}N_3O_5$	403.40	6.00 at 20 °C	-	2.50 at 20ºC
Bendiocarb[2]	22781-23-3	$C_{11}H_{13}NO_4$	223.22	260	-	1.70
Bifenthrin[1,2]	-	-	-	< $1.00x10^{-3}$ at 20 °C	Not applicable	6.00
Bromacil[2]	314-40-9	$C_9H_{13}BrN_2O_2$	261.12	g/100 mL 8.00x10-2	9.30	2.11
Bromoxynil[2]	1689-84-5	$C_7H_3Br_2NO$	276.91	130	3.86	2.70
Buprofezin[1]	69327-76-0	$C_{16}H_{23}N_3OS$	305.40	0.900	6.70	4.93
Carbaryl[2]	63-25-2	$C_{12}H_{11}NO_2$	201.22	Insoluble in water	-	2.36
Carbendazim[1,2]	10605-21-7	$C_9H_9N_3O_2$	191.19	8.00 at 24 °C	4.90	1.52
Carbofuran[1,2]	1563-66-2	$C_{12}H_{15}NO_3$	221.25	351	Not applicable	2.32
Carbofuran-3-OH (3-Hydroxycarbofuran)[1]	16655-82-6	$C_{12}H_{15}NO_4$	237.25	$6.21x10^3$ at 20 °C	-	1.45 at 20 °C
Chlorfenvinphos[1]	470-90-6	$C_{12}H_{14}Cl_3O_4P$	359.60	124 at 20 °C	-	3.81
Chlorpyrifos[1,2]	2921-88-2	$C_9H_{11}Cl_3NO_3PS$	350.60	1.40	Not applicable	4.96

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg L^{-1})	pKa	Log K_{ow} at 25 °C
Chlothianidin[1]	-	-	-	$3.27x10^2$ at 20 °C	11.1 at 20 °C	0.700
Clopyralid[2]	1702-17-6	$C_6H_3Cl_2NO_2$	192.00	-	2.32	1.06
Coumaphos[1]	56-72-4	$C_{14}H_{16}ClO_5PS$	362.80	1.50 at 20 °C	-	4.13
Cyanazine[2]	21725-46-2	$C_9H_{13}ClN_6$	240.69	$1.70x10^2$	0.870	2.22
Cyhalothrin[1]	-	-	-	$5.00x10^{-3}$ (temp not specified)	-	6.80
Cyproconazole[2]	94361-06-5	$C_{15}H_{18}ClN_3O$	291.77	140	-	2.90
Diazinon[1,2]	333-41-5	$C_{12}H_{21}N_2O_3PS$	304.35	40.0	2.60	3.81
3,4-Dichloroaniline[2]	95-76-1	$C_6H_5Cl_2N$	162.01	-	-	-
2,4-D (2,4-dichloro-phenoxyacetic acid)[2]	94-75-7	$C_8H_6Cl_2O_3$	221.03	-	2.73	2.81
Dichlofenthion[1]	97-17-6	$C_{10}H_{13}Cl_2O_3PS$	315.15	0.25	-	5.14 at 20 °C
Dichlorvos[2]	62-73-7	$C_4H_7Cl_2O_4P$	220.97	-	-	1.43
Difenoconazole[2]	119446-68-3	$C_{19}H_{17}Cl_2N_3O_3$	406.30	15.0	1.10	4.40
Diketonitrile[2]	143701-75-1	$C_{15}H_{12}F_3NO_4S$	359.30	-	-	-
Dimethoate[1]	60-51-5	$C_5H_{12}NO_3PS_2$	229.30	$2.50x10^4$	Not applicable	0.780
Diuron[1,2]	330-54-1	$C_9H_{10}Cl_2N_2O$	233.09	42.0	Not applicable	2.68
1-(3,4-Dichloro-phenyl)-3-methylurea DCPMU[2]	3567-62-2	$C_8H_8Cl_2N_2O$	219.06	-	-	-
DEET (Diethyltolua-mide)[2]	134-62-3	$C_{12}H_{17}NO$	191.27	912	-	2.02
DMA (2,4- dime-thylaniline)[1]	95-68-1	$C_8H_{11}N$	121.18	$1.00x10^4$	4.89	1.68
DMF (N,NDimethyl-formamide)[1]	68-12-2	C_3H_7NO	73.09	Miscible with water	-0.300	-1.01
DMPF (N'-(2,4- Dimethyl-phenyl)-N-methylfor-mamidine)[1]	33089-74-6	$C_{10}H_{14}N_2$	162.23	-	-	-
Ethion[1]	563-12-2	$C_9H_{22}O_4P_2S_4$	384.50	-	-	5.07
Etofenprox[1]	80844-07-1	$C_{25}H_{28}O_3$	376.50	$2.25x10^{-2}$ at 20 °C	Not applicable	6.90 at 20 °C
Fenitrothion[1]	122-14-5	$C_9H_{12}NO_5PS$	277.24	38.0	Not applicable	3.30
Fenamiphos[2]	22224-92-6	$C_{13}H_{22}NO_3PS$	303.36	400	10.5	3.23

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg L^{-1})	pKa	Log K_{ow} at 25 °C
Fenthion[1,2]	55-38-9	$C_{10}H_{15}O_3PS_2$	278.30	none at 20 °C	-	4.09
Fenthion sulfone[1]	3761-42-0	$C_{10}H_{15}O_5PS_2$	310.30	-	-	2.25 at 20 °C
Fenthion sulfoxide (Mesulfenfos)[1]	3761-41-9	$C_{10}H_{15}O_4PS_2$	294.30	3.72 at 20 °C	-	1.92 at 20 °C
Fipronil[1,2]	120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$	437.10	1.90 at 20 °C	Not applicable	4.00
Fluazifop[2]	69335-91-7	$C_{15}H_{12}F_3NO_4$	327.25	-	-	-
Fluazinam[2]	79622-59-6	$C_{13}H_4Cl_2F_6N_4O_4$	465.09	0.130 at 20 °C	7.34	4.10
Flumethrin[1]	69770-45-2	$C_{28}H_{22}Cl_2FNO_3$	510.40	200 at 20 °C	-	6.20 at 20 °C
Fluometuron[2]	2164-17-2	$C_{10}H_{11}F_3N_2O$	232.20	-	-	2.42
Fluroxypyr[2]	69377-81-7	$C_7H_5Cl_2FN_2O_3$	255.03	$9.10x10^{-2}$ g/L at 20 °C	2.94	-1.24
Fluvalinate[1]	69409-94-5	$C_{26}H_{22}ClF_3N_2O_3$	502.90	$1.20x10^{-2}$	-	5.50
Haloxyfop[2]	69806-34-4	$C_{15}H_{11}ClF_3NO_4$	361.70	-	-	-
Hexazinone[2]	51235-04-2	$C_{12}H_{20}N_4O_2$	252.31	$3.30x10^3$	2.20	1.85
Hexythiazox[1,2]	78587-05-0	$C_{17}H_{21}ClN_2O_2S$	352.90	0.500 at 20 °C	Not applicable	5.57
Hydroxysimazine[2]	2599-11-3	$C_7H_{13}N_5O$	183.21	-	-	-
Imazalil[1]	35554-44-0	$C_{14}H_{14}Cl_2N_2O$	297.20	180	6.53	3.82
Imazapic[2]	104098-48-8	$C_{14}H_{17}N_3O_3$	275.30	220	-	0.390
Imazapyr[2]	81334-34-1	$C_{13}H_{15}N_3O_3$	261.28	$1.13x10^3$	1.81	0.220
Imazethapyr[2]	81335-77-5	$C_{15}H_{19}N_3O_3$	289.33	-	-	1.49
Imidacloprid[1,2]	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	610 at 20 °C	1.56 (pKa1) 11.1 (pKa2)	0.570
Isoproturon[1]	34123-59-6	$C_{12}H_{18}N_2O$	206.28	70.0 at 20 °C	Not applicable	2.87
Malathion[1,2]	121-75-5	$C_{10}H_{19}O_6PS_2$	330.40	143 at 20 °C	Not applicable	2.36
4-Chloro-2-methyl-phenoxyacetic acid (MCPA)[2]	94-74-6	$C_9H_9ClO_3$	2010.62	270 g/l	3.13	3.25
Metalaxyl[2]	57837-19-1	$C_{15}H_{21}NO_4$	279.33	-	-	1.65
Methidathion[2]	950-37-8	$C_6H_{11}N_2O_4PS_3$	302.30	187 at 20 °C	-	2.20
Methiocarb[1,2]	2032-65-7	$C_{11}H_{15}NO_2S$	225.31	27.0 at 20 °C	Not applicable	2.92
Methomyl[2]	16752-77-5	$C_5H_{10}N_2O_2S$	162.21	58.0 mg/mL	-	0.600

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg L^{-1})	pKa	Log K_{ow} at 25 °C
Metolachlor[1,2]	51218-45-2	$C_{15}H_{22}ClNO_2$	283.79	588	Not applicable	3.13
Metribuzin[2]	21087-64-9	$C_8H_{14}N_4OS$	214.29	$1.05x10^3$ at 20 °C	10.0	1.70
Metsulfuron methyl[2]	74223-64-6	$C_{14}H_{15}N_5O_6S$	381.37	$9.50x10^3$	3.80	2.20
Molinate[1]	2212-67-1	$C_9H_{17}NOS$	187.30	970	Not applicable	3.21
Omethoate[1]	1113-02-6	$C_5H_{12}NO_4PS$	213.19	$5.00x10^5$ at 20 °C	-	-0.740 at 20 °C
Oryzalin[2]	19044-88-3	$C_{12}H_{18}N_4O_6S$	346.36	2.50	9.40	3.73
Parathion-ethyl[1]	56-38-2	$C_{10}H_{14}NO_5PS$	291.26	11.0 at 20 °C	-	3.83
Parathion-methyl[1]	298-00-0	$C_8H_{10}NO_5PS$	263.21	37.7 at 20 °C	7.15	2.86
Pencycuron[2]	66063-05-6	$C_{19}H_{21}ClN_2O$	328.80	-	-	-
Pendimethalin[2]	40487-42-1	$C_{13}H_{19}N_3O_4$	281.31	0.330 at 20 °C	-	5.20
Picloram[2]	1918-02-1	$C_6H_3Cl_3N_2O_2$	241.50	$4.30x10^2$	2.30 at 22 °C	0.300
Prochloraz[1]	67747-09-5	$C_{15}H_{16}Cl_3N_3O_2$	376.70	26.5 at 20 °C	3.80	3.50 at 20 °C
Prometryn[2]	7287-19-6	$C_{10}H_{19}N_5S$	241.36	33.0	4.05	3.51
Propachlor[2]	1918-16-7	$C_{11}H_{14}ClNO$	211.69	580	-	2.18
Propanil[1]	709-98-8	$C_9H_9Cl_2NO$	218.08	152	19.1	3.07
Propargite[2]	2312-35-8	$C_{19}H_{26}O_4S$	350.50	0.220	-	5.70
Propazine[1,2]	139-40-2	$C_9H_{16}N_5Cl$	229.71	8.60 at 22 °C	1.70 at 21 °C	2.93
Propiconazole[2]	60207-90-1	$C_{15}H_{17}Cl_2N_3O_2$	342.20	100	-	3.72
Propyzamide[2]	23950-58-5	$C_{12}H_{11}Cl_2NO$	256.12	-	-	3.43
Propoxur[2]	114-26-1	$C_{11}H_{15}NO_3$	209.24	-	-	1.52
Pyrimethanil[2]	53112-28-0	$C_{12}H_{13}N_3$	199.25	0.120 g/l	3.52	2.84
Pyriproxifen[1]	95737-68-1	$C_{20}H_{19}NO_3$	321.40	0.680	6.87	5.37
Simazine[1,2]	122-34-9	$C_7H_{12}ClN_5$	201.66	6.20 at 20 °C	1.62	2.18
Spinosad A (Spinosyn A)[1]	131929-60-7	$C_{41}H_{65}NO_{10}$	732.00	89.4	8.10	2.80
Spinosad D (Spinosyn D)[1]	131929-63-0	$C_{42}H_{67}NO_{10}$	746.00	0.76 at 20 °C	7.87	2.80
Sulfoxaflor[2]	946578-00-3	$C_{10}H_{10}F_3N_3OS$	277.27	809	-	0.800
Tebuconazole[1,2]	107534-96-3	$C_{16}H_{22}ClN_3O$	307.82	36.0 at 20 °C	2.30	3.70
Terbumeton[1]	33693-04-8	$C_{10}H_{19}N_5O$	225.29	130 at 20 °C	-	3.04 at 20 °C

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg L^{-1})	pKa	Log K_{ow} at 25 °C
Tebuthiuron[2]	34014-18-1	$C_9H_{16}N_4OS$	228.32	$2.50x10^3$	1.20	1.79
Terbumeton-desethyl[1]	30125-64-5	$C_8H_{15}N_5O$	197.24	-	-	-
Terbuthylazine[1,2]	5915-41-3	$C_9H_{16}ClN_5$	229.71	5.00 at 20 °C	2.00	3.40
Terbuthylazine-2-hydroxy (Terbutylazine-2-OH)[1]	66753-07-9	$C_9H_{17}N_5O$	211.26	7.19 at 20 °C	-	-
Terbuthylazine-desethyl[1,2]	30125-63-4	$C_7H_{12}ClN_5$	201.66	327 at 20 °C	-	2.30 at 20 °C
Terbutryn[1,2]	886-50-0	$C_{10}H_{19}N_5S$	241.36	25.0 at 20 °C	4.30	3.74
Thiabendazole[1]	148-79-8	$C_{10}H_7N_3S$	201.25	50.0	4.64	2.47
Thiamethoxam[1,2]	153719-23-4	$C_8H_{10}ClN_5O_3S$	291.72	$4.10x10^3$	Not applicable	-0.130
Tolclofos-methyl[1]	57018-04-9	$C_9H_{11}Cl_2O_3PS$	301.13	1.10	Not applicable	4.56
Triclopyr[2]	55335-06-3	$C_7H_4Cl_3NO_3$	256.50	440	2.68	0.420 (pH 5)
2,4,5-Trichlorophenoxyacetic acid (2,4,5 T)[2]	93-76-5	$C_8H_5Cl_3O_3$	255.50	Insoluble in water	2.88	4.00

Table S4. Characteristics of the pharmaceuticals and personal care products (PPCPs) analysed in the present study. Compounds were analyzed at the [1)] University of Valencia (UV) and/or [2)] The University of Queensland (UQ).

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg mL^{-1})	pKa	Log K_{ow} at 25 °C
Acesulfame[2]	33665-90-6	$C_4H_5NO_4S$	163.15	270 at 20 °C	2.00	-1.33
Acetaminophen[2]	103-90-2	$C_8H_9NO_2$	151.16	14.0	9.38	0.460
Atenolol[2]	29122-68-7	$C_{14}H_{22}N_2O_3$	266.34	13.3	9.58	0.160
Atorvastatin[2]	134523-00-5	$C_{33}H_{35}FN_2O_5$	558.60	$2.00x10^{-2}$ at 30º C	4.46	6.36
Bezafibrate[1]	41859-67-0	$C_{19}H_{20}ClNO_4$	361.80	$1.55x10^{-3}$	3.83	3.99
Bisphenol A[1]	80-05-7	$C_{15}H_{16}O_2$	228.29	$8.65x10^{-2}$	9.60	3.32
Butylparaben[1]	94-26-8	$C_{11}H_{14}O_3$	194.23	0.400	8.47	3.57
Caffeine[2]	58-08-2	$C_8H_{10}N_4O_2$	194.19	21.6	14.0	$-7.00x10^{-2}$
Carbamazepine[2]	298-46-4	$C_{15}H_{12}N_2O$	236.27	$2.00x10^{-2}$	13.9	2.45
Chloramphenicol[1]	56-75-7	$C_{11}H_{12}Cl_2N_2O_5$	323.13	2.50	7.49	1.14
Citalopram[2]	59729-33-8	$C_{20}H_{21}FN_2O$	324.40	$2.00x10^{-2}$	9.38	3.74
Clofibric Acid[1]	882-09-7	$C_{10}H_{11}ClO_3$	214.64	-	3.18	2.84
Codeine[2]	76-57-3	$C_{18}H_{21}NO_3$	299.40	Soluble in water	10.6	1.19
Cotinine[2]	486-56-6	$C_{10}H_{12}N_2O$	176.21	$1.00x10^3$	-	$7.00x10^{-2}$
Diclofenac[1,2]	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.10	$2.00x10^{-3}$	4.15	4.51
Demethylcitalopram[2]	62498-67-3	$C_{19}H_{19}FN_2O$	310.40	-	-	-
Desmethyldiazepam[2] (Nordazepam)	1088-11-5	$C_{15}H_{11}ClN_2O$	270.71	-	-	-
Ethylparaben[1]	120-47-8	$C_9H_{10}O_3$	166.17	2.49	8.34	2.47
Flufenamic Acid[1]	530-78-9	$C_{14}H_{10}F_3NO_2$	281.23	$9.00x10^{-3}$	3.88	5.25
Fluoxetine[2]	54910-89-3	$C_{17}H_{18}F_3NO$	309.33	-	-	-
Furosemide[1,2]	54-31-9	$C_{12}H_{11}ClN_2O_5S$	330.74	$7.30x10^{-2}$	3.90	2.03
Gabapentin[2]	60142-96-3	$C_9H_{17}NO_2$	171.24	$4.49x10^3$	3.70	-1.10

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg mL^{-1})	pKa	Log K_{ow} at 25 °C
Hydrochlorthiazide[2]	58-93-5	$C_7H_8ClN_3O_4S_2$	297.70	0.720	7.90	-7.00x10^{-2}
Hydroxycotinine[2]	34834-67-8	$C_{10}H_{12}N_2O_2$	192.21	-	-	-
Ibuprofen[1]	15687-27-1	$C_{13}H_{18}O_2$	206.28	2.10x10^{-2}	4.91	3.97
Indomethacin[1]	53-86-1	$C_{19}H_{16}ClNO_4$	357.80	9.00x10^{-4}	4.50	4.27
Iopromide[2]	73334-07-3	$C_{18}H_{24}I_3N_3O_8$	791.10	-	-	-
Lorazepam[1]	846-49-1	$C_{15}H_{10}Cl_2N_2O_2$	321.2	-	13.0	-
Methylparaben[1]	99-76-3	$C_8H_8O_3$	152.15	3.69	8.40	1.96
Naproxen[1,2]	22204-53-1	$C_{14}H_{14}O_3$	230.26	1.59x10^{-2}	4.15	3.18
Nicotine[2]	54-11-5	$C_{10}H_{14}N_2$	162.23	1.00x10^{3}	8.11	1.17
Paraxanthine[2]	611-59-6	$C_7H_8N_4O_2$	180.16	-	-	-
Ofloxacin[1]	82419-36-1	$C_{18}H_{20}FN_3O_4$	361.4	-	8.31	-0.390
Oxazepam[2]	604-75-1	$C_{15}H_{11}ClN_2O_2$	286.71	2.00x10^{-2}	-	2.24
Acetaminophen[1]	103-90-2	$C_8H_9NO_2$	151.16	-	9.38	0.460
Propylparaben[1]	94-13-3	$C_{10}H_{12}O_3$	180.20	0.960	8.50	3.04
Salicylic Acid[1,2]	69-72-7	$C_7H_6O_3$	138.12	2.40x10^{-3}	2.97	2.26
Sildenafil[2]	139755-83-2	$C_{22}H_{30}N_6O_4S$	474.60	5.00x10^{-3}	5.99	2.75
Sulfadiazine[2]	68-35-9	$C_{10}H_{10}N_4O_2S$	250.28	-	6.36	-
Sulfamethoxazole[2]	723-46-6	$C_{10}H_{11}N_3O_3S$	253.28	0.610 at 37 °C	-	0.890
Tadalafil[2]	171596-29-5	$C_{22}H_{19}N_3O_4$	389.40	0.220	0.850	1.42
Temazepam[2]	846-50-4	$C_{16}H_{13}ClN_2O_2$	300.74	-	-	-
Thiamphenicol[1]	15318-45-3	$C_{12}H_{15}Cl_2NO_5S$	356.20	2.27	7.65	0.330
Tramadol[2]	27203-92-5	$C_{16}H_{25}NO_2$	263.37	1.15	9.41	3.01
Triclocarban[1]	101-20-2	$C_{13}H_9Cl_3N_2O$	315.60	2.90x10^{-3}	12.7	4.34
Triclosan[1,2]	3380-34-5	$C_{12}H_7Cl_3O_2$	289.50	6.00x10^{-3}	7.90	4.76
Trimethoprim[2]	738-70-5	$C_{14}H_{18}N_4O_3$	290.32	0.400	7.12	0.910

Compound	CAS Number	Formula	Molecular Weight	Solubility in water at 25 °C (mg mL^{-1})	pKa	Log K_{ow} at 25 °C
Venlafaxine[2]	93413-69-5	$C_{17}H_{27}NO_2$	277.40	0.270	9.50	3.20
Verapamil[2]	52-53-9	$C_{27}H_{38}N_2O_4$	454.60	Practically insoluble in water	8.92	3.79 (pH 9)
Warfarin[1]	94-13-3	$C_{10}H_{12}O_3$	180.20	$1.70x10^{-2}$	5.00	2.70

Table S5. Description of the sampling points L´Albufera Natural Park (Valencia, Spain).

Point (Code)	City	Location (Coordinates, in decimal degrees)	Sampling point (name)	Samples[a]	Code[b]	Observation
1	Valencia	Lat: 39°18'39.43"N Long: 0°19'15.76"W	C.I.P El Palmar (fish farm)	W, PS	PW 1. PS 1	Control Point
2	Valencia	Lat: 39°18'34.91"N Long: 0°20'11.55"W	Obera Channel	W, PS	PW 2. PS 2	Irrigation/drainage channel-rice fields
3	Valencia	Lat: 39°18'18.40"N Long: 0°21'24.27"W	Els Campets Channel	W, PS	PW 3. PS 3	Irrigation/drainage channel-rice fields
4	Valencia	Lat: 39°18'19.41"N Long: 0°21'25.16"W	Tancat de Milia (entry)	W, PS	PW 4. PS 4	Treated WWTP effluent
5	Valencia	Lat: 39°18'39.68"N Long: 0°21'21.87"W	Tancat de Milia (exit)	W, PS	PW 5. PS 5	WWWTP effluent after green filter
6	Valencia	Lat: 39°18'3.45"N Long: 0°22'32.94"W	Alqueseria/Rizarbe Channel	W, PS	PW 6. PS 6	Irrigation/drainage channel-rice fields
7	Valencia	Lat: 39°14'16.50"N Long: 0°24'40.25"W	Sollana Channel	W, PS	PW 7. PS 7	Control (irrigation channel from Acequia Real)
8	Valencia	Lat: 39°20'47.18"N Long: 0°23'12.46"W	Font Nova Channel	W, PS	PW 8. PS 8	Irrigation/drainage channel-rice fields
9	Valencia	Lat: 39°21'53.72"N Long: 0°21'41.66"W	Comú Channel	W, PS	PW 9. PS 9	Irrigation/drainage channel-rice fields
10	Valencia	Lat: 39°21'43.25"N Long: 0°20'22.81"W	Tancaeta	W, PS	PW 10. PS 10	Irrigation/drainage channel-rice fields
11	Valencia	Lat: 39°20'39.09"N Long: 0°21'29.58"W	Albufera (north)	W, PS	PW 11. PS 11	Lake
12	Valencia	Lat: 39°19'14.45"N Long: 0°22'8.35"W	Albufera (south)	W, PS	PW 12. PS 12	Lake

[a] *W: Water; PS: Passive samplers; PW: code for water samples*

[b] *PW1 (considered as a control) was in an experimental fish farming center devoted to the recovery of native ichthyofauna. PW11 and PW12 were in the lake (north and south, next to the vegetated areas). PW2-5 were in the artificial wetlands that surround the lake, called Tancats by the locals (entry and exit) and PW6-10 was in the main drainage channels bringing water from the agricultural fields (where PW7 corresponds to a channel that carried out only surface water that could also be consider as a control).*

Table S6. Data of the physical-chemical parameters at the time of deployment of the passive samplers and 14, 28 days after deployment. T: temperature; Cond: conductivity; DO: disolved oxygen; Ch-a: chlorophyl-a; PE: phycoerythrin.

Point	Date	pH	T (ºC)	Cond (µS cm^{-1})	Salinity (PSU)	DO (%)	DO (mg L^{-1})	Ch-a (µg L^{-1})	PE (µg L^{-1})
Deployment day									
1	21/09/2020	7.86	22.1	1.46·10^3	0.74	80.2	6.99	2.22	4.46
2	22/09/2020	7.49	22.1	1.47·10^3	0.74	59.8	5.20	4.26	8.88
3	21/09/2020	7.49	21.9	1.76·10^3	0.89	56.4	4.94	2.70	6.16
4	21/09/2020	7.39	24.4	1.98·10^3	1.00	24.9	2.07	0.80	1.41
5	21/09/2020	8.22	26.6	3.13·10^3	1.63	153	12.5	13.0	28.3
6	22/09/2020	7.42	23.0	1.42·10^3	0.71	77.6	6.66	1.30	2.60
7	22/09/2020	8.27	24.9	1.07·10^3	0.53	117	9.61	0.20	0.78
8	23/09/2020	7.43	23.4	1.70·10^3	0.86	44.4	3.73	4.90	7.72
9	23/09/2020	7.59	23.2	1.87·10^3	0.95	66.4	5.65	6.74	14.7
10	23/09/2020	7.62	23.9	1.69·10^3	0.85	80.3	6.70	16.7	31.6
11	24/09/2020	8.25	23.2	2.00·10^3	1.02	117	9.25	13.9	35.0
12	24/09/2020	8.10	23.4	1.70·10^3	0.91	121	10.2	18.5	48.6
14 days after deployment									
1	05/10/2020	7.93	18.5	1.54·10^3	0.78	91.0	8.52	2.41	4.69
2	06/10/2020	7.64	20.3	1.49·10^3	0.75	70.6	6.38	1.91	4.13
3	05/10/2020	7.59	19.1	1.57·10^3	0.79	70.6	6.54	4.29	9.82
4	05/10/2020	7.34	23.2	2.08·10^3	1.06	22.5	1.93	0.87	2.03
5	05/10/2020	8.02	21.9	3.04·10^3	1.59	108	9.50	3.43	26.4
6	06/10/2020	7.52	21.1	1.44·10^3	0.72	90.4	8.03	0.74	1.80
7	06/10/2020	8.29	21.9	1.08·10^3	0.53	116	10.4	0.10	0.60
8	07/10/2020	7.53	20.0	1.68·10^3	0.85	62.5	5.62	4.21	6.46
9	07/10/2020	7.56	19.9	1.76·10^3	0.89	64.0	5.78	10.6	19.8
10	07/10/2020	7.59	20.9	2.00·10^3	1.02	68.8	6.08	30.3	65.6
11	08/10/2020	8.47	18.2	2.03·10^3	1.04	119	11.2	11.8	28.0
12	08/10/2020	8.43	18.3	1.89·10^3	0.96	118	11.1	11.1	27.8
28 days after deployment									
1	12/10/2020	8.13	15.6	1.60·10^3	0.81	96.6	9.59	1.96	4.04
2	13/10/2020	7.59	18.1	1.45·10^3	0.73	74.6	7.07	1.16	2.63
3	12/10/2020	7.71	17.7	1.42·10^3	0.72	73.3	6.93	0.95	1.45
4	12/10/2020	7.51	21.5	2.14·10^3	1.10	15.3	1.29	0.99	1.50
5	12/10/2020	8.30	19.3	3.00·10^3	1.57	127	11.9	37.5	73.3
6	13/10/2020	7.61	18.5	1.39·10^3	0.70	91.3	8.59	0.28	0.75

Point	Date	pH	T (ºC)	Cond (µS cm^{-1})	Salinity (PSU)	DO (%)	DO (mg L^{-1})	Ch-a (µg L^{-1})	PE (µg L^{-1})
28 days after deployment									
7	13/10/2020	8.28	19.6	$1.06 \cdot 10^3$	0.53	109	10.1	0.07	0.38
8	14/10/2020	7.63	19.5	$1.71 \cdot 10^3$	0.87	68.3	6.44	4.80	8.50
9	14/10/2020	7.65	18.1	$1.76 \cdot 10^3$	0.90	68.7	6.49	10.0	20.3
10	14/10/2020	7.51	18.4	$1.89 \cdot 10^3$	0.97	40.4	3.80	16.4	36.1
11	15/10/2020	8.38	19.5	$2.01 \cdot 10^3$	1.03	130	12.0	31.8	77.2
12	15/10/2020	8.37	19.8	$1.88 \cdot 10^3$	0.97	135	12.4	13.5	31.9

Table S7. Operational conditions for the analysis of the different organic contaminants by liquid chromatography (LC) at University of Valencia (UV).

LC CONDITIONS for OPFRs	
Analytical column	Kinetex X_B C18 (50 × 2.1 mm. particle size 1.7 mm) from Phenomenex (Torrance. CA. EEUU)
Column temperature	30° C
Volume injected	5 µL
Mobile phase	(A) water and (B) methanol. both containing 0.1% of formic acid working in gradient mode. Performed in positive ionization mode.
Flow rate	0.2 mL min^{-1}
Linear gradient	0 min (30% B). 0.5 min (30% B). 12 min (95% B). 18 min (98% B) and 25 min (98% B) and return to the initial conditions. An equilibration time of 15 min was applied to stabilize the columncon-ditions

LC CONDITIONS for PFAS	
Analytical column	Kinetex XB-C18: 50.0 × 4.6 mm. 1.7 µm particle size (Phenomenex. Torrance. USA)
Column temperature	30° C
Volume injected	20 µL
Mobile phase	(A) Ultra –pure water – (B) methanol both with 10 mM Ammonium Formate working in gradient mode. Performed in negative ionization mode.
Flow rate	0.5 mL min^{-1}
Linear gradient	10–80% B over 5 min. then 80–90% B over other 5 min followed by an isocratic hold at 90% B for 8 min. At 18 min B was returned to 10% in 2 min. The total run time for each injection was 20 min.

LC CONDITIONS for pesticides	
Analytical column	Luna C18 (15.0 cm × 0.21 cm) with a 3 µm particle size (Phenomenex. Torrance. USA)
Column temperature	30° C
Volume injected	5 µL
Mobile phase	(A) Ultra –pure water – (B) methanol both with 10 mM Ammonium Formate (positive mode) working in gradient mode.
Flow rate	0.3 mL min^{-1}
Gradient mode	0 min (50 % B). 10 min (83 % B). 12 min (83 % B). 12.5 min (98 % B) and 15.5 min (98 % B)

LC CONDITIONS for PPCPs

Analytical column	Kinetex XB-C18: 50.0 × 4.6 mm. 1.7 µm particle size (Phenomenex. Torrance. USA)
Column temperature	30° C
Volume injected	5 µL
Mobile phase	(A) Ultra –pure water – (B) methanol both with 0.1% formic acid (for positive mode) and (A) Ultra –pure water – (B) methanol both with 2.5mM ammonium fluoride (for negative mode) working in gradient mode.
Flow rate	0.2 mL min^{-1}
Gradient mode	Started with a 30% of A and ended with a 95% of A in 12 min that was maintained for 8 min. And then. the system was stabilized 15 min more to reach to the initial conditions

Table S8. Sampling rates (R_s; mL day^{-1}) for detected pesticides, PFAS and PPCPs.

Pesticides	**R_s**	**PPCPs**	**R_s**	**PFAS**	**Rs**
MCPA	3.10	Hydroxycotinine	3.40	6:2 FTS	21.7
Atrazine desisopropyl	4.90	Carbamazepine	3.60	PFBA	15.2
Atrazine	8.70	Venlafaxine	6.60	PFBS	28.4
Tebuconazole	4.16	Citalopram	3.50	PFDA	29.3
Imidacloprid	5.20	Iopromide	2.00	PFHpA	23.8
Diuron	7.20	Temazepam	2.90	PFHxA	19.3
Propiconazole	8.70	Hydrochlorthiazide	2.30	PFHxS	22.0
2,4-D	3.60	Tramadol	2.00	PFNA	24.0
Metsulfuron methyl	26.0	Cotinine	6.50	PFOA	18.8
Simazine	10.0	Citalopram desmethyl	7.40	PFOS	18.6
Atrazine desethyl	5.90	Atenolol	3.00	PFPeA	20.8

The sampling rates for pesticides were obtained from (Clokey et al.. 2023; Hageman et al.. 2019). Sampling rates for carbamazepine, atenolol, venlafaxine, hydrochlorthiazide, cotinine, hydroxycotinine, tramadol and citalopram were obtained from (Cárdenas-Soracá et al.. 2020). Temazepan, iopromide and citalopram desmethyl were obtained from (McKay et al.. 2020). Sampling rates for PFAS were obtained during calibrations studies but previously unpublished data.

Table S9. Predicted No Effect Concentrations (PNEC) values of the detected contaminants obtained via database Lowest PNEC extracted from the NORMAN Ecotoxicology Database.

Contaminant	Lowest PNEC Freshwater (ng L^{-1})
OPFRs	
TCEP	$6.50 \cdot 10^{4}$
TnBP	$1.70 \cdot 10^{2}$
TPhP	$3.70 \cdot 10^{4}$
Pesticides	
Acetamiprid	$2.40 \cdot 10^{1}$
Atrazine	$6.00 \cdot 10^{2}$
Atrazine-Desethyl	$2.60 \cdot 10^{2}$
Atrazine-Desisopropyl	$3.90 \cdot 10^{2}$
Carbendazim	$4.40 \cdot 10^{2}$
Diazinon	$1.20 \cdot 10^{1}$
Dimethoate	$7.00 \cdot 10^{1}$
Diuron	$7.00 \cdot 10^{1}$
Imazalil	$4.30 \cdot 10^{3}$
Imidacloprid	$1.30 \cdot 10^{1}$
Prochloraz	$1.56 \cdot 10^{3}$
Propanil	$1.68 \cdot 10^{3}$
Simazine	$1.00 \cdot 10^{3}$
Tebuconazole	$2.40 \cdot 10^{2}$
Terbumeton	$1.70 \cdot 10^{3}$
Terbumeton desethyl	$6.50 \cdot 10^{1}$
Terbutryn	$6.50 \cdot 10^{1}$
Thiabendazole	$7.70 \cdot 10^{2}$
PFAS	
PFBA	$2.78 \cdot 10^{4}$
PFBS	$4.08 \cdot 10^{3}$
PFDA	$1.70 \cdot 10^{2}$
PFDS	$1.60 \cdot 10^{2}$
PFHpA	$5.00 \cdot 10^{2}$
PFHpS	$4.80 \cdot 10^{2}$
PFHxS	$8.70 \cdot 10^{2}$
PFNA	$2.10 \cdot 10^{2}$
PFOA	$2.90 \cdot 10^{2}$
PFODA	$6.90 \cdot 10^{1}$
PFOS	2.00
PFTrDA	$1.00 \cdot 10^{2}$
PFUnDA	$1.30 \cdot 10^{2}$

Contaminant	Lowest PNEC Freshwater (ng L^{-1})
PPCPs	
Atenolol	$1.25 \cdot 10^{5}$
Bezafibrate	$2.30 \cdot 10^{3}$
Caffeine	$1.38 \cdot 10^{4}$
Diclofenac	$5.00 \cdot 10^{1}$
Ethylparaben	$1.33 \cdot 10^{4}$
Flufenamic acid	$4.00 \cdot 10^{2}$
Ibuprofen	$1.10 \cdot 10^{1}$
Lorazepam	$9.60 \cdot 10^{1}$
Methylparaben	$2.91 \cdot 10^{4}$
Naproxen	$1.70 \cdot 10^{3}$
Ofloxacin	$1.39 \cdot 10^{3}$
Acetaminophen	$4.60 \cdot 10^{4}$
Propylparaben	$8.19 \cdot 10^{3}$
Salicylic acid	$3.79 \cdot 10^{4}$
Tramadol	$8.65 \cdot 10^{3}$
Triclosan	$1.10 \cdot 10^{2}$

Table S10. Minimum, maximum (ng $sampler^{-1}$), median, frequency of detection (nº of occurrences, Freq) and limit of reporting (LOR) for pesticides, per- and polyfluoroalkyl sunstanses (PFAS) and pharmaceuticals and personal care products (PPCPs) in MPT passives samplers (ng $sampler^{-1}$) analyzed at UQ (after a 28 days deployment period).

Compounds	Min	Max	Median	Freq	LOR
Pesticides					
3.4-Dichloroaniline	<LOR	6.67	2.40	10	1.00
Atrazine desisopropyl	<LOR	0.180	<LOR	3	0.100
Atrazine desethyl	<LOR	0.530	<LOR	2	0.100
DEET	2.00	7.54	3.53	12	0.100
Pyrimethanil	<LOR	4.62	<LOR	4	0.500
Terbuthylazine desethyl	<LOR	7.03	<LOR	3	1.00
Atrazine	<LOR	0.270	<LOR	4	0.100
DCPMU	<LOR	0.600	<LOR	4	0.100
Terbuthylazine	<LOR	1.93	0.480	8	0.100
Diuron	<LOR	4.68	<LOR	4	0.100
Fluroxypyr	<LOR	10.8	<LOR	4	0.100
Imidacloprid	<LOR	1.73	0.280	8	0.100
Bromacil	<LOR	0.110	<LOR	1	0.100
Metalaxyl	<LOR	0.890	<LOR	4	0.100
Propiconazole	<LOR	25.3	6.32	11	1.00
Metsulfuron methyl	<LOR	0.370	<LOR	1	0.100

Compounds	Min	Max	Median	Freq	LOR
Pesticides					
Difenoconazole	1.46	106	28.6	12	1.00
MCPA	<LOR	39.4	4.47	11	0.100
2.4 D	<LOR	0.290	<LOR	2	0.100
Propyzamide	<LOR	0.820	<LOR	2	0.100
Fenamiphos	<LOR	0.520	<LOR	4	0.100
Diazinon	<LOR	1.87	0.450	11	0.100
Hexythiazox	<LOR	0.820	<LOR	4	0.100
Glyphosate	<LOR	43.7	0.740	8	0.100
AMPA	<LOR	147	3.12	8	0.100
PFAS					
PFBA	<LOR	0.420	<LOR	2	0.100
PFPeA	<LOR	0.590	0.250	9	0.100
FBSA	<LOR	0.200	<LOR	1	0.100
PFBS	<LOR	0.610	<LOR	4	0.100
PFHxA	<LOR	0.330	0.190	7	0.100
PFHpA	<LOR	0.240	0.103	6	0.100
PFHxS	<LOR	0.990	<LOR	5	0.120
PFOA	<LOR	0.690	0.150	6	0.120
6:2 FTS	<LOR	0.590	0.280	10	0.100
PFHpS	<LOR	0.100	<LOR	1	0.100
PFNA	<LOR	0.290	0.0950	6	0.120
PFOS	0.420	5.44	2.07	12	0.330
PFDA	<LOR	0.850	<LOR	1	0.100
PFUnDA	<LOR	0.110	<LOR	2	0.100
PFTeDA	<LOR	0.130	<LOR	1	0.100
PFHxDA	<LOR	0.240	<LOR	1	0.100
PFODA	<LOR	1.72	<LOR	5	0.100
PFOPA	<LOR	10.2	1.17	10	0.0100
6:6 PFPiA	<LOR	0.290	<LOR	5	0.100
6:2 FTAB	<LOR	4.94	0.680	7	0.100
PPCPs					
Caffeine	<LOR	3.74	0.480	9	0.250
Carbamazepine	<LOR	1.66	0.230	7	0.100
Sulfadiazine	<LOR	0.250	<LOR	4	0.100
Sulfamethoxazole	<LOR	2.10	<LOR	4	0.100
Atenolol	<LOR	0.350	<LOR	3	0.100
Venlafaxine	<LOR	4.55	<LOR	4	0.500
Oxazepam	<LOR	3.77	<LOR	5	0.500
Diclofenac	<LOR	5.47	<LOR	4	0.100
Temazepam	<LOR	3.26	0.170	9	0.100
Iopromide	<LOR	5.43	<LOR	3	0.500
Salicylic acid	<LOR	13.5	<LOR	5	0.100
Acesulfame	0.330	5.76	0.67	12	0.100

Compounds	Min	Max	Median	Freq	LOR
PPCPs					
Hydrochlorthiazide	<LOR	7.13	<LOR	3	0.100
Gabapentin	<LOR	10.6	1.21	10	0.100
Cotinine	<LOR	1.25	0.15	11	0.100
Hydroxycotinine	<LOR	1.98	<LOR	3	0.100
Tramadol	<LOR	6.61	0.330	11	0.100
Citalopram desmethyl	<LOR	1.49	<LOR	3	0.100
Citalopram	<LOR	3.04	<LOR	3	0.330
Triclosan	<LOR	4.24	<LOR	4	0.330

<LOR: detected below the reporting limit

Table S11. Minimum, maximum (ng sampler^{-1}), median and frequency (Freq) of detection for pesticides, PFAS and PPCPs in passives samplers analyzed in UV (after a 14 days deployment period).

Compounds	(ng sampler^{-1})			Freq (number of occurrences)
	Min	Max	Median	
Pesticides				
Atrazine desisopropyl	<LOD	0.920	<LOD	3
Atrazine desethyl	<LOD	1.01	0.280	8
Terbuthylazine desethyl	<LOD	4.50	0.580	6
Atrazine	<LOD	0.310	<LOD	4
Terbuthylazine	<LOD	1.69	0.270	6
Diuron	<LOD	6.03	<LOD	5
Imidacloprid	<LOD	5.08	<LOD	2
Terbutryn	<LOD	5.28	0.380	7
Chlorpyrifos	0.600	5.68	0.930	12
Chlothianidin	<LOD	4.16	2.34	7
Acetamiprid	<LOD	4.45	1.04	8
Dimethoate	<LOD	0.830	<LOD	1
Carbendazim	<LOD	1.63	0.180	6
Thiabendazole	<LOD	2.94	<LOD	5
Simazine	<LOD	2.50	<LOD	1
Fenthion sulfoxide	<LOD	0.490	<LOD	2
Terbumeton desethyl	<LOD	8.28	3.80	8
Terbuthylazine-2OH	<LOD	3.12	0.210	6
Terbumeton	<LOD	1.25	0.350	8
Imazalil	<LOD	4.17	<LOD	5
Tebuconazole	<LOD	92.4	5.39	10
Prochloraz	<LOD	26.2	0.350	9
Buprofezin	<LOD	0.540	<LOD	5
Dichlofenthion	<LOD	3.58	<LOD	2

Compounds	(ng sampler^{-1})			Freq (number of occurrences)
	Min	Max	Median	
Pesticides				
Hexythiazox	<LOD	0.730	<LOD	2
Fluvalinate	<LOD	0.210	<LOD	1
Flumethrin	<LOD	1.68	1.04	9
PFAS				
PFHxS	<LOD	2.11	0.450	7
PFOA	<LOD	0.890	0.140	6
PFOS	<LOD	4.56	1.80	9
PFDA	<LOD	1.23	<LOD	1
PPCPs				
Diclofenac	<LOD	4.98	<LOD	3
Salicylic acid	<LOD	11.3	<LOD	4
Triclosan	<LOD	6.15	1.28	9
OPFRs				
TCIPP	<LOD	4.30	1.29	8
TDCIPP	<LOD	3.18	0.700	9
TPhP	<LOD	1.35	0.260	7
TnBP	<LOD	2.05	<LOD	2

<LOD: detected below the detection limit.

Table S12. Minimum, maximum (ng sampler^{-1}), median and frequency of detection (Freq) for pesticides, PFAS and PPCPs in passives samplers (ng sampler^{-1}) analyzed in UV (after a 28 days deployment period).

Compounds	Min	Max	Median	Freq	LOQ
Pesticides					
Atrazine desisopropyl	<LOD	0.950	<LOD	3	0.100
Atrazine desethyl	<LOD	1.09	<LOD	5	0.100
Terbuthylazine desethyl	<LOD	2.80	<LOD	3	0.330
Atrazine	<LOD	0.230	<LOD	1	0.100
Terbuthylazine	<LOD	1.54	<LOD	3	0.100
Diuron	<LOD	4.06	<LOD	3	0.100
Imidacloprid	<LOD	2.50	<LOD	2	1.00
Terbutryn	<LOD	6.29	<LOD	5	0.150
Chlorpyrifos	2.60	16.1	7.92	12	0.330
Chlothianidin	<LOD	2.97	<LOD	4	0.100
DMPF	<LOD	8.91	<LOD	1	1.30
Acetamiprid	<LOD	5.43	0.150	6	0.250
Dimethoate	<LOD	0.720	<LOD	1	0.100
Carbendazim	<LOD	1.80	<LOD	5	0.100
Thiabendazole	<LOD	4.03	<LOD	5	0.150

Compounds	Min	Max	Median	Freq	LOQ
Pesticides					
Fenthion sulfoxide	<LOD	0.310	<LOD	1	0.300
Terbumeton desethyl	<LOD	10.8	0.990	10	0.0150
Terbuthylazine-2OH	<LOD	3.19	0.178	6	0.150
Terbumeton	<LOD	1.60	<LOD	5	0.0150
Imazalil	<LOD	3.17	<LOD	2	0.300
Tebuconazole	<LOD	153	14.1	8	0.150
Prochloraz	<LOD	31.5	0.345	8	0.100
Buprofezin	<LOD	0.350	<LOD	3	0.100
Dichlofenthion	<LOD	7.23	1.66	8	0.500
Hexythiazox	<LOD	0.560	<LOD	3	0.100
Fluvalinate	<LOD	0.220	<LOD	1	0.0200
Flumethrin	<LOD	1.96	0.950	9	0.300
PFAS					
PFBA	<LOD	0.680	<LOD	2	0.120
PFBS	<LOD	0.670	<LOD	6	0.150
PFHxA	<LOD	0.650	0.340	7	0.100
PFHpA	<LOD	0.830	0.120	6	0.150
PFHxS	<LOD	1.89	0.140	6	0.120
PFOA	<LOD	0.920	0.190	6	0.100
PFOS	<LOD	5.65	1.78	8	0.100
PFUnDA	<LOD	1.48	<LOD	2	0.100
PPCPs					
Diclofenac	<LOD	5.36	<LOD	3	0.100
Salicylic acid	<LOD	11.0	<LOD	4	0.100
Triclosan	<LOD	6.97	1.64	9	0.100
OPFRs					
TCIPP	<LOD	1.48	<LOD	5	0.250
TDCIPP	<LOD	1.14	0.730	11	0.030
TPhP	<LOD	1.26	0.490	11	0.250
TnBP	<LOD	0.640	<LOD	5	0.100

<LOD: detected below the detection limit.

Table S13. Minimum, maximum, average concentrations (ngL^{-1}) and frequency of detection (nº of occurrences) for OPFRs, pesticides, PFAS and PPCPs in water (grab samples) considering samples taken at 0, 14 and 28 days.

Compound	Min	Max	Mean	Median	[a] Freq
Pesticides					
Imidacloprid	<LOD	45.1	8.18	6.65	7
DMPF	<LOD	21.1	3.06	<LOD	3
Atrazine-Desisopropyl	<LOD	8.91	2.85	<LOD	4
Acetamiprid	3.52	71.0	16.2	11.3	12
Dimethoate	<LOD	9.30	0.890	<LOD	2
Atrazine-Desethyl	<LOD	15.3	4.03	3.03	8
Carbendazim	0.250	11.9	3.06	1.47	12
Thiabendazole	<LOD	21.1	5.66	2.98	11
Simazine	<LOD	4.41	0.95	<LOD	3
Fenthion sulfoxide	<LOD	6.01	0.770	<LOD	3
Terbumeton desethyl	<LOD	60.2	20.0	17.0	11
Terbuthylazine-2OH	<LOD	14.2	6.95	6.51	11
Terbuthylazine-desethyl	<LOD	50.6	15.6	11.1	11
Atrazine	<LOD	1.31	0.720	<LOD	1
Diuron	<LOD	28.6	4.30	<LOD	4
Terbumeton	<LOD	2.62	0.660	0.530	7
Terbuthylazine	<LOD	3.85	1.10	0.800	10
Propanil	<LOD	11.8	1.77	<LOD	2
Terbutryn	<LOD	8.58	1.50	0.75	7.
Imazalil	<LOD	17.7	2.49	<LOD	5
Tebuconazole	<LOD	10.9	5.38	3.38	11
Diazinon	<LOD	4.20	0.470	<LOD	2
Prochloraz	<LOD	21.5	6.04	4.52	8
Spinosad A	<LOD	0.530	0.050	<LOD	1
PFAS					
PFBA	<LOD	2.66	0.940	<LOD	4
PFPeA	<LOD	4.30	1.50	0.940	6
PFBS	<LOD	1.34	0.390	0.290	10
PFHpA	<LOD	1.53	0.580	0.560	7
PFHxS	0.130	1.43	0.680	0.710	12
PFOA	1.42	4.51	2.63	2.38	12
PFHpS	<LOD	1.19	0.690	<LOD	2
PFNA	<LOD	3.30	0.830	<LOD	4
PFOS	<LOD	10.2	2.27	<LOD	3

Compound	Min	Max	Mean	Median	[a] Freq
PFAS					
PFDA	<LOD	5.03	0.790	<LOD	3
PFUnDA	<LOD	4.26	1.40	<LOD	4
PFDS	<LOD	1.20	0.660	<LOD	3
PFTrDA	<LOD	1.44	0.740	<LOD	2
PFODA	<LOD	0.750	0.300	<LOD	4
PPCPs					
Salicylic acid	20.0	103	61.8	52.5	12
Methylparaben	<LOD	12.3	6.67	8.35	7
Ethylparaben	5.76	20.1	12.8	12.3	12
Naproxen	<LOD	158	35.9	12.2	10
Bezafibrate	<LOD	82.1	7.91	<LOD	3
Propylparaben	<LOD	11.8	3.82	3.20	7
Diclofenac	<LOD	688	124	81.3	10
Ibuprofen	<LOD	1470	202	81.4	8
Flufenamic acid	<LOD	93.7	20.2	<LOD	5
Triclosan	<LOD	23.3	8.21	<LOD	5
Atenolol	<LOD	2.97	0.360	<LOD	1
Acetaminophen	<LOD	18.4	2.55	<LOD	5
Ofloxacin	<LOD	26.4	3.43	<LOD	2
Tramadol	<LOD	82.1	23.0	7.27	9
Caffeina	1.34	66.3	9.71	2.33	12
Lorazepam	<LOD	5.54	1.32	<LOD	2
OPFRs					
TCEP	<LOD	131	18.4	<LOD	2
TPP	<LOD	1.55	0.420	<LOD	3
TClPP	<LOD	816	72.7	<LOD	2
TDClPP	<LOD	57.1	5.30	<LOD	1
TPhP	<LOD	2.88	0.790	<LOD	1
TnBP	<LOD	105	12.1	1.45	9
TBEP	<LOD	15.8	3.35	0.54	6

[a] *Freq. = Frequency of detection as number of occurrences in the samples. <LOD: detected below the detection limit.*

Table S14. Concentration of pesticides, PPCPs and PFAS in water C_w (ngL^{-1}) inferred from passive samplers (using Equation 1) analyzed at UQ and UV.

Compounds	Sampling point											
	PS1	PS2	PS3	PS4	PS5	PS6	PS7	PS8	PS9	PS10	PS11	PS12
Pesticides												
Atrazine desisopropyl UQ	n.d.	<LOR	n.d.	1.31	n.d.	n.d.	0.730	0.870	n.d	n.d	n.d	n.d
UV 14 d	n.d.	n.d.	n.d.	8.31	5.54	n.d.	n.d.	13.4	n.d.	n.d.	n.d.	n.d.
UV 28 d	n.d.	n.d.	n.d.	3.79	6.92	n.d.	n.d.	2.70	n.d.	n.d.	n.d.	n.d.
Atrazine Desethyl UQ	<LOR	n.d.	n.d.	n.d.	n.d.	n.d.	3.21	1.94	n.d.	n.d.	n.d.	n.d.
UV 14 d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.21	1.94	n.d.	n.d.	n.d.	n.d.
UV 28 d	n.d.	n.d.	n.d.	6.60	2.72	3.33	1.45	n.d.	5.27	n.d	n.d	n.d
Atrazine UQ	n.d.	1.11	n.d.	0.990	<LOR	n.d.	0.900	1.11	n.d	n.d.	n.d.	n.d.
UV 14 d	n.d	2.55	1.48	1.48	n.d	n.d	n.d	1.64	n.d	n.d	n.d	n.d
UV 28 d	n.d	n.d	n.d	0.940	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Diuron. UQ	n.d.	n.d.	n.d.	23.2	7.99	5.51	n.d.	n.d.	n.d.	7.29	n.d.	n.d.
UV 14 d	n.d.	6.95	n.d.	59.8	14.5	22.9	n.d.	n.d.	n.d.	20.3	n.d.	n.d.
UV 28 d	n.d	n.d	n.d	20.1	13.5	n.d.	n.d.	n.d.	n.d.	11.7	n.d.	n.d.
Imidacloprid. UQ	n.d.	1.99	1.79	11.9	3.85	3.43	3.43	1.24	n.d.	4.05	n.d.	n.d.
UV 14 d	n.d.	n.d.	n.d.	69.8	n.d.	n.d.	n.d.	n.d.	n.d.	27.8	n.d.	n.d.
UV 28 d	n.d.	n.d.	n.d.	17.2	n.d.	n.d.	n.d.	n.d.	n.d.	12.4	n.d.	n.d.
Propiconazole UQ	104	18.4	12.6	19.3	69.3	6.5	<LOR	6.7	85.3	32.6	52.1	53.8
Metsulfuron methyl UQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.510	n.d.	n.d.	n.d.	n.d.	n.d.
MCPA UQ	49.4	48.6	92.4	n.d.	5.99	75.9	454	6.11	13.9	393	53.6	56.2
24 D UQ	<LOR	n.d.	n.d.	2.88	n.d.	<LOR	1.88	n.d.	n.d.	<LOR	n.d.	n.d.
Tebuconazole UV 14 d	77.1	1590	642	102	1160	83.1	n.d.	285	29.2	1380	n.d.	22.8
UV 28 d	18.1	n.d	n.d	12.8	657	n.d	n.d.	224	377	1300	1310	1270
PPCPs (UQ)												
Carbamazepine	n.d.	<LOR	n.d.	16.5	7.54	2.48	2.18	<LOR	<LOR	6.75	2.28	5.56
Atenolol	n.d.	n.d.	n.d.	4.17	n.d.	1.19	n.d.	n.d.	n.d.	1.19	n.d.	n.d.
Venlafaxine	n.d.	n.d.	n.d.	24.5	4.98	7.95	n.d.	n.d.	n.d.	6.98	n.d.	n.d.
Temazepam	n.d.	1.35	n.d.	40.2	13.6	7.76	1.85	1.23	<LOR	13.7	2.22	5.79
Iopromide	n.d.	n.d.	n.d.	60.0	n.d.	n.d.	n.d.	n.d.	n.d.	97.0	n.d.	14.8
Hydrochlorthiazide	n.d.	n.d.	n.d.	111	n.d.	25.3	n.d.	n.d.	n.d.	4.81	n.d.	n.d.
Cotinine	0.820	0.820	0.600	2.20	0.710	<LOR	1.65	0.660	0.600	6.87	0.820	1.37
Hydroxycotinine	n.d.	2.42	n.d.	n.d.	n.d.	n.d.	3.15	n.d.	n.d.	20.8	n.d.	n.d.
Tramadol	n.d.	3.75	2.86	118	27.9	34.3	5.36	3.21	3.39	46.1	6.25	14.6
Citalopram desmethyl	n.d.	n.d.	n.d.	7.19	n.d.	1.11	0.720	n.d.	n.d.	n.d.	n.d.	n.d.
Citalopram	n.d.	n.d.	n.d.	31.0	n.d.	14.7	n.d.	n.d.	n.d.	10.3	n.d.	n.d.

Compounds	Sampling point											
	PS1	PS2	PS3	PS4	PS5	PS6	PS7	PS8	PS9	PS10	PS11	PS12
PFAS												
PFBA UQ	n.d.	n.d.	<LOR	n.d.	n.d.	n.d.	n.d.	n.d.	0.630	0.990	<LOR	n.d.
PFBA UV	n.d.	n.d.	n.d.	0.657	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.60
PFPeA UQ	0.410	<LOR	<LOR	0.360	0.910	0.450	0.690	0.450	<LOR	1.02	0.550	0.410
PFBS UQ	0.130	0.140	<LOR	<LOR	n.d	<LOR	<LOR	0.770	<LOR	0.180	<LOR	<LOR
PFBS UV	n.d.	n.d.	0.180	0.315	n.d.	0.300	n.d.	0.840	0.210	n.d.	0.310	n.d.
PFHxA UQ	<LOR	<LOR	<LOR	<LOR	0.520	0.310	0.410	0.420	<LOR	0.61	0.390	0.480
PFHxA UV	0.960	n.d	n.d	1.20	0.590	n.d	n.d	0.700	n.d	0.850	0.650	0.680
PFHpA UQ	<LOR	<LOR	n.d	<LOR	0.210	<LOR	0.350	0.360	n.d	0.301	0.240	0.260
PFHpA UV	0.620	n.d.	n.d.	n.d.	1.25	n.d.	n.d.	0.480	n.d.	0.376	0.320	0.390
PFHxS UQ	1.61	0.830	<LOR	<LOR	0.890	<LOR	1.09	0.970	<LOR	<LOR	<LOR	<LOR
PFHxS UV 14 d	2.79	4.84	n.d.	n.d.	6.86	3.18	1.04	1.92	n.d.	2.50	n.d.	n.d.
UV 28 d	1.84	1.09	n.d.	n.d.	3.07	1.15	n.d.	0.410	n.d.	0.410	n.d.	n.d.
PFOA UQ	0.490	<LOR	<LOR	<LOR	0.760	<LOR	0.460	1.31	<LOR	<LOR	0.420	0.550
PFOA UV 14 d	1.02	n.d.	n.d.	n.d.	1.18	n.d.	n.d.	3.38	n.d.	1.10	1.33	1.40
UV 28 d	0.720	n.d.	n.d.	n.d.	0.680	n.d.	n.d.	1.74	n.d.	0.780	0.780	0.970
6:2 FTS UQ	0.330	0.460	<LOR	0.690	0.540	0.490	0.460	<LOR	0.210	0.330	0.920	0.970
PFNA UQ	0.370	<LOR	n.d.	<LOR	0.430	n.d.	0.240	0.160	n.d.	n.d.	0.160	0.190
PFOS UQ	7.19	3.67	0.810	2.04	5.93	1.5	4.29	10.5	9.58	5.94	2.96	3.66
PFOS UV 14 d	n.d	9.86	n.d	4.92	9.85	n.d	8.93	17.5	15.2	9.85	4.66	4.58
UV 28 d	n.d	6.06	n.d.	3.19	7.77	n.d.	n.d.	10.9	9.68	7.41	3.64	2.54
PFDA UQ	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR	1.04	<LOR	<LOR	<LOR	<LOR	<LOR
PFDA UV 14 d	n.d	n.d	n.d	n.d	n.d	n.d	3.00	n.d	n.d	n.d	n.d	n.d

[a] *Freq. = Frequency of detection as number of occurrences in the samples. n.d.: no detected, <LOR: detected below the reporting limit.*

Table S15. Concentration of PPCPs, OPFRs, pesticides and PFAS in grab samples (ngL^{-1}) at t=0 days.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PPCPs												
Salicylic acid	208	176	98.0	96.9	67.6	49.9	60.1	101	25.9	40.5	21.8	74.0
Methylparaben	8.21	19.3	6.98	n.d.	15.8	n.d.	n.d.	8.47	n.d.	6.14	9.29	6.84
Ethylparaben	21.2	42.8	11.3	17.9	34.5	8.25	8.05	12.6	9.26	4.55	15.9	3.48
Naproxen	<LOQ	95.9	79.0	<LOQ	29.9	28.5	8.79	9.97	4.82	156	10.3	15.1
Bezafibrate	<LOQ	4.19	82.0	<LOQ	<LOQ	<LOQ	<LOQ	1.87	<LOQ	<LOQ	<LOQ	<LOQ
Propylparaben	5.68	9.74	4.51	n.d.	21.2	n.d.	n.d.	2.23	2.89	2.42	n.d.	n.d.
Diclofenac	46.0	86.8	94.2	698	n.d.	150	48.6	53.0	n.d.	87.6	125	128
Ibuprofen	n.d.	55.4	48.2	265	88.1	75.8	122	n.d.	257	1260	n.d.	n.d.
Flufenamic acid	n.d.	n.d.	29.1	78.8	7.48	33.4	n.d.	n.d.	n.d.	12.7	n.d.	n.d.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PPCPs												
Triclosan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30.7	19.7	13.5	21.9	20.5
Atenolol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.97	n.d.	n.d.
Acetaminophen	1.43	2.10	1.75	n.d.	n.d.	n.d.	n.d.	n.d.	1.98	18.4	n.d.	n.d.
Ofloxacin	n.d.	n.d.	n.d.	11.5	n.d.	n.d.	n.d.	n.d.	n.d.	26.4	n.d.	n.d.
Tramadol	<LOQ	3.33	5.35	93.1	26.0	22.1	<LOQ	n.d.	32.5	71.0	6.76	2.46
Caffeina	1.72	0.990	1.60	2.16	4.39	2.11	0.810	1.35	3.08	2.11	4.37	3.19
Lorazepam	<LOQ	<LOQ	<LOQ	5.22	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.02	<LOQ	<LOQ
OPFRs												
TCEP	<LOQ	<LOQ	<LOQ	126	64.1	<LOQ	<LOQ	25.1	<LOQ	<LOQ	<LOQ	<LOQ
TPP	<LOQ	<LOQ	<LOQ	1.81	1.52	<LOQ	<LOQ	<LOQ	<LOQ	1.05	<LOQ	<LOQ
TClPP	<LOQ	<LOQ	<LOQ	546	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	55.3	<LOQ	<LOQ
TDClPP	<LOQ	<LOQ	<LOQ	55.0	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
TPhP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.88	<LOQ	<LOQ	<LOQ
TnBP	2.14	<LOQ	<LOQ	24.9	4.18	0.110	<LOQ	4.11	2.02	289	2.59	1.76
TBEP	<LOQ	<LOQ	0.500	12.0	1.64	3.88	2.03	<LOQ	<LOQ	4.97	<LOQ	<LOQ
Pesticides												
Imidacloprid	<LOQ	4.90	12.8	50.3	6.64	12.0	<LOQ	<LOQ	13.5	13.8	<LOQ	<LOQ
DMPF	n.d.	n.d.	5.08	n.d.	n.d.	n.d.	n.d.	n.d.	5.1	21.1	n.d.	n.d.
Atrazine-Desi-sopropyl	n.d.	n.d.	6.14	9.25	n.d.	n.d.	n.d.	7.50	4.93	n.d.	n.d.	n.d.
Acetamiprid	17.3	4.69	8.25	86.3	20.6	7.25	7.11	1.43	5.19	12.7	22.0	19.8
Dimethoate	n.d.	n.d.	n.d.	5.35	0.840	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine-Dese-thyl	n.d.	3.78	3.07	12.9	3.98	3.40	2.77	3.95	13.0	n.d.	n.d.	n.d.
Carbendazim	1.00	0.770	1.49	10.8	5.10	1.57	0.270	0.580	1.56	9.42	1.76	1.4
Thiabendazole	2.98	1.94	16.2	9.89	4.02	2.45	n.d.	1.73	26.5	9.74	2.89	2.72
Simazine	n.d.	<LOQ	<LOQ	4.58	<LOQ	<LOQ	n.d.	3.36	1.12	<LOQ	<LOQ	<LOQ
Fenthion sul-foxide	n.d.	n.d.	1.41	8.57	n.d.	0.110	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbumeton desethyl	10.5	19.2	37.2	26.1	26.0	14.3	<LOQ	52.7	40.0	2.53	7.85	11.0
Terbuthylazi-ne-2OH	11.4	5.81	8.16	8.78	18.1	3.19	<LOQ	6.17	14.5	6.78	9.12	8.34
Terbuthylazi-ne-desethyl	7.58	20.1	29.5	19.8	9.53	13.9	<LOQ	50.1	41.1	2.99	5.34	6.45
Atrazine	n.d.	n.d.	n.d.	1.34	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	n.d.	n.d.	n.d.	27.6	5.37	5.13	n.d.	n.d.	n.d.	5.94	n.d.	n.d.
Terbumeton	<LOQ	0.290	1.48	2.58	1.40	0.690	n.d.	0.910	0.940	<LOQ	<LOQ	<LOQ
Terbuthylazine	<LOQ	0.900	1.53	4.78	1.10	1.37	n.d.	3.27	0.490	0.75	0.460	0.580
Propanil	n.d.	n.d.	n.d.	n.d.	11.7	n.d.	n.d.	n.d.	n.d.	3.41	n.d.	n.d.
Terbutryn	n.d.	n.d.	1.02	9.21	2.43	1.22	n.d.	n.d.	n.d.	3.26	1.04	0.650
Imazalil	n.d.	n.d.	3.02	19.1	n.d.	4.97	n.d.	n.d.	2.87	1.49	n.d.	n.d.
Tebuconazole	1.22	2.66	2.21	3.92	1.06	3.63	n.d.	11.7	10.3	8.98	10.7	9.9

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
Pesticides												
Diazinon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.30	n.d.	n.d.	0.330	n.d.	n.d.
Prochloraz	9.92	14.2	12.6	n.d.	n.d.	<LOQ	n.d.	4.00	27.3	7.82	3.86	7.14
Spinosad A	n.d.	n.d.	n.d.	n.d.	n.d.	0.650	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFAS												
PFBA	1.97	n.d.	2.07	1.29	n.d.	1.46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	n.d.	n.d.	n.d.	n.d.	n.d.	3.88	2.11	1.70	n.d.	2.10	3.99	3.14
PFBS	0.120	n.d.	0.160	0.240	0.350	n.d.	0.570	1.52	0.150	0.250	0.340	0.260
PFHpA	0.660	n.d.	n.d.	0.500	1.16	n.d.	n.d.	0.910	n.d.	0.750	1.57	0.910
PFHxS	1.32	0.460	0.260	0.740	0.930	0.290	0.130	0.890	0.940	0.940	0.910	0.510
PFOA	4.36	1.91	4.07	4.99	4.11	1.85	1.55	2.36	3.40	3.00	3.44	2.07
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.00	0.450	<LOQ
PFNA	0.870	0.900	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.51	2.80	<LOQ
PFOS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.83	n.d.	n.d.	n.d.	9.50	8.27
PFDA	4.90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.98	1.21	n.d.
PFUnDA	<LOQ	<LOQ	<LOQ	3.90	<LOQ	<LOQ	<LOQ	<LOQ	1.99	2.74	<LOQ	2.12
PFDS	<LOQ	1.20	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.23	<LOQ	0.150	<LOQ	<LOQ
PFTrDA	<LOQ	<LOQ	1.42	1.44	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFODA	0.760	n.d.	n.d.	n.d.	0.750	n.d.	0.580	0.690	n.d.	n.d.	<LOQ	<LOQ

n.d.: no detected,<LOQ: detected below the limit of quantification.

Table S16. Concentration of PPCPs, OPFRs, pesticides and PFAS in grab samples (ngL^{-1}) at t=14 days.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PPCPs												
Salicylic acid	47.3	30.7	97.9	93.0	39.5	42.3	104	31.0	32.5	59.7	21.5	12.1
Methylparaben	10.1	5.35	7.74	n.d.	9.81	n.d.	n.d.	8.68	n.d.	17.1	8.23	6.21
Ethylparaben	14.7	5.52	11.1	6.63	8.46	9.94	5.38	6.28	4.18	18.6	10.6	8.50
Naproxen	<LOQ	93.7	79.2	<LOQ	9.65	31.2	11.0	7.98	2.89	159	9.27	13.8
Bezafibrate	<LOQ	3.89	82.2	<LOQ	<LOQ	<LOQ	<LOQ	3.37	<LOQ	<LOQ	<LOQ	<LOQ
Propylparaben	2.92	5.26	2.09	n.d.	11.8	n.d.	n.d.	3.49	4.70	24.0	n.d.	n.d.
Diclofenac	48.1	72.3	75.8	774	n.d.	104	47.7	55.0	n.d.	236	124	127
Ibuprofen	n.d.	10.1	46.9	265	87.1	73.6	61.9	n.d.	300	1950	n.d.	n.d.
Flufenamic acid	n.d.	n.d.	33.6	15.2	6.11	7.73	n.d.	n.d.	n.d.	250	n.d.	n.d.
Triclosan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	23.3	8.16	15.6	20.9	18.9
Atenolol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.09	n.d.	n.d.
Acetaminophen	1.48	1.75	3.49	n.d.	n.d.	n.d.	n.d.	n.d.	7.14	28.7	n.d.	n.d.
Ofloxacin	n.d.	n.d.	n.d.	3.53	n.d.	n.d.	n.d.	n.d.	n.d.	26.9	n.d.	n.d.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PPCPs												
Tramadol	<LOQ	3.56	8.06	36.0	38.4	19.7	<LOQ	n.d.	39.3	87.8	6.94	5.54
Caffeina	2.54	3.26	1.43	1.28	4.14	1.47	1.55	1.29	19.3	128	7.09	4.19
Lorazepam	<LOQ	<LOQ	<LOQ	5.53	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.50	<LOQ	<LOQ
OPFRs												
TCEP	<LOQ	<LOQ	<LOQ	166	60.2	<LOQ	<LOQ	28.1	<LOQ	<LOQ	<LOQ	<LOQ
TPP	<LOQ	<LOQ	<LOQ	1.88	0.690	<LOQ	<LOQ	<LOQ	<LOQ	0.400	<LOQ	<LOQ
TClPP	<LOQ	<LOQ	<LOQ	933	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	53.7	<LOQ	<LOQ
TDClPP	<LOQ	<LOQ	<LOQ	78.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
TPhP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.65	<LOQ	<LOQ	<LOQ
TnBP	0.230	<LOQ	<LOQ	9.81	3.18	0.110	<LOQ	4.45	0.880	10.7	2.78	1.13
TBEP	<LOQ	<LOQ	0.890	14.5	0.910	4.64	1.99	<LOQ	<LOQ	32.5	<LOQ	<LOQ
Pesticides												
Imidacloprid	<LOQ	7.90	4.75	32.7	7.29	5.11	<LOQ	<LOQ	5.40	13.8	<LOQ	<LOQ
DMPF	n.d.	n.d.	7.90	n.d.	n.d.	n.d.	n.d.	n.d.	5.34	22.1	n.d.	n.d.
Atrazine-Desiso-propyl	n.d.	n.d.	6.02	8.91	n.d.	n.d.	n.d.	6.01	4.98	n.d.	n.d.	n.d.
Acetamiprid	9.18	9.62	3.87	43.0	15.7	5.65	22.4	5.62	3.37	6.12	20.1	21.9
Dimethoate	n.d.	n.d.	n.d.	18.1	1.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine-Desethyl	n.d.	2.22	3.14	16.2	3.85	3.11	2.88	3.2	9.23	n.d.	n.d.	n.d.
Carbendazim	0.970	0.680	1.07	13.5	4.09	1.47	0.230	0.740	1.84	10.2	2.42	2.01
Thiabendazole	1.54	1.68	2.82	8.79	2.55	2.06	n.d.	1.66	24.3	11.8	3.34	2.95
Simazine	n.d.	<LOQ	<LOQ	3.33	<LOQ	<LOQ	n.d.	3.16	1.49	<LOQ	<LOQ	<LOQ
Fenthion sul-foxide	n.d.	n.d.	1.58	0.750	n.d.	0.220	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbumeton dese-thyl	11.3	18.9	17.5	30.3	21.7	15.4	<LOQ	67.8	48.3	5.58	9.94	11.5
Terbuthylazi-ne-2OH	7.18	2.04	1.71	5.61	10.3	2.55	<LOQ	5.13	9.37	4.85	11.3	9.92
Terbuthylazi-ne-desethyl	6.07	16.7	13.5	20.8	8.45	11.4	<LOQ	51.1	29.1	5.28	13.9	7.74
Atrazine	n.d.	n.d.	n.d.	1.32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	n.d.	n.d.	n.d.	32.1	4.60	5.56	n.d.	n.d.	n.d.	8.71	n.d.	n.d.
Terbumeton	<LOQ	0.240	0.410	2.86	1.21	0.880	n.d.	1.22	1.34	<LOQ	<LOQ	<LOQ
Terbuthylazine	<LOQ	0.880	0.850	2.40	0.990	0.870	n.d.	2.57	0.520	0.670	0.490	0.650
Propanil	n.d.	n.d.	n.d.	n.d.	12.8	n.d.	n.d.	n.d.	n.d.	14.5	n.d.	n.d.
Terbutryn	n.d.	n.d.	0.430	6.65	1.87	0.870	n.d.	n.d.	n.d.	3.45	1.03	1.07
Imazalil	n.d.	n.d.	3.98	15.0	n.d.	3.31	n.d.	n.d.	1.27	1.58	n.d.	n.d.
Tebuconazole	1.24	2.80	2.91	3.72	1.42	2.28	n.d.	7.59	10.1	9.20	10.9	9.82
Diazinon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.99	n.d.	n.d.	0.520	n.d.	n.d.
Prochloraz	5.90	5.07	3.01	n.d.	n.d.	<LOQ	n.d.	2.01	15.7	7.08	2.39	2.95
Spinosad A	n.d.	n.d.	n.d.	n.d.	n.d.	0.520	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PFAS												
PFBA	1.26	n.d.	2.66	1.97	n.d.	1.68	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	n.d.	n.d.	n.d.	n.d.	n.d.	3.38	1.88	1.82	n.d.	1.79	4.30	2.99
PFBS	0.270	n.d.	0.400	0.360	0.580	n.d.	0.460	1.17	0.350	0.480	0.450	0.260
PFHpA	0.590	n.d.	n.d.	0.500	1.24	n.d.	n.d.	0.330	n.d.	0.910	1.49	1.32
PFHxS	1.54	0.560	0.380	0.830	0.590	0.390	0.120	0.410	0.850	0.490	0.840	0.700
PFOA	2.53	0.930	0.720	4.04	2.98	2.36	2.26	1.80	1.35	2.03	3.01	2.03
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.19	0.460	<LOQ
PFNA	0.740	0.890	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.30	2.15	<LOQ
PFOS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.01	n.d.	n.d.	n.d.	10.9	7.92
PFDA	5.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.47	1.56	n.d.
PFUnDA	<LOQ	<LOQ	<LOQ	4.26	<LOQ	<LOQ	<LOQ	<LOQ	2.18	3.33	<LOQ	1.92
PFDS	<LOQ	1.10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.09	<LOQ	0.200	<LOQ	<LOQ
PFTrDA	<LOQ	<LOQ	1.56	1.29	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFODA	0.580	n.d.	n.d.	n.d.	0.680	n.d.	0.690	0.580	n.d.	n.d.	<LOQ	<LOQ

n.d.: no detected, <LOQ: detected below the limit of quantification.

Table S17. Concentration of PPCPs, OPFRs, pesticides and PFAS in grab samples (ngL^{-1}) at t=28 days.

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PPCPs												
Salicylic acid	21.6	103	97.9	94.9	40.0	57.5	16.5	33.8	77.0	21.3	16.7	14.1
Methylparaben	11.9	12.4	8.48	n.d.	5.51	n.d.	n.d.	8.26	n.d.	10.1	7.17	16.0
Ethylparaben	12.3	11.9	10.9	16.3	17.2	9.83	3.86	14.3	13.1	22.3	22.3	7.52
Naproxen	<LOQ	98.2	79.1	<LOQ	19.8	29.8	9.89	8.98	3.85	158	8.25	14.5
Bezafibrate	<LOQ	4.49	82.1	<LOQ	<LOQ	<LOQ	<LOQ	2.62	<LOQ	<LOQ	<LOQ	<LOQ
Propylparaben	2.02	7.51	12.4	n.d.	2.52	n.d.	n.d.	2.86	3.79	2.13	n.d.	n.d.
Diclofenac	24.1	101	57.3	592	n.d.	94.9	46.9	57.1	n.d.	56.5	122	125
Ibuprofen	n.d.	270	47.6	266	89.0	74.7	91.9	n.d.	279	1190	n.d.	n.d.
Flufenamic acid	n.d.	n.d.	31.3	165	8.85	21.5	n.d.	n.d.	n.d.	18.3	n.d.	n.d.
Triclosan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15.9	31.3	14.5	19.9	17.3
Atenolol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.85	n.d.	n.d.
Acetaminophen	1.55	2.43	5.20	n.d.	n.d.	n.d.	n.d.	n.d.	4.55	8.07	n.d.	n.d.
Ofloxacin	n.d.	n.d.	n.d.	24.4	n.d.	n.d.	n.d.	n.d.	n.d.	25.9	n.d.	n.d.
Tramadol	<LOQ	3.13	10.7	117	22.0	24.5	<LOQ	n.d.	46.1	74.2	5.76	4.61
Caffeina	1.99	1.83	4.44	3.10	2.63	1.49	2.27	1.38	48.1	68.5	4.44	5.67
Lorazepam	<LOQ	<LOQ	<LOQ	5.86	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.29	<LOQ	<LOQ

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
OPFRs												
TCEP	<LOQ	<LOQ	<LOQ	102	59.2	<LOQ	<LOQ	26.2	<LOQ	<LOQ	<LOQ	<LOQ
TPP	<LOQ	<LOQ	<LOQ	0.950	0.430	<LOQ	<LOQ	<LOQ	<LOQ	0.980	<LOQ	<LOQ
TClPP	<LOQ	<LOQ	<LOQ	968	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	57	<LOQ	<LOQ
TDClPP	<LOQ	<LOQ	<LOQ	37.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
TPhP	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.11	<LOQ	<LOQ	<LOQ
TnBP	1.19	<LOQ	<LOQ	36.0	2.17	0.120	<LOQ	4.78	1.45	15.8	2.98	1.45
TBEP	<LOQ	<LOQ	1.65	21.0	0.740	4.52	2.09	<LOQ	<LOQ	9.16	<LOQ	<LOQ
Pesticides												
Imidacloprid	<LOQ	6.25	6.75	52.2	6.89	11.6	<LOQ	<LOQ	5.6	11.5	<LOQ	<LOQ
DMPF	n.d.	n.d.	4.94	n.d.	n.d.	n.d.	n.d.	n.d.	4.88	20.1	n.d.	n.d.
Atrazine-Desisopropyl	n.d.	n.d.	5.93	8.58	n.d.	n.d.	n.d.	6.24	3.99	n.d.	n.d.	n.d.
Acetamiprid	13.2	7.16	4.28	83.8	18.2	6.45	14.7	3.52	2.46	9.43	21	20.8
Dimethoate	n.d.	n.d.	n.d.	4.48	0.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Atrazine-Desethyl	n.d.	2.89	3.11	16.8	3.89	3.25	2.74	3.77	5.81	n.d.	n.d.	n.d.
Carbendazim	0.991	0.730	0.760	11.5	4.59	1.52	0.241	0.660	0.840	9.80	2.09	1.70
Thiabendazole	2.26	1.81	8.04	10.4	3.28	2.25	n.d.	1.7	12.5	10.8	3.12	2.84
Simazine	n.d.	<LOQ	<LOQ	5.31	<LOQ	<LOQ	n.d.	3.26	1.81	<LOQ	<LOQ	<LOQ
Fenthion sulfoxide	n.d.	n.d.	1.49	8.70	n.d.	0.394	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbumeton desethyl	10.9	19.1	16.7	27.3	23.8	14.9	<LOQ	60.2	17.3	4.05	8.9	11.3
Terbuthylazine-2OH	9.30	3.93	3.71	7.21	14.2	2.87	<LOQ	5.65	7.12	5.81	10.2	9.13
Terbuthylazine-desethyl	6.82	18.4	14.5	19.2	8.99	12.6	<LOQ	50.6	18.6	4.13	9.64	7.09
Atrazine	n.d.	n.d.	n.d.	1.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	n.d.	n.d.	n.d.	26.2	4.98	5.34	n.d.	n.d.	n.d.	7.32	n.d.	n.d.
Terbumeton	<LOQ	0.320	0.580	2.41	1.31	0.780	n.d.	1.07	0.550	<LOQ	<LOQ	<LOQ
Terbuthylazine	<LOQ	0.890	0.820	4.36	1.04	1.12	n.d.	2.92	0.600	0.710	0.470	0.610
Propanil	n.d.	n.d.	n.d.	n.d.	11	n.d.	n.d.	n.d.	n.d.	8.97	n.d.	n.d.
Terbutryn	n.d.	n.d.	0.500	9.87	2.15	1.05	n.d.	n.d.	n.d.	3.35	1.08	0.860
Imazalil	n.d.	n.d.	3.60	19	n.d.	4.14	n.d.	n.d.	1.30	1.39	n.d.	n.d.
Tebuconazole	1.23	2.99	2.80	3.74	1.98	2.96	n.d.	9.67	10.3	8.6	11	9.84
Diazinon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.30	n.d.	n.d.	0.390	n.d.	n.d.
Prochloraz	7.91	9.61	7.83	n.d.	n.d.	<LOQ	n.d.	3.01	21.5	7.45	3.12	5.05
Spinosad A	n.d.	n.d.	n.d.	n.d.	n.d.	0.410	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFAS												
PFBA	1.61	n.d.	3.24	2.65	n.d.	1.90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PFPeA	n.d.	n.d.	n.d.	n.d.	n.d.	4.39	2.35	1.76	n.d.	2.41	4.61	3.31
PFBS	0.200	n.d.	0.280	0.300	0.460	n.d.	0.690	1.34	0.250	0.360	0.400	0.260
PFHpA	0.740	n.d.	n.d.	0.520	1.20	n.d.	n.d.	0.620	n.d.	0.830	1.53	1.12

Compound	Sampling point (for the location see Figure 1)											
	1	2	3	4	5	6	7	8	9	10	11	12
PFAS												
PFHxS	1.43	0.380	0.500	0.780	0.760	0.500	0.140	0.650	0.890	0.710	0.880	0.900
PFOA	3.44	1.42	2.40	4.51	3.54	2.11	1.90	2.08	2.37	2.51	3.22	2.05
PFHpS	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.37	0.460	<LOQ
PFNA	0.980	0.920	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.09	3.46	<LOQ
PFOS	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7.21	n.d.	n.d.	n.d.	10.2	8.60
PFDA	5.16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.96	1.90	n.d.
PFUnDA	<LOQ	<LOQ	<LOQ	4.62	<LOQ	<LOQ	<LOQ	<LOQ	2.39	3.03	<LOQ	2.02
PFDS	<LOQ	1.31	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.930	<LOQ	0.210	<LOQ	<LOQ
PFTrDA	<LOQ	<LOQ	1.29	1.59	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
PFODA	0.800	n.d.	n.d.	n.d.	0.840	n.d.	0.790	0.790	n.d.	n.d.	<LOQ	<LOQ

n.d.: no detected, <LOQ: detected below the limit of quantification

Table S18. Mean and standard deviation (SD) of each OC detected at different time points (t=0, t=14 and t=28) at each sampling point indicating the sampling day on which the maximum concentrations were detected (only for OCs quantifiable at more than three sampling points).

Compounds	Parameters	Sampling point (for the location see Figure 1)											
		1	2	3	4	5	6	7	8	9	10	11	12
PPCPs													
Caffeine	Mean (ng L^{-1})	2.08	2.03	2.49	2.18	3.72	1.69	1.54	1.34	23.5	66.3	5.30	4.35
	SD	0.426	1.14	1.69	0.911	0.948	0.363	0.733	$4.82 \cdot 10^{-2}$	22.8	63.13	1.55	1.25
	Sampling time at max. C_w (day)	*14*	*14*	*28*	*28*	*0*	*0*	*28*	*28*	*28*	*14*	*14*	*28*
Diclofenac	Mean (ng L^{-1})	39.4	86.8	75.8	688	1.17	116	47.7	55.0	1.17	127	124	127
	SD	13.3	14.5	18.4	91.4	-	29.6	0.825	2.01	-	95.8	1.51	1.76
	Sampling time at max. C_w (day)	*14*	*28*	*0*	*14*	*-*	*0*	*0*	*28*	*-*	*14*	*0*	*0*
Ethylparaben	Mean (ng L^{-1})	16.1	20.1	11.1	13.6	20.1	9.34	5.76	11.1	8.83	15.1	16.3	6.50
	SD	4.60	19.91	0.213	6.09	13.3	0.940	2.12	4.23	4.45	9.35	5.84	2.66
	Sampling time at max. C_w (day)	*0*	*0*	*0*	*0*	*0*	*14*	*14?*	*28*	*28*	*28*	*28*	*14*
Flufenamic acid	Mean (ng L^{-1})	0.333	0.333	31.3	86.2	7.48	20.9	0.333	0.333	0.333	93.7	0.333	0.333
	SD	-	-	2.25	75.0	1.37	12.8	-	-	-	136	-	-
	Sampling time at max. C_w (day)	-	-	*14*	*28*	*28*	*0*	-	-	-	*14*	-	-
Ibuprofen	Mean (ng L^{-1})	0.333	112	47.6	266	88.1	74.7	91.9	0.333	279	1470	0.333	0.333
	SD	-	139	0.642	0.490	0.950	1.08	29.9	-	21.6	421	-	-

Compounds	Parameters	Sampling point (for the location see Figure 1)											
		1	2	3	4	5	6	7	8	9	10	11	12
PPCPs													
	Sampling time at max. C_w (day)	-	*28*	*28?*	*28*	*28*	*0*	-	-	*14*	*14*	-	-
Methylparaben	Mean (ng L^{-1})	10.1	12.3	7.73	0.500	10.4	0.500	0.500	8.47	0.500	11.1	8.23	9.69
	SD	1.86	6.98	0.749	-	5.18	-	-	0.208	-	5.52	1.06	5.49
	Sampling time at max. C_w (day)	28	0	28	-	0	-	-	14	-	14	0	28
Naproxen	Mean (ng L^{-1})	1.34	95.9	79.1	1.34	19.8	29.8	9.89	8.98	3.85	158	9.27	14.5
	SD	-	2.22	0.180	-	10.1	1.39	1.10	1.00	0.97	1.19	1.02	0.670
	Sampling time at max. C_w (day)	-	*28*	*14*	-	*0*	*14*	*14*	*0*	*0*	*14*	*0*	*0*
Propylparaben	Mean (ng L^{-1})	3.54	7.50	6.33	0.100	11.8	0.100	0.100	2.86	3.79	9.53	0.100	0.100
	SD	1.91	2.24	5.39	-	9.32	-	-	0.630	0.910	12.6	-	-
	Sampling time at max. C_w (day)	*0*	*0*	*28*	-	*0*	-	-	*14*	*14*	*14*	-	-
Salicylic acid	Mean (ng L^{-1})	92.4	103	97.9	94.9	49.0	49.9	60.1	55.2	45.1	40.5	20.0	33.4
	SD	101	72.6	0.07	1.94	16.1	7.64	43.6	39.4	27.8	19.2	2.88	35.1
	Sampling time at max. C_w (day)	0	0	0	0	0	28	14	0	28	14	0	0
Tramadol	Mean (ng L^{-1})	2.00	3.34	8.05	82.12	28.80	22.11	2.00	0.50	39.30	77.63	6.49	4.20
	SD	-	0.210	2.70	41.69	8.58	2.37	-	-	6.77	8.92	0.630	1.58
	Sampling time at max. C_w (day)	*Constant*	*14*	*28*	*28*	*14*	*28*	-	-	*28*	*14*	*14*	*14*
Triclosan	Mean (ng L^{-1})	0.150	0.150	0.150	0.150	0.150	0.150	0.150	23.3	19.7	14.5	20.9	18.9
	SD	-	-	-	-	-	-	-	7.38	11.6	1.07	1.01	1.60
	Sampling time at max. C_w (day)	-	-	-	-	-	-	-	*0*	*28*	*14*	*0*	*0*
Pesticides													
Acetamiprid	Mean (ng L^{-1})	13.2	7.16	5.47	71.0	18.2	6.45	14.7	3.52	3.67	9.43	21.0	20.8
	SD	4.06	2.47	2.42	24.3	2.43	0.802	7.62	2.10	1.39	3.31	0.912	1.04
	Sampling time at max. C_w (day)	*0*	*14*	*0*	*0*	*0*	*0*	*14*	*14*	*0*	*0*	*0*	*14*
Imidacloprid	Mean (ng L^{-1})	0.200	6.35	8.09	45.1	6.94	9.58	0.200	0.200	8.16	13.0	0.20	0.200
	SD	-	1.50	4.17	10.7	0.327	3.88	-	-	4.61	1.37	-	-
	Sampling time at max. C_w (day)	-	*14*	*0*	*14*	*14*	*0*	-	-	*0*	*0*	-	-
Atrazine-Desethyl	Mean (ng L^{-1})	1.00	2.96	3.11	15.3	3.91	3.25	2.80	3.64	9.33	1.00	1.00	1.00
	SD	-	0.781	$3.74 \cdot 10^{-2}$	2.11	$6.79 \cdot 10^{-2}$	0.146	$7.39 \cdot 10^{-2}$	0.391	3.58	-	-	-
	Sampling time at max. C_w (day)	-	*0*	*14*	*28*	*0*	*0*	*14*	*0*	*0*	-	-	-

Compounds	Parameters	Sampling point (for the location see Figure 1)											
		1	2	3	4	5	6	7	8	9	10	11	12
Pesticides													
Atrazine-De-sisopropyl	Mean (ng L^{-1})	1.00	1.00	6.03	8.91	1.00	1.00	1.00	6.58	4.63	1.00	1.00	1.00
	SD	-	-	0.104	0.338	-	-	-	0.802	0.555	-	-	-
	Sampling time at max. C_w (day)	-	-	*0*	*0*	-	-	-	*0*	*14*	-	-	-
Diuron	Mean (ng L^{-1})	0.665	0.665	0.665	28.6	4.98	5.34	0.665	0.665	0.665	7.32	0.665	0.665
	SD	-	-	-	3.11	0.386	0.215	-	-	-	1.38	-	-
	Sampling time at max. C_w (day)	-	-	-	*14*	*0*	*14*	-	-	-	*14*	-	-
Terbumeton	Mean (ng L^{-1})	$3.00 \cdot 10^{-2}$	0.283	0.822	2.62	1.31	0.783	$3.00 \cdot 10^{-2}$	1.07	0.939	$3.00 \cdot 10^{-2}$	$3.00 \cdot 10^{-2}$	$3.00 \cdot 10^{-2}$
	SD	-	$4.00 \cdot 10^{-2}$	0.580	0.230	$9.00 \cdot 10^{-2}$	$9.00 \cdot 10^{-2}$	-	0.150	0.400	-	-	-
	Sampling time at max. C_w (day)	-	*28.00*	*0.00*	*14.00*	*0.00*	*14.00*	-	*14.00*	*14.00*	-	-	-
Terbume-ton-desethyl	Mean (ng L^{-1})	10.1	19.1	23.8	27.9	23.8	14.9	$3.00 \cdot 10^{-2}$	60.2	35.2	4.05	8.90	11.3
	SD	0.424	0.136	11.6	2.14	2.16	0.562	-	7.57	16.1	1.53	1.04	0.252
	Sampling time at max. C_w (day)	*14*	*0*	*0*	*14*	*0*	*14*	-	*14*	*14*	*14*	*14*	*14*
Terbuthylazine	Mean (ng L^{-1})	$3.00 \cdot 10^{-2}$	0.889	1.07	3.85	1.04	1.12	$3.00 \cdot 10^{-2}$	2.92	0.537	0.708	0.471	0.608
	SD	-	$9.05 \cdot 10^{-2}$	0.400	1.27	$5.29 \cdot 10^{-2}$	0.251	-	0.348	$5.55 \cdot 10^{-2}$	$3.83 \cdot 10^{-2}$	$1.38 \cdot 10^{-2}$	$3.35 \cdot 10^{-2}$
	Sampling time at max. C_w (day)	-	0	0	0	0	0	-	0	28	0	14	14
Terbuthylazi-ne-2OH	Mean (ng L^{-1})	9.30	3.93	4.53	7.20	14.2	2.87	0.300	5.65	10.3	5.81	10.2	9.13
	SD	2.12	1.88	3.30	1.59	3.90	0.318	-	0.517	3.79	0.966	1.08	0.791
	Sampling time at max. C_w (day)	0	0	0	0	0	0	-	0	0	0	14	14
Terbutryn	Mean (ng L^{-1})	$8.00 \cdot 10^{-2}$	$8.00 \cdot 10^{-2}$	0.648	8.58	2.15	1.05	$8.00 \cdot 10^{-2}$	$8.00 \cdot 10^{-2}$	$8.00 \cdot 10^{-2}$	3.35	1.05	0.860
	SD	-	-	0.326	1.70	0.279	0.174	-	-	-	$9.44 \cdot 10^{-2}$	$2.80 \cdot 10^{-2}$	0.211
	Sampling time at max. C_w (day)	-	-	0	28	0	0	-	-	-	14	28	14
Carbendazim	Mean (ng L^{-1})	0.990	0.730	1.11	11.9	4.59	1.52	0.250	0.660	1.41	9.81	2.09	1.70
	SD	$1.00 \cdot 10^{-2}$	$4.00 \cdot 10^{-2}$	0.370	1.41	0.510	$5.00 \cdot 10^{-2}$	$2.00 \cdot 10^{-2}$	$8.00 \cdot 10^{-2}$	0.520	0.390	0.330	0.300
	Sampling time at max. C_w (day)	*0*	*0*	*0*	*14*	*0*	*0*	*0*	*14*	*14*	*14*	*14*	*14*
Imazalil	Mean (ng L^{-1})	0.170	0.170	3.54	17.7	0.170	4.14	0.170	0.170	1.81	1.49	0.170	0.170
	SD	-	-	0.484	2.36	-	0.834	-	-	0.913	$9.46 \cdot 10^{-2}$	-	-

Compounds	Parameters	Sampling point (for the location see Figure 1)											
		1	2	3	4	5	6	7	8	9	10	11	12
Pesticides													
	Sampling time at max. C_w (day)	-	-	14	0	-	0	-	-	0	14	-	-
Prochloraz	Mean (ng L^{-1})	7.91	9.61	7.82	1.00	1.00	4.00	1.00	3.01	21.5	7.45	3.12	5.05
	SD	2.01	4.54	4.80	-	-	-	-	0.994	5.82	0.374	0.734	2.10
	Sampling time at max. C_w (day)	*0*	*0*	*0*	-	-	-	-	*0*	*0*	*0*	*0*	*0*
Tebuconazole	Mean (ng L^{-1})	1.23	2.82	2.64	3.80	1.49	2.96	$8.00 \cdot 10^{-2}$	9.67	10.3	8.93	10.9	9.85
	SD	$9.44 \cdot 10^{-3}$	0.169	0.376	0.112	0.464	0.671	-	2.08	0.110	0.305	0.176	$4.32 \cdot 10^{-2}$
	Sampling time at max. C_w (day)	*14*	*28*	*14*	*0*	*28*	*0*	-	*0*	*0*	*14*	*28*	*0*
Thiabendazole	Mean (ng L^{-1})	2.26	1.81	9.02	9.69	3.28	2.25	$8.00 \cdot 10^{-2}$	1.70	21.1	10.8	3.12	2.84
	SD	0.720	0.128	6.74	0.817	0.734	0.197	-	$3.21 \cdot 10^{-2}$	7.55	1.03	0.226	0.115
	Sampling time at max. C_w (day)	*0*	*0*	*0*	*28*	*0*	*0*	-	*0*	*0*	*14*	*14*	*14*
PFASs													
PFBA	Mean (ng L^{-1})	1.61	0.425	2.65	1.97	0.425	1.68	0.425	0.425	0.425	0.425	0.425	0.425
	SD	0.356	-	0.585	0.679	-	0.220	-	-	-	-	-	-
	Sampling time at max. C_w (day)	*0*	-	*28*	*28*	-	*28*	-	-	-	-	-	-
PFPeA	Mean (ng L^{-1})	0.125	0.125	0.125	0.125	0.125	3.88	2.11	1.76	0.125	2.10	4.30	3.14
	SD	-	-	-	-	-	0.509	0.238	$6.44 \cdot 10^{-2}$	-	0.312	0.309	0.159
	Sampling time at max. C_w (day)	-	-	-	-	-	*28*	*28*	*14*	-	*28*	*28*	*28*
PFHpA	Mean (ng L^{-1})	0.665	0.100	0.100	0.505	1.20	0.100	0.100	0.620	0.100	0.830	1.53	1.12
	SD	$7.50 \cdot 10^{-2}$	-	-	$1.22 \cdot 10^{-2}$	$3.95 \cdot 10^{-2}$	-	-	0.288	-	$8.25 \cdot 10^{-2}$	$4.13 \cdot 10^{-2}$	0.206
	Sampling time at max. C_w (day)	28	-	-	28	14	-	-	0	-	14	0	14
PFOA	Mean (ng L^{-1})	3.44	1.42	2.40	4.51	3.54	2.11	1.90	2.08	2.37	2.51	3.22	2.05
	SD	0.916	0.490	1.67	0.473	0.565	0.258	0.354	0.281	1.02	0.485	0.214	$1.85 \cdot 10^{-2}$
	Sampling time at max. C_w (day)	0	0	0	0	0	14	14	0	0	0	0	0
PFNA	Mean (ng L^{-1})	0.865	0.902	0.260	0.260	0.260	0.260	0.260	0.260	0.260	3.30	2.80	0.260
	SD	0.120	$1.40 \cdot 10^{-2}$	-	-	-	-	-	-	-	0.790	0.658	-
	Sampling time at max. C_w (day)	28	28	-	-	-	-	-	-	-	*28*	*28*	-
PFUnDA	Mean (ng L^{-1})	0.670	0.670	0.670	4.26	0.670	0.670	0.670	0.670	2.18	3.03	0.670	2.02
	SD	-	-	-	0.361	-	-	-	-	0.199	0.295	-	0.105

Compounds	Parameters	Sampling point (for the location see Figure 1)											
		1	2	3	4	5	6	7	8	9	10	11	12
PFASs													
	Sampling time at max. C_w (day)	-	-	-	*28.00*	-	-	-	-	*28.00*	*14.00*	-	*0.00*
PFBS	Mean (ng L^{-1})	0.198	0.125	0.279	0.301	0.462	0.125	0.574	1.34	0.252	0.362	0.397	0.258
	SD	$7.72 \cdot 10^{-2}$	-	0.124	$6.32 \cdot 10^{-2}$	0.112	-	0.117	0.176	$9.98 \cdot 10^{-2}$	0.114	$5.55 \cdot 10^{-2}$	$2.47 \cdot 10^{-3}$
	Sampling time at max. C_w (day)	*14*	-	*14*	*14*	*14*	-	*28*	*0*	*14*	*14*	*14*	*14*
PFHxS	Mean (ng L^{-1})	1.43	0.466	0.378	0.782	0.760	0.392	0.131	0.649	0.892	0.713	0.876	0.705
	SD	0.112	$9.18 \cdot 10^{-2}$	0.120	$4.72 \cdot 10^{-2}$	0.168	0.104	$9.10 \cdot 10^{-2}$	0.239	$4.74 \cdot 10^{-2}$	0.223	$3.15 \cdot 10^{-2}$	0.195
	Sampling time at max. C_w (day)	14	14	28	14	0	28	28	0	0	0	0	28
OPFRs													
TBEP	Mean (ng L^{-1})	$6.00 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	1.01	15.8	1.10	4.34	2.04	$6.00 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$	15.5	$6.00 \cdot 10^{-2}$	$6.00 \cdot 10^{-2}$
	SD	-	-	0.586	4.65	0.481	0.409	$5.00 \cdot 10^{-2}$	-	-	14.8	-	-
	Sampling time at max. C_w (day)	-	-	28	28	0	14	28	-	-	14	-	-
TnBP	Mean (ng L^{-1})	1.19	0.600	0.600	23.6	3.18	0.110	0.60	4.45	1.45	105	2.78	1.45
	SD	0.955	-	-	13.1	1.01	$6 \cdot 10^{-3}$	-	0.342	0.574	159	0.202	0.311
	Sampling time at max. C_w (day)	0	-	-	28	0	*28*	-	28	0	0	28	0
For the calculations n.d. were considered as LOD/2 and <LOQ were established as ((LOD+LOQ)/2)													

Table S19. Mean of the differences of concentrations (ng samplers^{-1}), standard deviation, standard error of the mean and p value and 95% confidence interval showing differences between MPT passive sampler results observed at the UQ and UV laboratories.

Compound	1	2	3	4	5	6	7	8	9	10	11	12	Mean	S.d.	SEM*	t	*p* value	95% c.i inferior difference	95% c.i superior difference
Pesticides																			
Atrazine	0.00	0.253	0.00	0.0100	0.0500	0.00	0.203	0.253	0.00	0.00	0.00	0.00	0.06	0.11	0.03	2.11	0.06	-0.002	0.13
Atrazine desisopropyl	0.00	0.0500	0.00	-0.340	-0.933	0.00	0.0830	-0.250	0.00	0.00	0.00	0.00	-0.12	0.29	0.08	-1.40	0.20	-0.30	0.07
Atrazine desethyl	0.0500	0.00	0.00	-1.07	-0.433	-0.533	0.290	0.303	-0.853	0.00	0.00	0.00	-0.19	0.44	0.13	-1.48	0.17	-0.47	0.09

Compound	1	2	3	4	5	6	7	8	9	10	11	12	Mean	S.d.	SEM*	t	*p* value	95% c.i inferior difference	95% c.i superior difference
Pesticides																			
Terbuthylazine	0.0500	0.793	0.463	0.00	-0.870	0.463	0.173	1.07	0.493	0.00	0.0500	0.00	0.22	0.49	0.14	1.59	0.14	-0.09	0.54
Terbuthylazine desethyl	0.112	1.09	0.112	-0.810	-2.23	0.112	0.112	4.23	-0.053	-0.0530	-0.0530	-0.053	0.21	1.49	0.43	0.49	0.64	-0.73	1.15
Diuron	0.00	0.00	0.00	0.620	-1.11	1.09	0.00	0.00	0.00	-0.880	0.00	0.00	-0.02	0.57	0.17	-0.14	0.89	-0.39	0.34
Imidacloprid	-0.150	0.123	0.0930	-0.770	0.393	0.333	0.333	0.0130	-0.150	-1.21	-0.150	-0.150	-0.11	0.47	0.14	-0.80	0.44	-0.41	0.19
Hexythiazox	-0.163	0.193	0.173	-0.133	0.00	0.273	0.260	0.00	0.00	0.00	0.00	0.00	0.05	0.14	0.04	1.23	0.25	-0.04	0.14
PPCPs																			
Diclofenac	0.00	0.213	0.00	0.110	0.00	0.200	0.00	0.00	0.00	0.170	0.00	0.00	0.06	0.09	0.03	2.26	0.05	0.001	0.12
Salicylic acid	0.00	-2.183	0.00	0.0900	0.00	-0.803	2.520	0.00	0.00	0.313	0.0830	0.443	0.04	1.05	0.30	0.13	0.90	-0.63	0.70
Triclosan	0.153	-1.41	-1.34	-2.73	0.153	-0.710	-1.42	-0.950	0.153	-0.910	-1.00	-1.47	-0.96	0.84	0.24	-3.95	0.00	-1.49	-0.42
PFAS																			
PFBA	-0.003	-0.003	0.047	-0.263	-0.003	-0.003	-0.003	-0.003	0.250	0.400	0.047	-0.663	-0.02	0.26	0.07	-0.23	0.83	-0.18	0.16
PFBS	0.075	0.085	-0.073	-0.183	-0.008	-0.173	0.042	-0.060	-0.103	0.115	-0.183	0.042	-0.04	0.11	0.03	-1.13	0.28	-0.10	0.05
PFHxA	-0.453	0.050	0.050	-0.583	-0.040	0.153	0.203	-0.150	0.050	-0.130	-0.140	-0.110	-0.09	0.23	0.07	-1.37	0.20	-0.24	0.07
PFHpA	-0.343	0.042	-0.008	0.042	-0.690	0.042	0.205	-0.080	-0.008	-0.050	-0.050	-0.090	-0.08	0.23	0.07	-1.25	0.24	-0.23	0.08
PFHxS	-0.140	-0.160	0.060	0.060	-1.34	-0.630	0.650	0.350	0.060	-0.170	0.060	0.060	-0.10	0.50	0.14	-0.66	0.52	-0.41	0.23
PFOA	-0.120	0.063	0.063	0.063	0.040	0.063	0.223	-0.230	0.063	-0.330	-0.190	-0.220	-0.04	0.17	0.05	-0.88	0.40	-0.15	0.08
PFOS	3.72	-1.24	0.403	-0.600	-0.960	0.763	2.21	-0.210	-0.050	-0.760	-0.350	0.580	0.29	1.43	0.41	-0.71	0.49	-0.61	1.21
PFUnDA	-0.973	-0.050	0.00	-0.050	0.093	0.00	0.00	0.083	0.00	-1.41	-0.050	-0.050	-0.20	0.48	0.14	-1.46	0.17	-0.50	0.10

Mean= Mean of the differences between the observations. S.d.= Standard deviation. SEM= standard error of the mean. 95% c.i of the superior difference= 95% confidence interval of the superior difference. 95% c.i of the inferior difference= 95% confidence interval of the inferior difference.*

Table S20. Normalised differences (%) between MPT Passive sampler results obtained at the University of Queensland (UQ) and the University of Valencia (UV) for each compound and sampling point.

Compound	Normalised differences (%)												Mean of the normalised differences (%)	Standard deviation of the normalized differences (%)
	1	2	3	4	5	6	7	8	9	10	11	12		
Pesticides														
Atrazine	2	177	2	4	120	2	172	177	2	2	2	2	55	80
Atrazine desisopropyl	2	120	2	-97	-193	2	143	-102	2	2	2	2	-10	91
Atrazine desethyl	120	2	2	-194	-185	-188	75	180	-192	2	2	2	-31	130
Terbuthylazine	120	192	187	0	-79	187	168	77	187	0	120	0	97	95
Terbuthylazine desethyl	101	142	101	-52	-174	101	101	86	-27	-27	-27	-27	25	94
Diuron	2	2	2	14	-51	194	2	2	2	-46	2	2		
Imidacloprid	-163	54	44	-36	108	100	100	7	-163	-101	-163	-163	11	61
Hexythiazox	-165	171	168	-100	2	178	38	2	2	2	2	2	-31	114
PPCPs														
Diclofenac	0	173	0	2	0	9	0	0	0	34	0	0		
Salicylic acid	0	-188	0	8	0	-172	21	0	0	140	77	154	18	50
Triclosan	107	-152	-151	-49	107	-33	-153	-30	107	-28	-139	-154	3	102
PFAS														
PFBA	-18	-18	108	-177	-18	-18	-18	-18	172	182	108	-190		
PFBS	120	126	-71	-116	-40	-113	91	-9	-87	139	-116	91	8	119
PFHxA	-155	120	120	-163	-13	164	172	-49	120	-33	-50	-35	1	104
PFHpA	-144	91	-40	91	-142	91	161	-29	-40	-22	-27	-42	17	118
PFHxS	-13	-27	120	120	-110	-159	188	82	120	-103	120	120	-4	95
PFOA	-38	131	131	131	11	131	174	-29	131	-135	-60	-55	38	115
PFOS	198	-49	185	-44	-27	192	197	-4	-1	-22	-20	36	44	105
PFUnDA	-193	-120	0	-120	147	0	0	143	0	-183	-120	-120	53	105

*Normalised differences (ND, %) = ((value a-value b)/average a,b)*100), where a and b are the concentrations from passive samplers of samples collected in UQ and UV, respectively.*

Table S21. Mean of the differences of concentrations (ng L^{-1}), standard deviation, standard error of the mean and p value and 95% confidence interval showing difference between the Grab samples and passive samplers.

Compound	1	2	3	4	5	6	7	8	9	10	11	12	Mean	S.d.	SEM*	t	p value	95% c.i inferior difference	95% c.i superior difference
Pesticide																			
Atrazine	0.498	-0.443	0.498	0.321	0.498	0.498	-0.238	-0.443	0.498	0.498	0.498	0.498	0.27	0.39	0.11	2.34	0.04	$2.00 \cdot 10^{-2}$	0.51
Atrazine desiso-propyl	0.833	0.833	5.86	5.12	-5.92	0.833	0.833	3.88	4.47	0.833	0.833	0.833	1.60	3.08	0.89	1.80	0.10	-0.36	3.56
Atrazine desethyl	0.833	2.80	2.94	8.71	1.19	-0.075	1.35	3.48	4.06	0.833	0.833	0.833	2.32	2.39	0.70	3.36	0.01	0.80	3.83
Diuron	0.498	0.498	0.498	8.49	-8.51	5.18	0.498	0.498	0.498	-4.34	0.498	0.498	0.40	4.16	1.20	0.33	0.75	-2.24	3.04
Imidacloprid	0.033	6.18	7.92	27.9	6.78	9.42	0.033	0.033	8.00	0.672	0.033	0.033	5.59	7.80	2.31	2.42	0.03	0.50	10.7
PPCPs																			
Atenolol	0.065	0.065	0.065	-3.50	0.065	-0.525	0.065	0.065	0.065	1.78	0.065	0.065	-0.14	1.19	0.34	-0.40	0.690	-0.89	0.62
Tramadol	-	-0.407	5.19	-35.9	0.941	-12.2	-4.76	-2.61	35.9	31.6	0.238	-10.4	0.63	18.8	5.43	0.12	0.91	-11.3	12.6
PFAS																			
PFBA	1.10	-0.091	2.14	1.31	-0.091	1.16	-0.091	-0.091	-0.091	-0.091	-0.091	-1.17	0.33	0.91	0.26	1.24	0.24	-0.25	0.90
PFPeA	-0.285	-0.042	-0.042	-0.235	-0.785	3.43	1.42	1.31	-0.042	1.04	3.75	2.73	1.02	1.55	0.45	2.29	0.04	$4.00 \cdot 10^{-2}$	2.01
PFBS	0.030	-0.042	0.098	-0.015	0.295	-0.175	0.407	0.503	0.044	0.196	0.087	0.090	0.12	0.19	0.06	2.26	0.05	0.00	0.25
PFHpA	0.044	-0.067	-0.067	0.330	-0.049	-0.067	-0.067	0.140	-0.067	0.453	1.212	0.727	0.21	0.41	0.12	1.79	0.10	$-5.00 \cdot 10^{-2}$	0.47
PFHxS	-0.179	-0.372	0.208	0.617	-0.130	0.225	-0.960	-0.322	0.726	0.547	0.709	0.535	0.13	0.53	0.15	0.87	0.40	-0.20	0.47
PFOA	2.72	1.25	2.23	4.35	2.86	1.94	1.73	0.339	2.20	1.73	2.44	1.08	2.07	1.01	0.29	7.08	0.00	1.43	2.72
PFNA	0.500	0.736	0.098	0.098	-0.165	0.098	0.025	0.105	0.098	3.13	2.64	0.075	0.62	1.09	0.31	1.97	0.07	$-7.00 \cdot 10^{-2}$	1.31
PFOS	-0.088	-5.860	-0.088	-2.990	-7.570	-0.088	6.718	-10.67	-9.48	-7.21	6.57	5.73	-2.09	6.22	1.80	-1.16	0.27	-6.04	1.86
PFDA	4.96	-0.017	-0.017	-0.017	-0.017	-0.017	-2.95	-0.017	-0.017	2.41	1.49	-0.017	0.4	1.87	0.54	0.89	0.39	-0.70	1.70

Mean= Mean of the differences between the observations. S.d.= Standard deviation. SEM= standard error of the mean. 95% c.i of the superior difference= 95% confidence interval of the superior difference. 95% c.i of the inferior difference= 95% confidence interval of the inferior difference.*

Table S22. Normalised differences (%) between grab samples and passive samplers for each compound and sampling point.

Compound	Normalised differences (%)											
	P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**
Pesticide												
Atrazine	120	-50	120	28	120	120	-30	-50	120	120	120	120
Atrazine desisopropyl	143	143	189	81	-149	143	143	84	186	143	143	143
Atrazine desethyl	143	179	180	79	36	-2	63	182	56	143	143	143
Diuron	120	120	120	35	-92	188	120	120	120	-46	120	120
Imidaclo-prid	18.0	189.7	191.9	89.6	190.6	193.1	18.0	18.0	192.0	5.3	18.0	18.0
PPCPs												
Atenolol	10	10	10	-145	10	-57	10	10	10	86	10	10
Tramadol	0	-11	95	-36	3	-43	-160	-137	168	51	4	-111
PFAS												
PFBA	103	-19	135	100	-19	106	-19	-19	-19	-19	-19	-116
PFPeA	-107	-29	-29	-97	-152	158	101	119	-29	69	155	154
PFBS	17	-29	43	-5	94	-82	110	46	19	74	25	43
PFHpA	7	-50	-50	99	-4	-50	-50	26	-50	75	131	96
PFHxS	-12	-58	77	130	-16	80	-157	-40	137	124	136	123
PFOA	131	158	174	186	136	171	168	18	174	105	122	71
PFNA	81	138	45	45	-47	45	10	49	45	181	178	33
PFOS	-36	-187	-36	-176	-190	-36	184	-193	-192	-189	95	106
PFDA	195	-29	-29	-29	-29	-29	-193	-29	-29	189	184	-29

*Normalised differences (%) = ((value a-value b)/average a,b)*100), where a and b are the concentrations from grab water samples and passive samplers, respectively. [a]Passive samplers results are the values of samples collected at 28 day. [b]Grab samples results are the average values of samples collected on days 0, 14 and 28.*

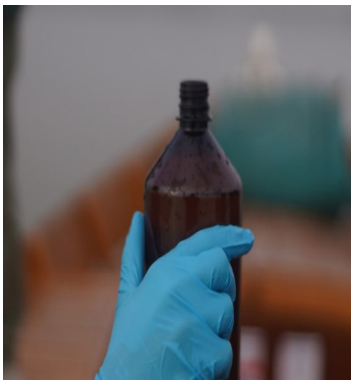
Figure S1. Pictures highlighting the overview of the sampling procedure.



MPT Passive samplers



Lake sampling point



Water sample



L'albufera natural park canal



Tancat MPT samplers retrieval



Sediment sampling



Channel sampling



Water sampling

Figure S2. Differences between laboratories expressed as (A) normalized mean of the differences and the standard error and (B) ratio of the mean normalized mass differences of the 12 sampling points (ng sampler-1) for each of the nineteen compounds analysed at the University of Queensland (UQ) and the University of Valencia (UV), sorted in ascending order within the groups: pesticides (blue), per- and polyfluoroalkyl substances (PFAS) (pink) and pharmaceuticals and personal care products (PPCP) (yellow). Dashed orange line shows >33% deviation between labs. The ratios have been extracted from the Table S20 considering that ND (%) = (a-b)/[(a+b)/2]*100 and r=b/a.

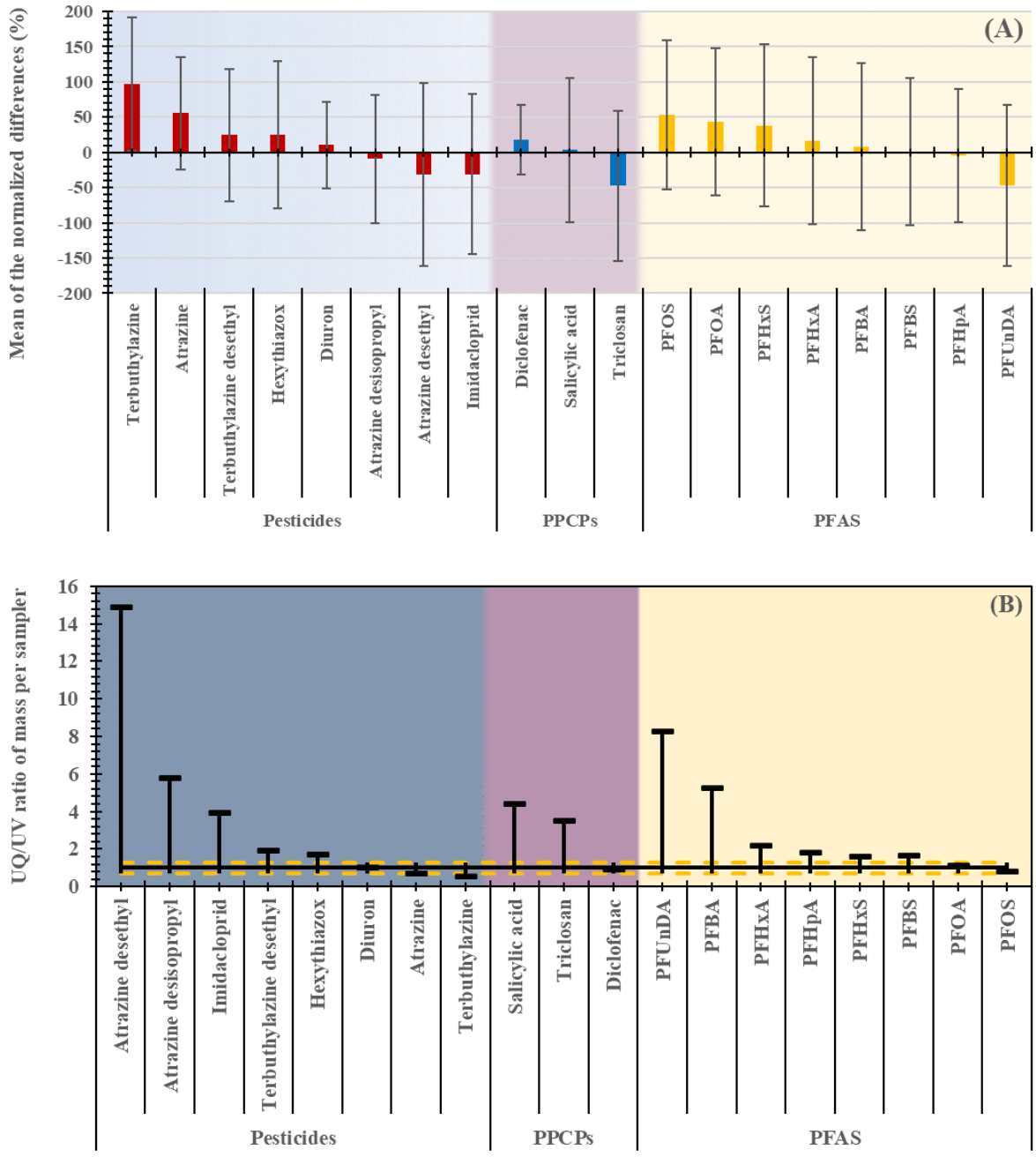


Figure S3. Ratio C_w grab samples/C_w passive samplers vs C_w grab samples for each individual pesticide. The points in orange (●) indicate the n.d. that were substituted by the LODs/2, the points in blue (●) indicated those value obtained for the points were the compound was detected. C_w is the concentration value expressed in (ng L^{-1}).

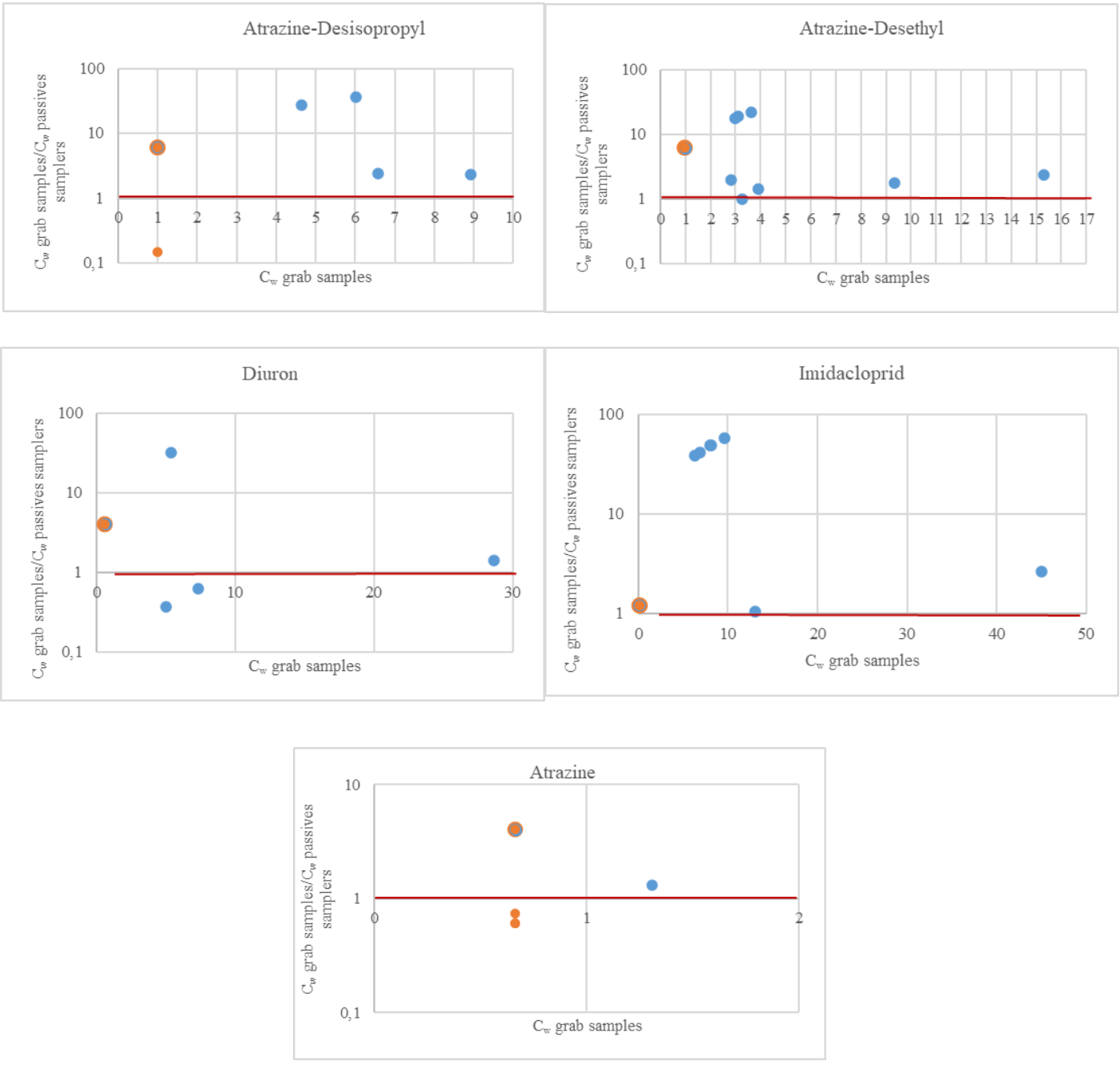


Figure S4. Ratio C_w grab samples/C_w passive samplers vs C_w grab samples for each individual PFAS. The points in orange (●) indicate the n.d. that were substituted by the LODs/2, the points in blue (●) indicated those value obtained for the points were the compound was detected. C_w is the concentration value.expressed in (ng L^{-1}).

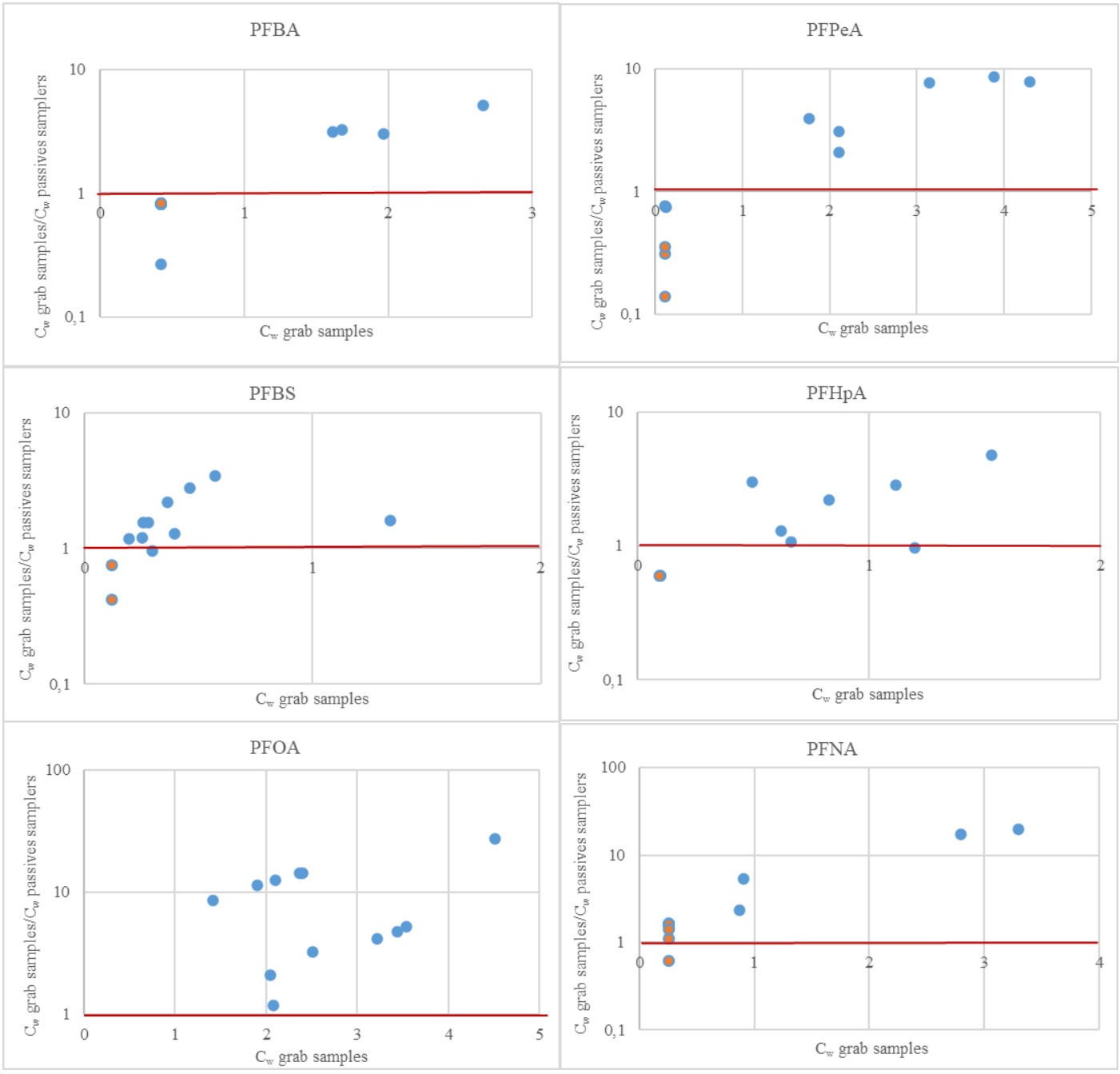


Figure S5. Ratio C_w grab samples/C_w passive samplers vs C_w grab samples for the other PFAS and PPCPs. The points in orange (●) indicate the n.d. that were substituted by the LODs/2, the points in blue (●) indicated those value obtained for the points were the compound was detected. C_w is the concentration value expressed in (ng L^{-1}).

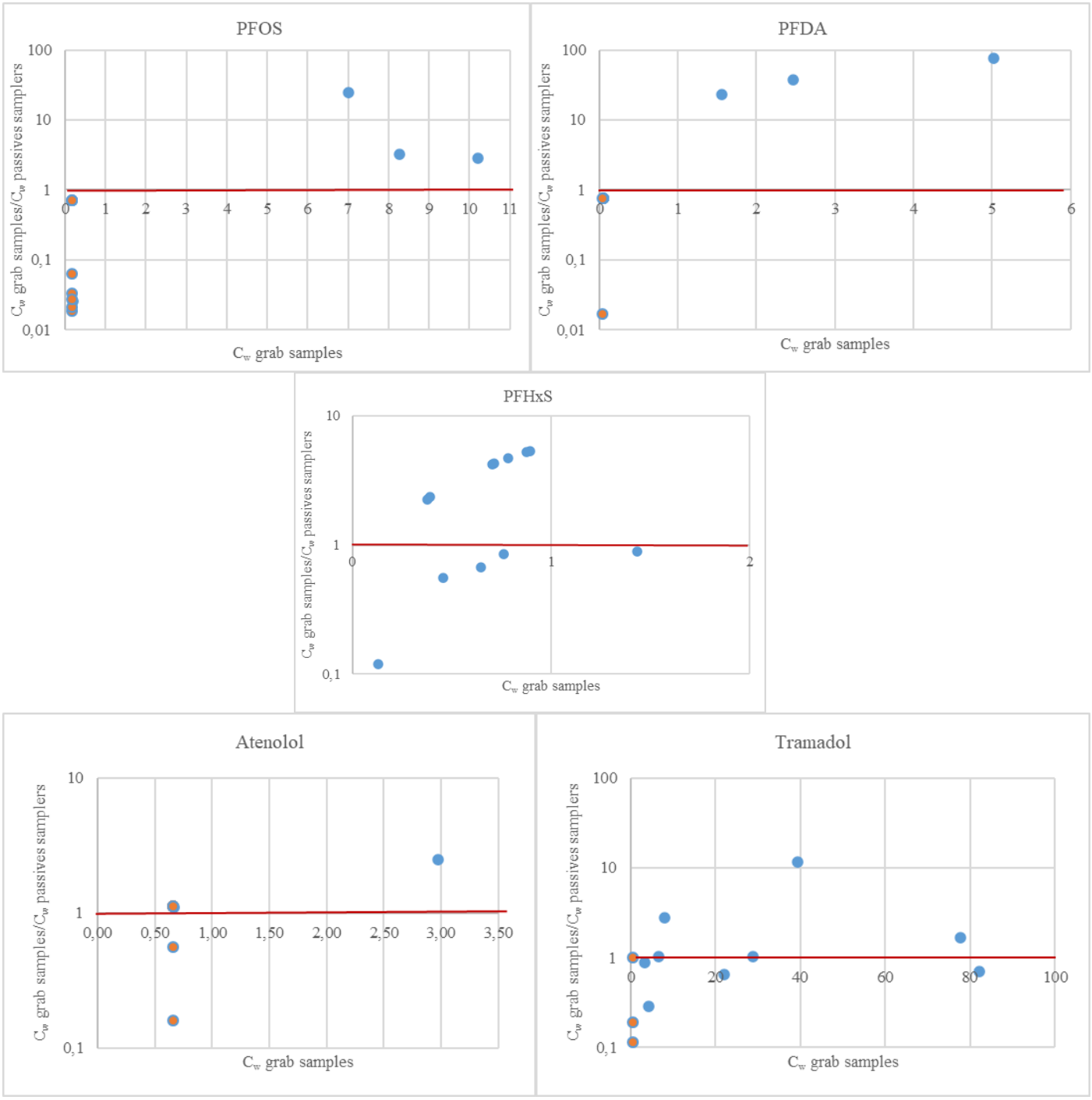
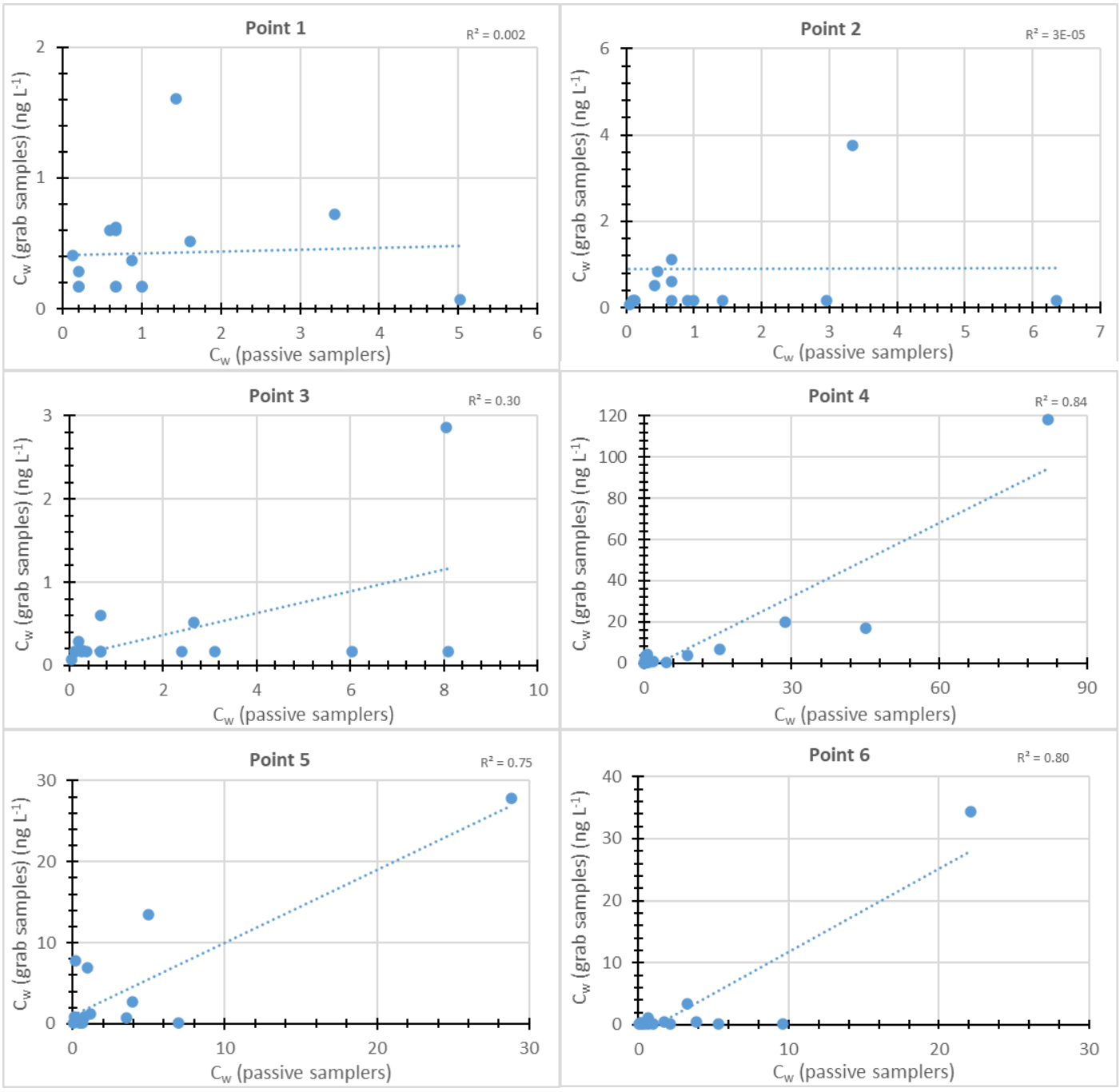


Figure S6. Water concentration estimates (C_w), in ng L^{-1}, for pesticides, PPCPs and PFAS in grab samples and in passives samplers showing site-by-site corerlations.



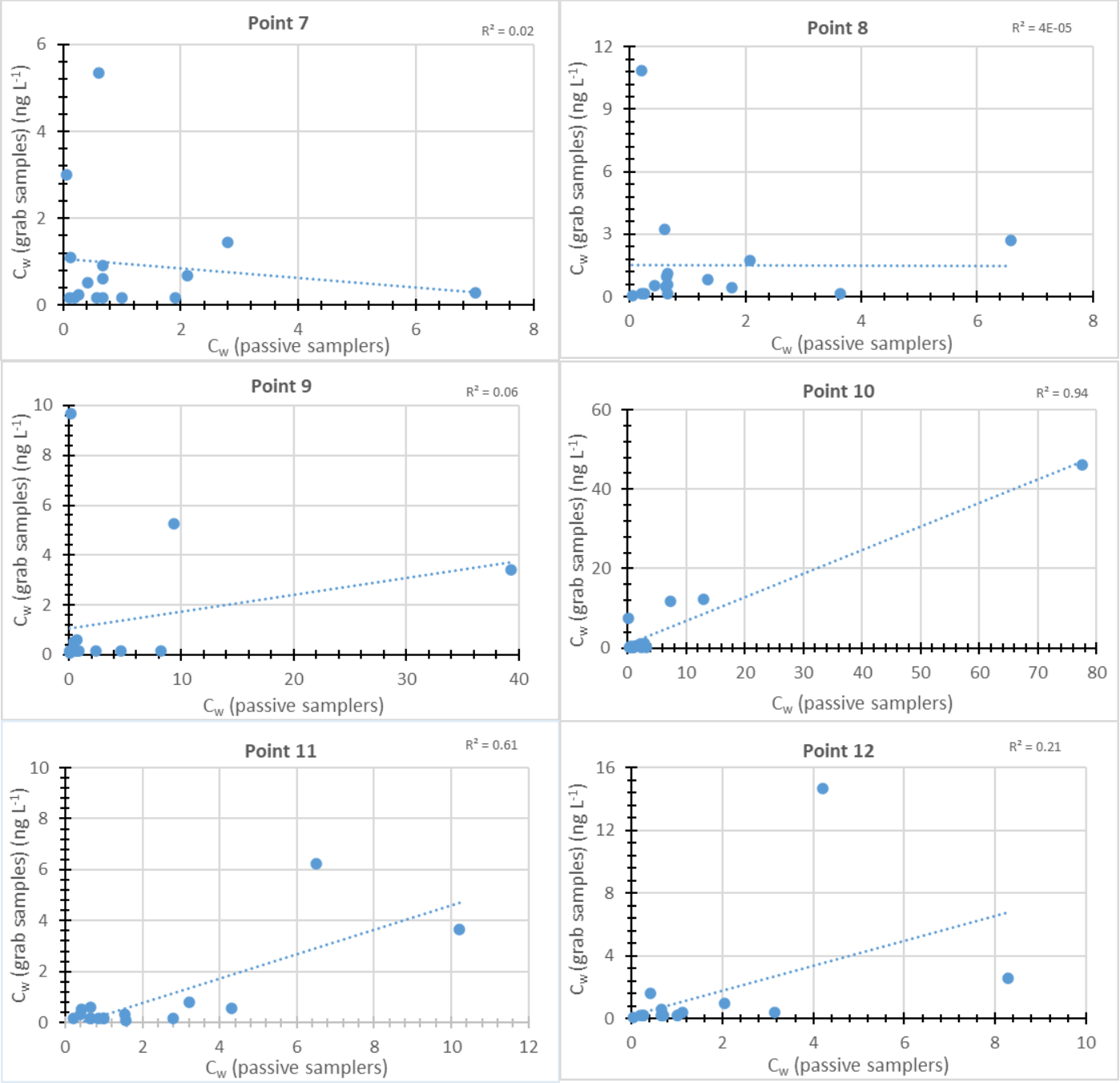

Point 7
R² = 0.02
Cw (grab samples) (ng L-1)
Cw (passive samplers)
Point 8
R² = 4E-05
Cw (grab samples) (ng L-1)
Cw (passive samplers)
Point 9
R² = 0.06
Cw (grab samples) (ng L-1)
Cw (passive samplers)
Point 10
R² = 0.94
Cw (grab samples) (ng L-1)
Cw (passive samplers)
Point 11
R² = 0.61
Cw (grab samples) (ng L-1)
Cw (passive samplers)
Point 12
R² = 0.21
Cw (grab samples) (ng L-1)
Cw (passive samplers)

Figure S7. Correlation of water concentration estimates (C_w), in ng L^{-1}, for pesticides and PPCPs in grab samples and in passives samplers.

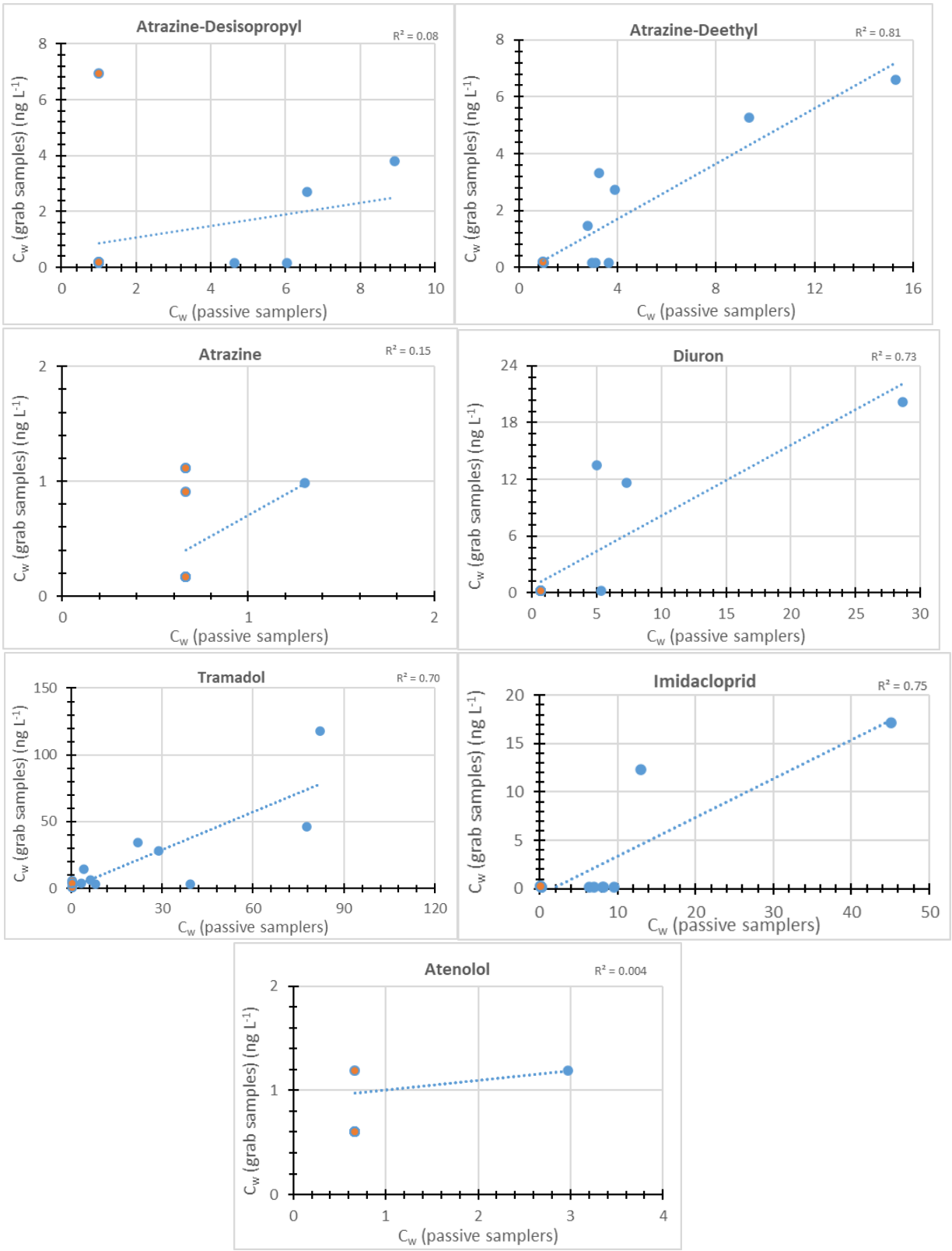


Figure S8. Correlation of water concentration estimates (C_w), in ng L^{-1}, for PFAS in grab samples and in passives samplers. The points in orange (●) indicate the n.d. that were substituted by the LODs/2, the points in blue (●) indicated those value obtained for the points were the compound was detected. C_w is the concentration value expressed in (ng L^{-1}).

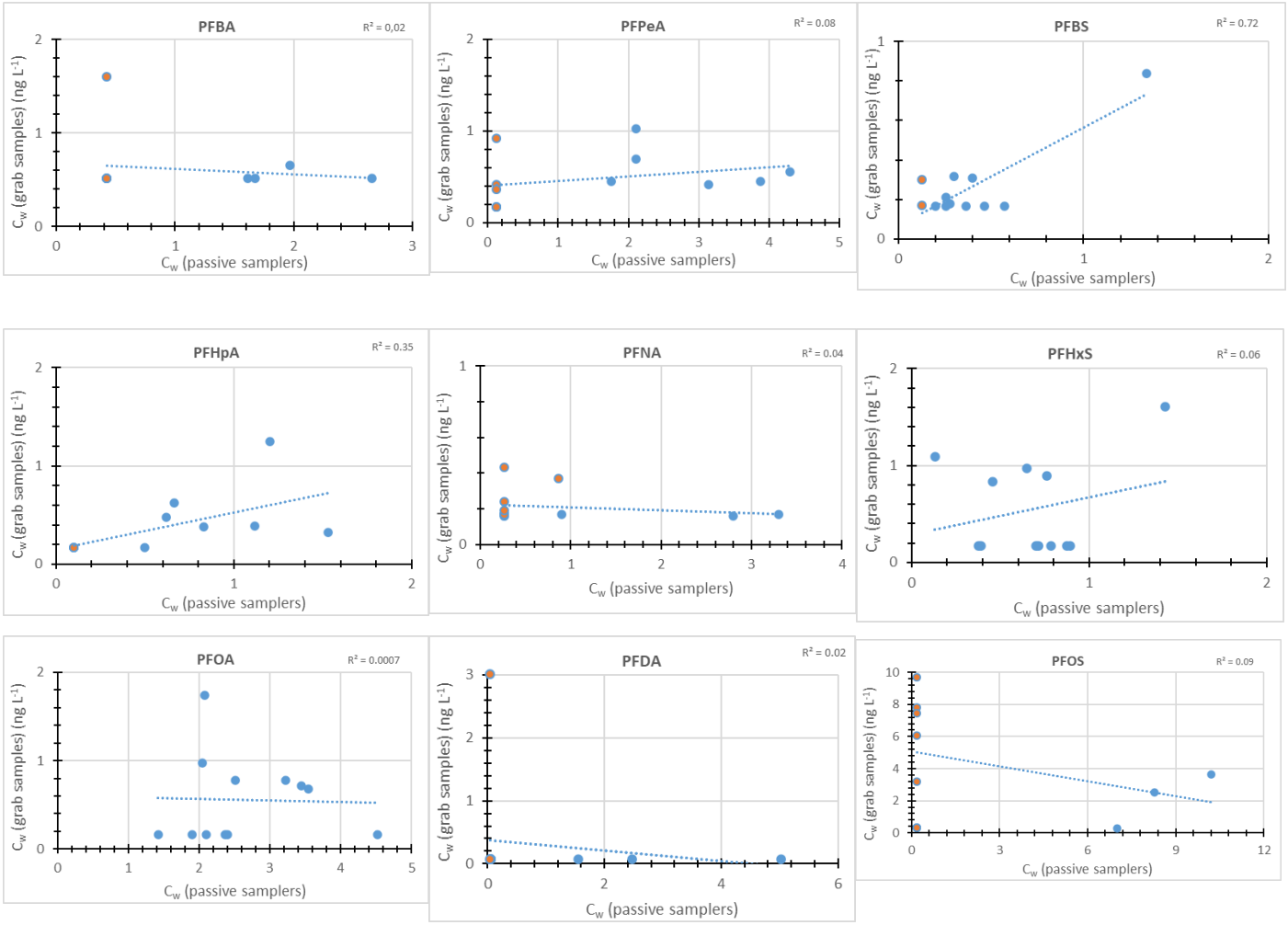


Figure S9. Side-by-side comparison of water concentration estimates (C_w) for pesticides from grab samples and passives samplers.

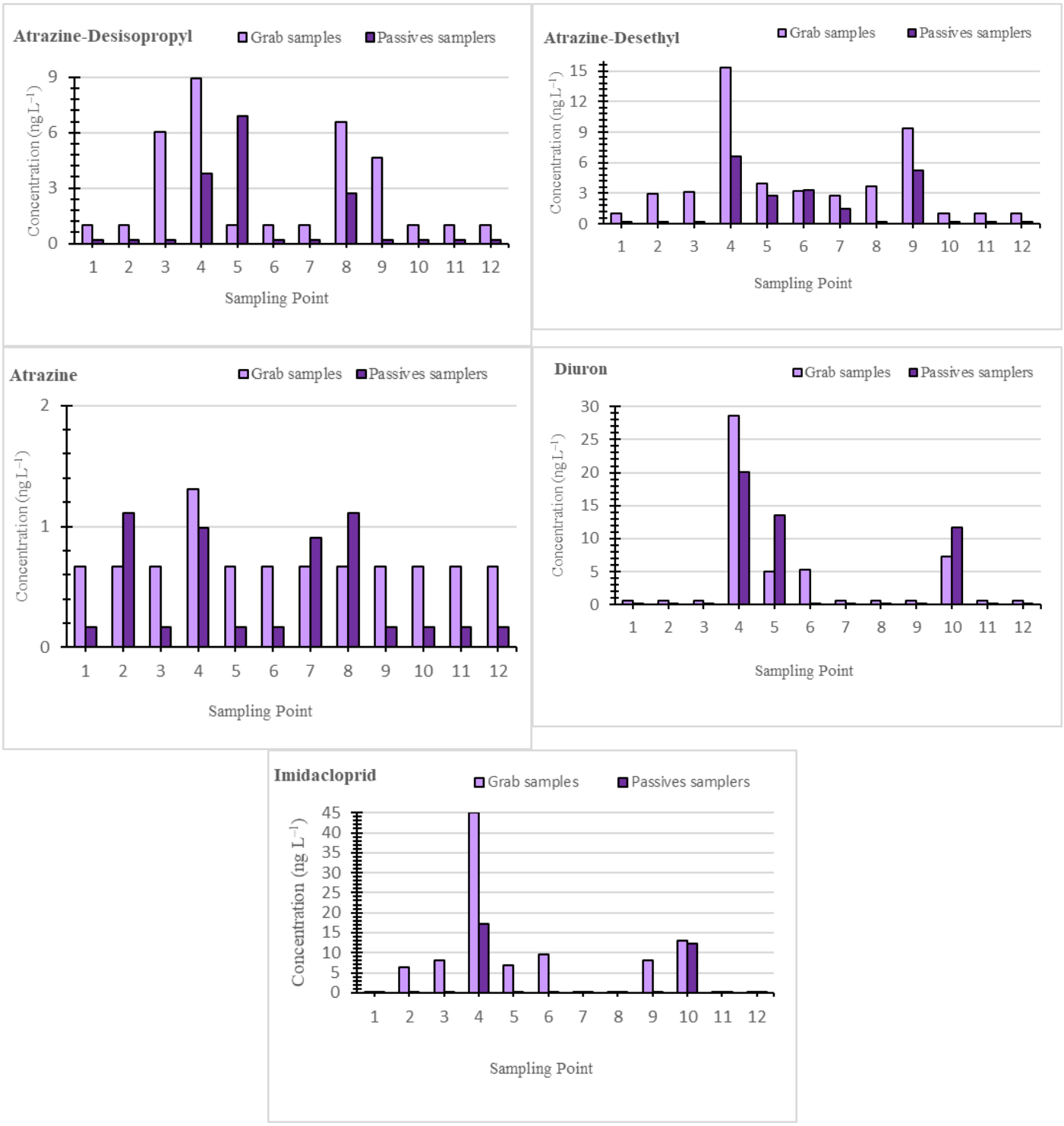


Figure S10. Side-by-side comparison of water concentration estimates (C_w) for PFAS from grab samples and passives samplers.

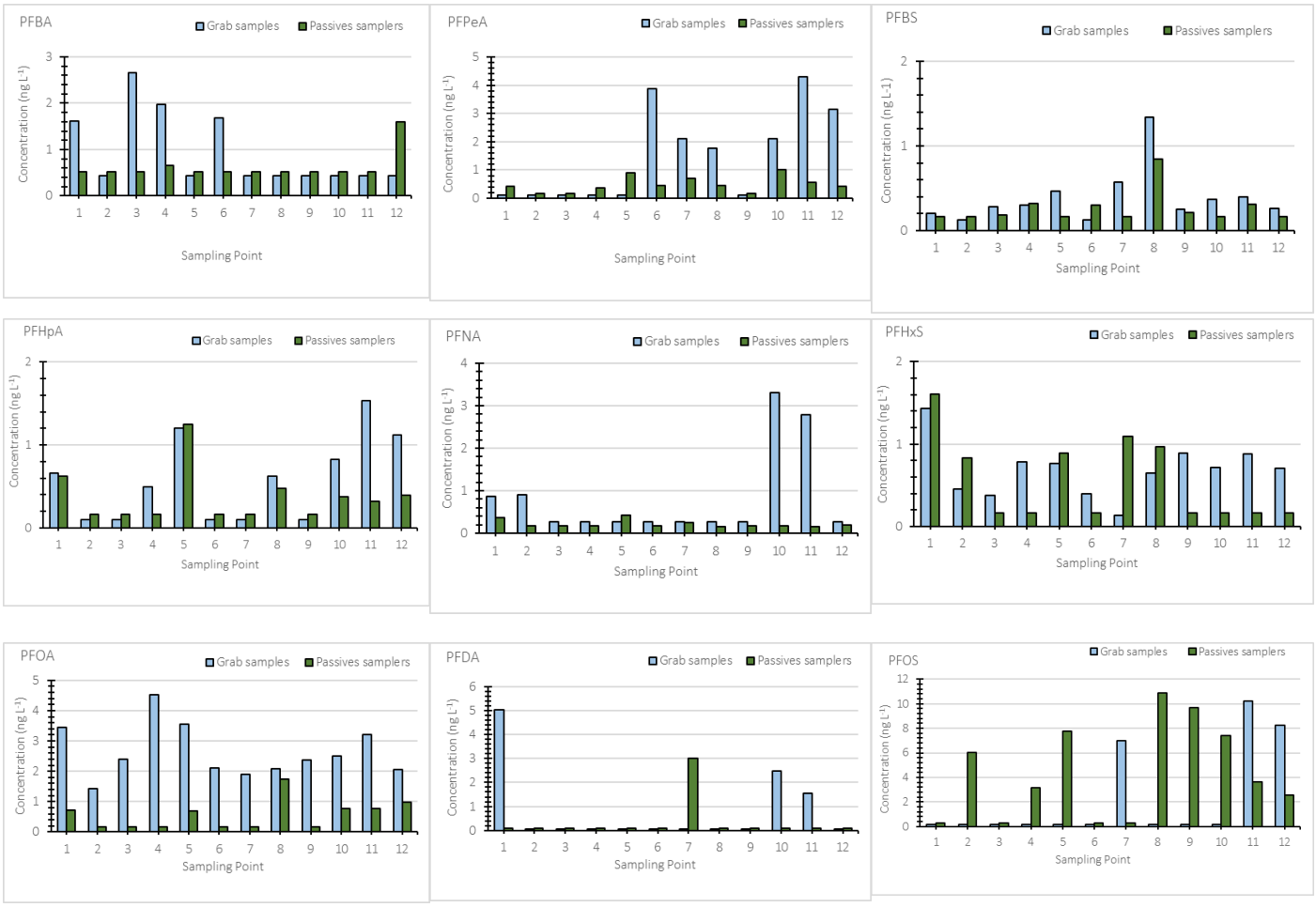


Figure S11. Side-by-side comparison of water concentration estimates (C_w) for PPCPs from grab samples and passives samplers.

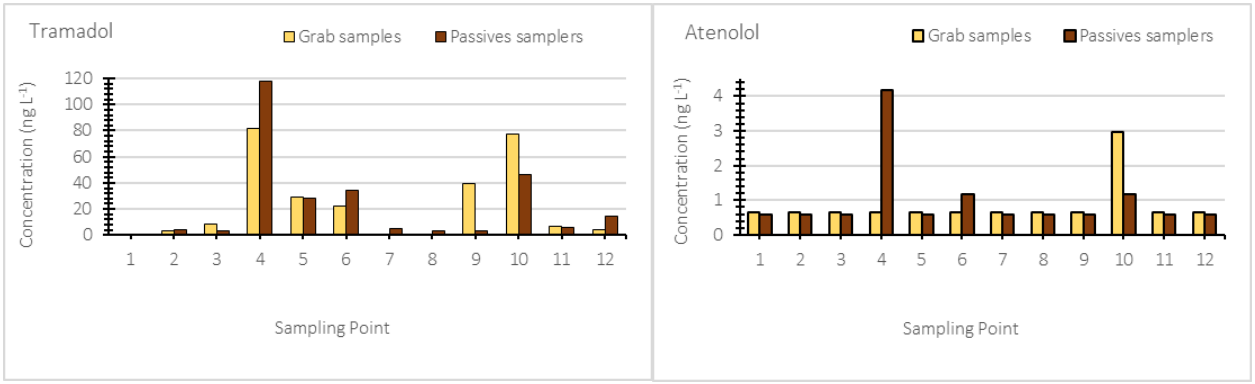


Figure S12. Comparison of average water concentrations (ng L^{-1}) and standard deviation in MPT passive samplers and grab samples for a range of pesticides, PPCPs and PFAS. Grab samples results are the average values of samples collected across the 12 sites on days 0, 14 and 28. Passive sampler results are the average values of samples collected at the 12 sites.

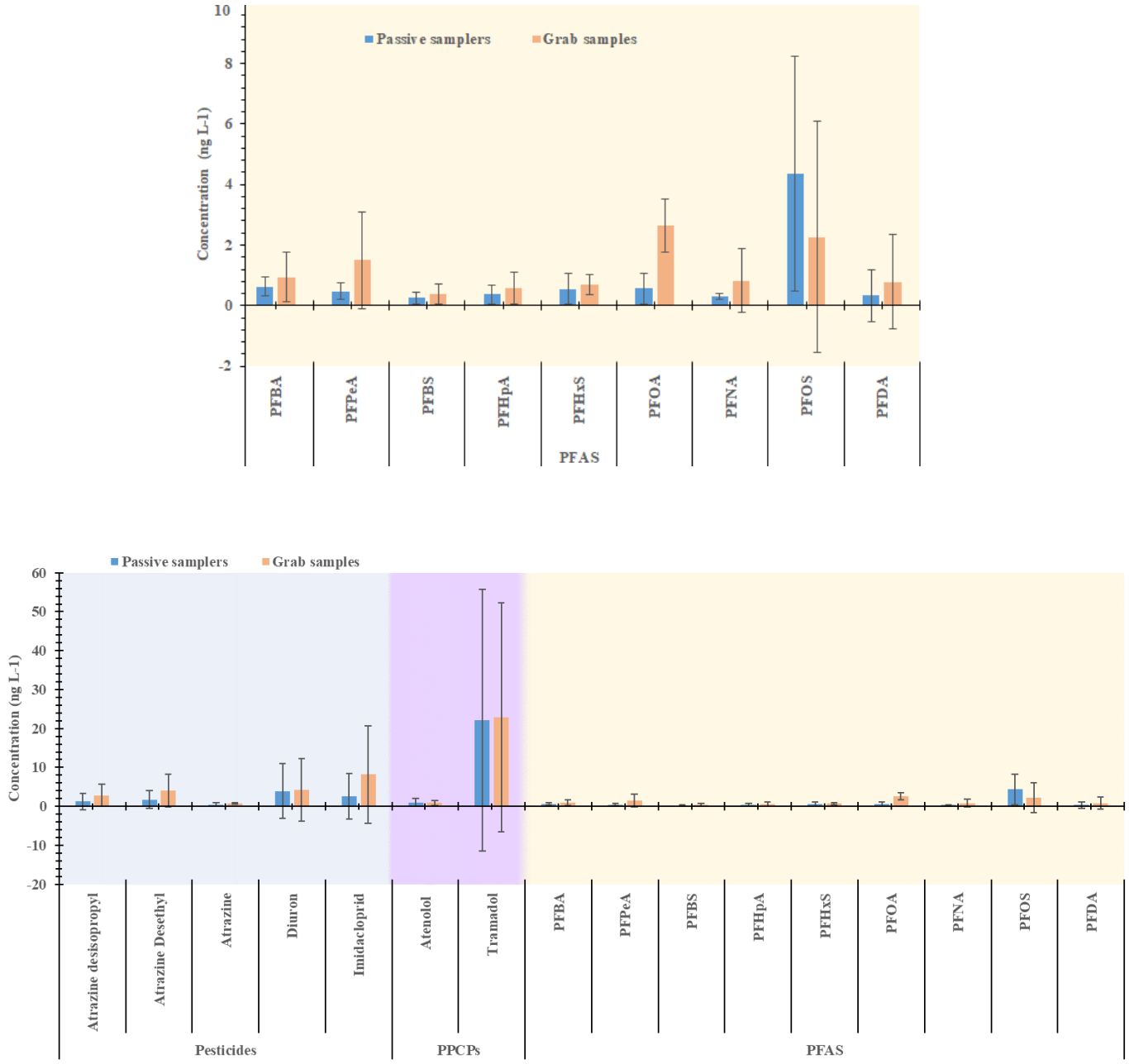
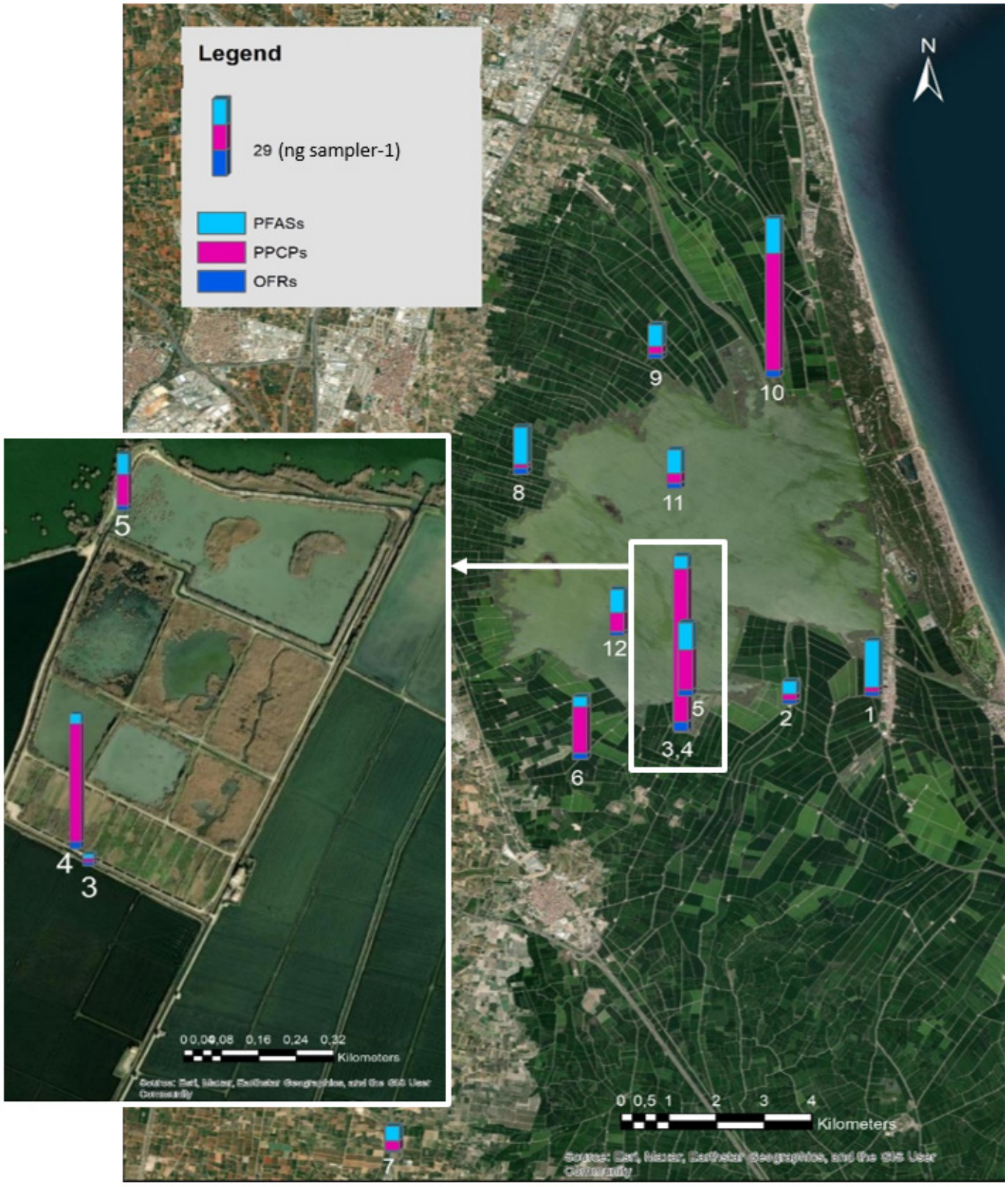


Figure S13. Sum of the mass of target PPCPs, PFAS and OPFRs accumulated in MPT passive samplers across three sampling sites of the Albufera Natural Park, Valencia, Spain.



ANNEX I

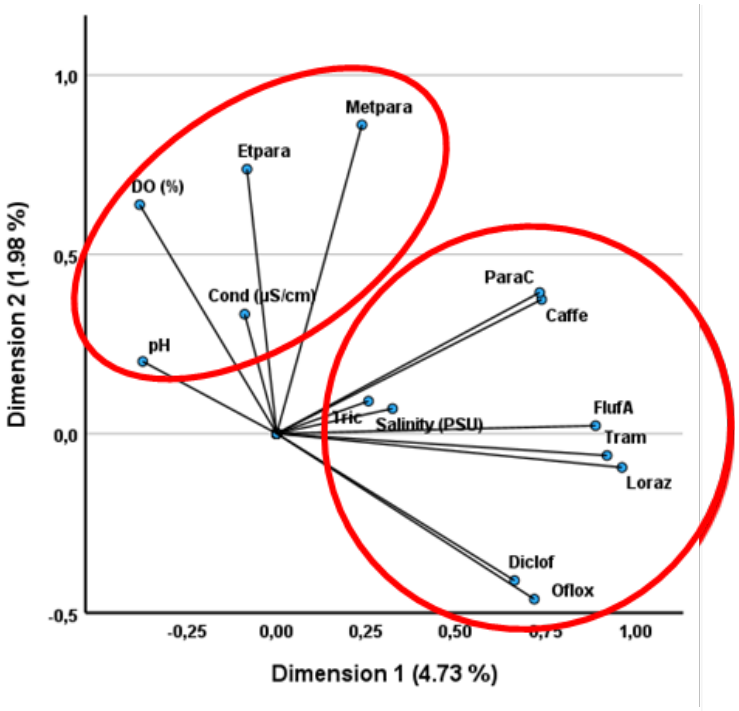
Statistical treatment applied to the spatial assessment (section 3.3.) to establish the weight and dependence among variables and behavioral patterns

GRAB SAMPLES FOR PPCPs

ANOVA

There are no differences for PPCPs in each treatment (ZONE, TIME, METHOD).

Figure S14. Biplot of the Principal Component Analysis related to PPCPs in grab water samples of L'Albufera Natural Park.



Variance explained: 6.71%

CAPCA cannot explain enough the variance but two groups were formed. However, pH, DO, Salinity and Conductivity seem to be the parameters that most influenced the dynamics of the majority of these compounds according the correlation analysis.

GRAB SAMPLES FOR PESTICIDES

ANOVA

Statistical significant differences were observed in the two treatments.

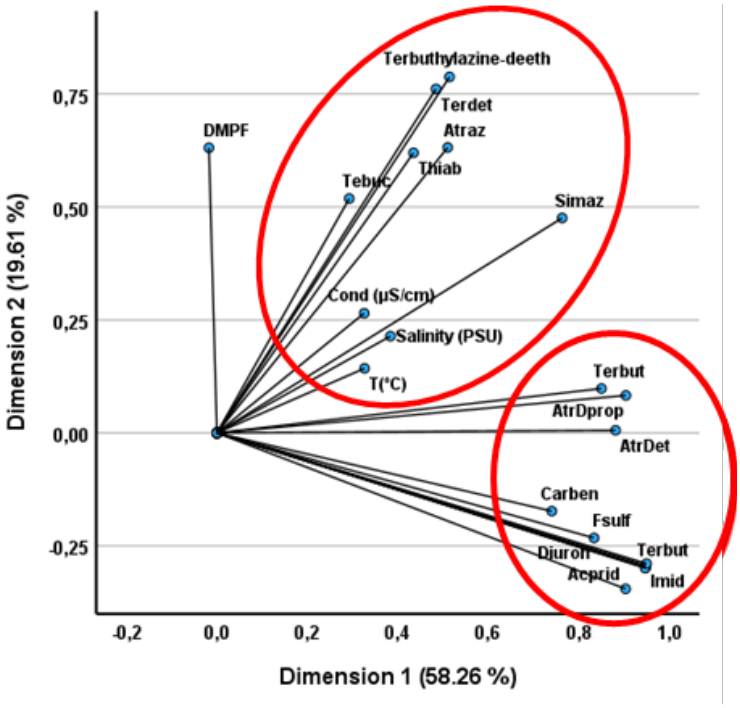
According ZONES, differences were observed for:

Atrazine	Control ≈ Channels ≠ Lake
Tebuconazol	Control ≠ Channels ≠ Lake
Diazepam	Lake ≈ Channels ≠ Control

According TIME, differences were observed for:

Terbumeton deethyl	14′ ≈ 0′ ≈ 28	14′ ≠ 28′
Terbuthylazine 2OH	28′ ≠14′ ≈ 0′	
Terbuthylazine detthyl	0′ ≈ 14′ ≈ 28	0′ ≠ 28′

Figure S15. Biplot of the Principal Component Analysis related to Pesticides in grab water samples of L'Albufera Natural Park.



Variance explained: 77.87%

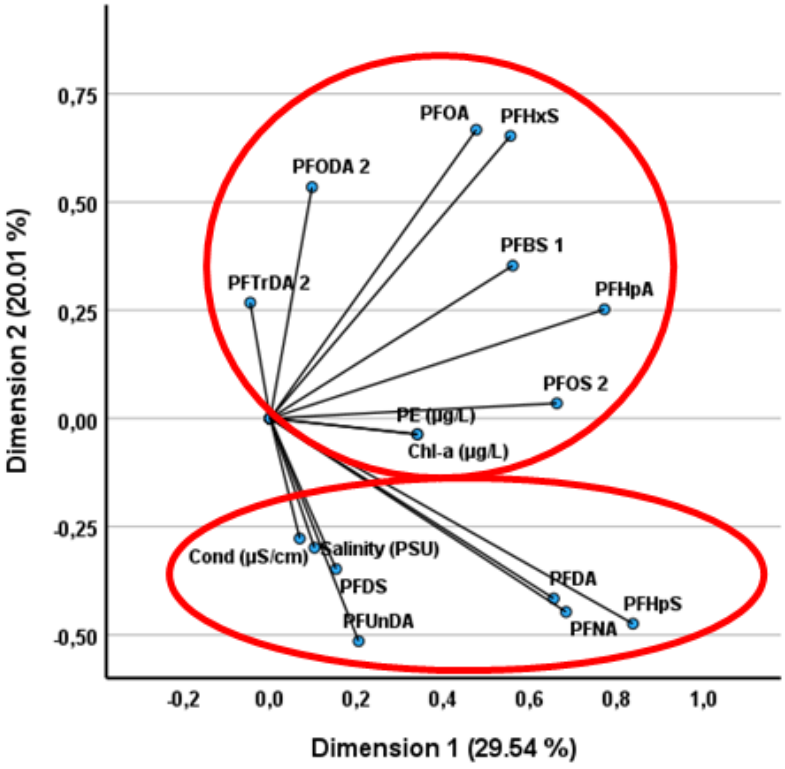
The water salinization and T are the factors that strongly influenced the the majority of compounds in the area.

GRAB SAMPLES FOR PFAS

ANOVA

Statistical significant differences were observed for ZONE but only for:
PFOA Channels ≈ Lake ≠ Control
No differences were observed for TIME.

Figure S16. Biplot of the Principal Component Analysis related to PFASs in grab water samples of L'Albufera Natural Park.



Variance explained: 49.56%

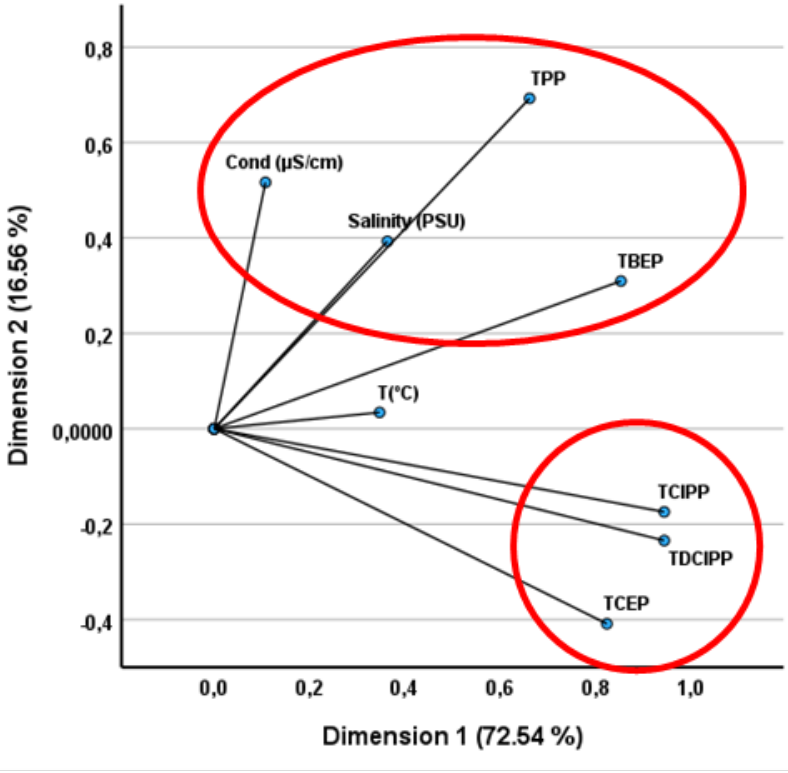
Although the percentage of variance explained is not significant, two groups are well defined. Each one influenced by a pair of water variables (PE: phycoerythrin/Chl-a and Salinity/conductivity), which is also reflected by the correlation analysis.

GRAB SAMPES FOR OPFRs

ANOVA

No significant correlations were observed in any treatment.

Figure S17. Biplot of the Principal Component Analysis related to OPFRs in grab water samples of L'Albufera Natural Park.



Variance explained: 89.10%

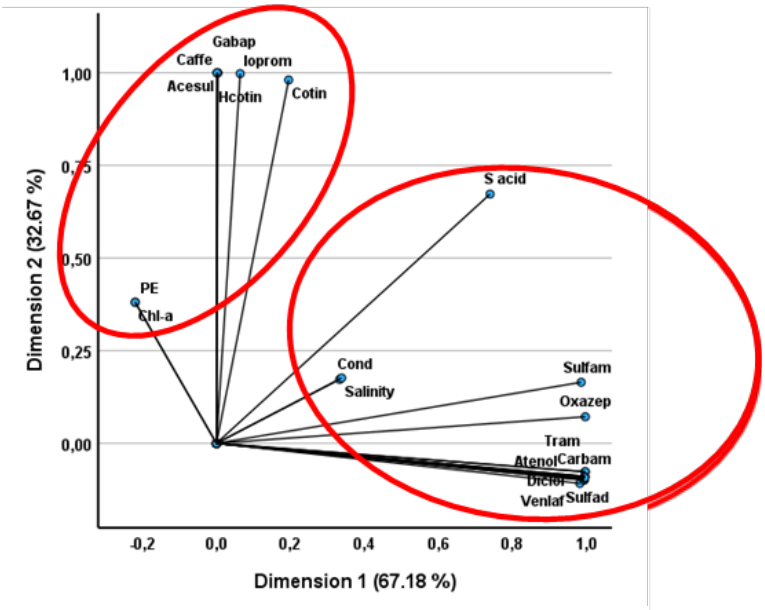
According CAPCA and the correlations analysis the salinization conditions are driving the variability for these compounds.

PASSIVE SAMPLERS FOR PPCPs

ANOVA

There are no observed statistical differences between ZONES or between TIME in this case.

Figure S18. Biplot of the Principal Component Analysis related to PPCPs in passive samplers of L'Albufera Natural Park.



Variance explained: 89.10%

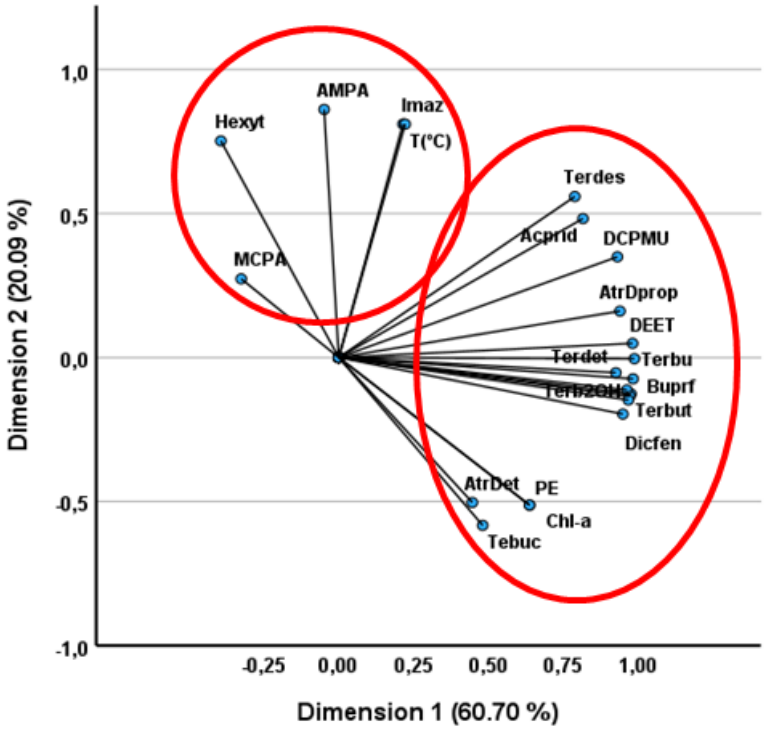
According CAPCA and the correlations analysis the salinization conditions are driving the variability for these compounds.

PASSIVE SAMPLERS FOR PESTICIDES

ANOVA

Significant differences were only observed in the analysis of ZONE. In this case for Tebuconazol
Channels ≈ Lake/Control and Lake ≠ CControl

Figure S19. Biplot of the Principal Component Analysis related to Pesticides in passive samplers of L'Albufera Natural Park.



Variance explained: 80.79%

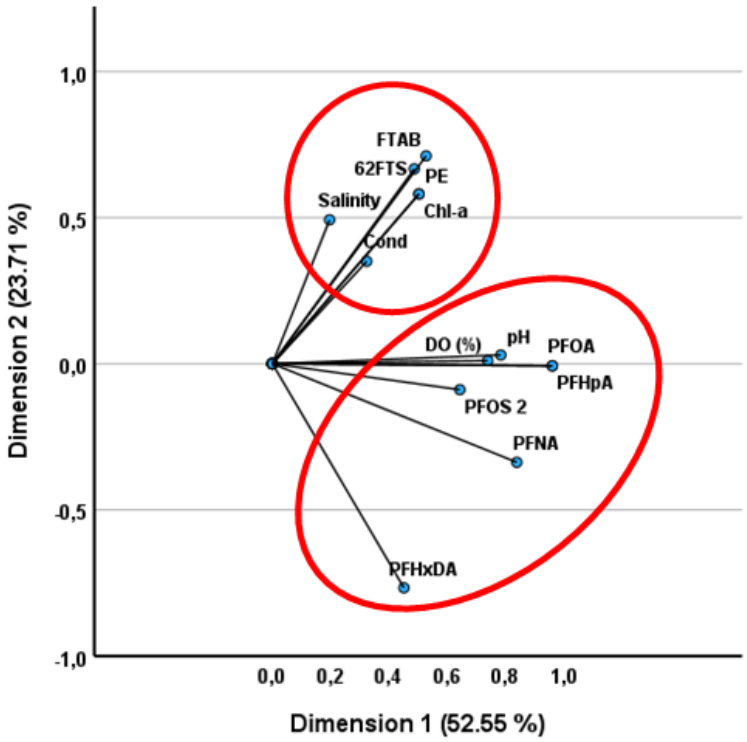
The potential influence of eutrophication in the dynamics of some compounds are observed in the CAPCA through phycoerythrin and Chl-a. This is accompanied by the influence of temperature on pesticides in the area.

PASIVE SAMPLERS FOR PFAS

ANOVA

Significant differences has been observed in the analysis of ZONE. In this case for 6:2 FTS Channels ≈ Control ≠ Lake

Figure S20. Biplot of the Principal Component Analysis related to PFASs in passive samplers of L'Albufera Natural Park.



Variance explained: 76.26%

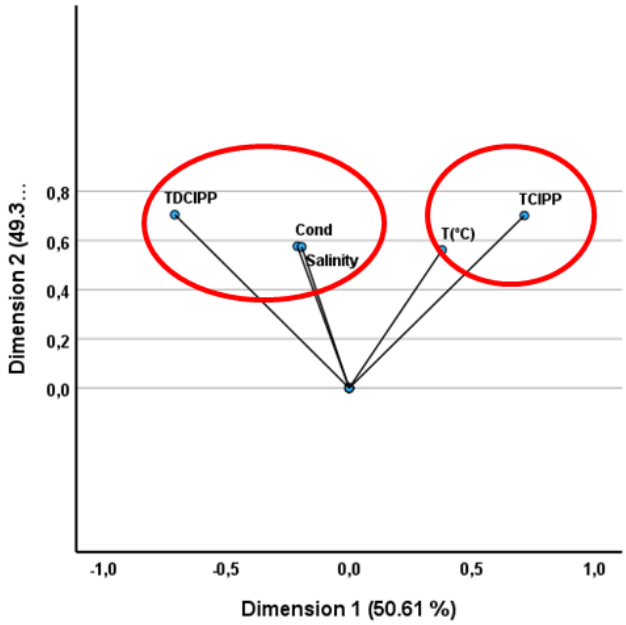
The net alteration of the water conditions and their effect on the dynamics of these compounds can be observed in this CAPCA. Mainly in the influence of two groups of parameters (Salinity, Conductivity, phycoerythrin and Chl-a, and the group formed by pH and DO) on different compounds.

PASIVE SAMPLERS FOR OPFRs

ANOVA

Statistically significant differences were not observed on ZONES and TIME. In the same way no correlations appeared between compounds and environmental characteristics.

Figure S21. Biplot of the Principal Component Analysis related to OPFRs in passive samplers of L'Albufera Natural Park.



Variance explained: 100.00%

Salinity, Conductivity and T are the driving variable that influence more the behavior of these compounds.

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SECCIÓN 4

Detección simultánea de contaminantes antropogénicos en núcleos de sedimentos utilizando análisis dirigidos y no dirigidos

ARTICLE 04

Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: accounting for site/area dependent factors

Journal of Hazardous Materials 470 (2024) 134168

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: Accounting for site/area dependent factors

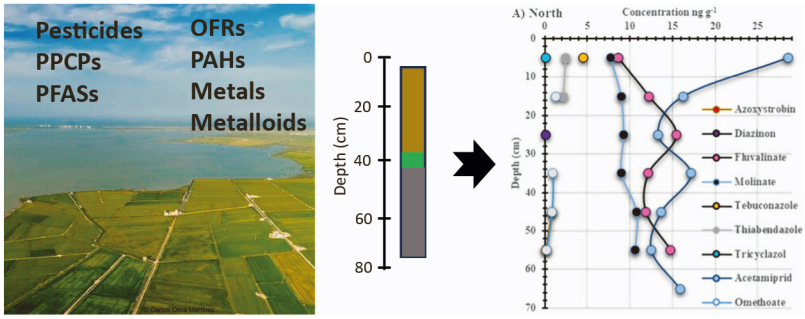
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HIGHLIGHTS

- HMs, PAHs, PFASs, OPFRs, pesticides, PPCPs were detected in sediment cores.
- Challenging to study historical trends due to compound properties and area dynamics.
- PFOS increase sharply in the upper layers of sediments.
- L'Albufera Lake sediment cores exhibit homogeneous distribution of contaminants.
- Need of better sediment characteristics definition for contamination chronology.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Sediment cores
Contaminants of emerging concern
Metals
Non-Target
Mediterranean coastal wetland
Lake

ABSTRACT

Sedimentary records help chronologically identify anthropogenic contamination in environmental systems. This study analysed dated sediment cores from L'Albufera Lake (Valencia, Spain), to assess the occurrence of heavy metals (HMs), polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFASs), organophosphorus flame retardants (OPFRs), pesticides and pharmaceuticals and personal care products (PPCPs). The results evidence the continuing vertical presence of all types of contaminants in this location. The sediment age was difficult to establish. However, the presence of shells together with an historical estimation and the knowledge of sedimentary rates could help. HMs contents are higher in the upper layer reflecting the most recent increase of the industrial and agricultural practices in the area since the middle 20th century. Higher availability index of these HMs in the upper sediment layers is associated with point and diffuse contamination sources in the area. PAHs and OPFRs were homogeneous distributed through the sediments with few exceptions such as phenanthrene in the North and fluoranthene in the South. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) were detected throughout the sediment core while short-chain PFASs (except perfluoropentanoic acid (PFPeA)) were detected only in the top layer. Pesticides and PPCPs showed appreciable down-core mobility. The vertical concentration profiles of organic contaminants did not exhibit a clear trend with depth, then, it is difficult to develop a direct relationship between sediment age and contaminant concentrations, and to elucidate the historical trend of contamination based on dated sediment core. Consequently, linking contaminant

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https://doi.org/10.1016/j.jhazmat.2024.134168
Received 8 January 2024; Received in revised form 4 March 2024; Accepted 28 March 2024
Available online 7 April 2024
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occurrence in sediments directly to their historical use is somewhat speculative at least in the conditions of L'Albufera Lake.

1. Introduction

The Anthropocene represents an informal geological epoch, denoting the contemporary period in Earth's history marked by the substantial influence of human activities on the planet's climate and ecosystems [1, 2]. Contaminants are one of the human contributions to the environment that define the Anthropocene. Most authors consider that the industrial revolution in the 19th century in Europe is the beginning of the Anthropocene, with a distinct and quantifiable contamination signature behind it. However, no long-term monitoring data are available from that period. It is hypothesized that sediment layers in lakes and aquatic environments could function as historical records [3,4], documenting through their accurate dating the evolution of environmental conditions and human disturbances in their vertical profile. Thus, sedimentary records along with the data on contaminants accumulated for each time interval could be used to identify and quantify chronologically the occurrence of anthropogenic contamination on environmental systems [5,6].

This information could be more straightforward in coastal and estuarine areas with elevated anthropogenic activity. Several studies have demonstrated that historical contamination for heavy metals (HMs) [7-9] and persistent organic contaminants (POPs) including polycyclic aromatic hydrocarbons (PAHs) [10-12] and perfluoroalkyl substances (PFASs) [13] can be determined using dated sediments. As examples, Bai et al. [14], Zhang et al. [15], and Lorgeoux et al. [16] provided historical PAHs records in lake, tidal flat, and river basin sediment cores, respectively, establishing correlations between PAHs concentrations and sediment age. MacInnis et al. [17] also correlated PFASs presence with sediment age, revealing temporal trends mirroring historical market changes in PFASs manufacturing inventory. However, the long-term presence of contaminants of emerging concern (CECs) such as pharmaceuticals and personal care products (PPCPs), industrial contaminants, and pesticides in sediments has been scarcely studied, particularly for those characterized as moderately polar or polar. Chiaia-Hernandez et al. [1] conducted a thorough evaluation of contamination patterns related to these organic contaminants (OCs) in sediments but found no direct correlation with sediment age. In contrast, Deng et al. [18] established a link between concentration peaks and anthropogenic effects for various OCs. There is no indication of the influence that sedimentation rate, sediment type, or zone characteristics may have on the validity of the results. In the same way, there is no information on the influence of the physico-chemical characteristics of the contaminant, such as mobility or in its interaction with the characteristics of the sediments (% of clay, salt, etc.). Therefore, the establishment of whether this hypothesis is general or necessitates specific sediments characteristics for its validity or only works with contaminants of defined properties remains uncertain. On the other hand, there is hardly any data on the study of the long-term history of contamination in the Mediterranean area —a zone profoundly influenced by human activities dating back to Roman times.

L'Albufera (including the Natural Park around it) is a typical Mediterranean wetland ecosystem modified since the 128 BD that suffered its most important transformation after 1800 (with the landings to introduce rice cultivation and the change in salinity of the area due to the input of more fresh water for this crop) [19]. Its ecological status deteriorated seriously in the 1970 s due to diverse pressures, such as urban and industrial discharges making it today a highly eutrophic lake [20]. Land-use practices and the proximity of the lake to industrial areas and densely populated cities, together with touristic and recreational activities have contributed to the degradation of this vital habitat. Several studies on the Natural Park have documented the continuous occurrence of pesticides [21-24], PPCPs [25,24,26], drugs of abuse [27, 28], PFASs [24,29] or organophosphorus flame retardants (OPFRs) [24, 30]. Regarding the existence of contaminants in sediment cores, just few studies focused on organic matter and metals have been carried out so far [31,32]. Therefore, there is still a knowledge gap concerning the distribution in depth of multiple types of CECs in the sediments of the lake.

The main objective of this study is to characterize the vertical distribution patterns of a diverse range of contaminants, including HMs, POPs (PAHs, PFASs and OPFRs) and CECs (PPCPs and pesticides), within sediment cores of L'Albufera Lake (Valencia, Spain). This aims to establish connections between contamination patterns, transformation processes, sediment characteristics, and the lake's historical evolution. To this end, three key partial objectives were considered: (i) dating L'Albufera Lake sediments and characterizing their physicochemical attributes; (ii) analyzing 71 pesticides, 37 PPCPs, 24 PFASs, 11 OPFRs, 16 PAHs, and 25 HMs and using non-target screening for other CECs; and (iii) investigating the feasibility of constructing a historical record of lake contamination through its dated sediments. This study will provide new information regarding the vertical variations of contaminants, the influence of the area and characteristics of the sediments as well as the properties of the contaminant and will determine if there is a relationship between contaminant levels and sediment age, providing insights into the Anthropocene's origin and development.

2. Materials and methods

2.1. Study area and sampling

L'Albufera Lake, located 10 km Southeast of Valencia City (Spain), lies in a vast alluvial plain shaped by the Turia and Júcar Rivers. The area experiences local subsidence and has a gentle slope. Nowadays, the lake covers an area of 2400 ha, with water depth ranging between 0.5 to 2.0 m, and an average sediment thickness of 70 cm [31]. The surface area of the lake, estimated at more than 30000 ha in Roman times, has decreased to 2433 ha (20% of the original area) mainly due to silting to introduce rice cultivation from 1761 to 1927 [20].

During the late Quaternary, the entire area was a marine embayment with a developing barrier island [33]. The closure of this barrier took place about the 1110 ± 115 BD. Nowadays, the barrier that separates the lagoon from the sea has 30 km length and 500–1000 m width (Fig. 1). Intensive irrigation farming over the past five centuries and the climatic fluctuations of the Little Ice Age (s. XIV-XIX) have transformed the original brackish lagoon into a freshwater ecosystem [20].

Currently, the area balances the maintenance of its intrinsic natural importance (endemic species, biodiversity and hydrological buffering) with human activities (traditional agriculture, hinterland industrial and settlement development). Major pressures come from the activities of a population of 1500000 inhabitants, of which, almost 1000000 live in the thirteen municipalities included within the limits of the Natural Park [34].

The lagoon receives discharges from ravines, drainage and irrigation channels, local springs (ullals), and major rivers (Turia and Júcar) [34]. The water level is controlled to maintain the freshwater quality as well as to assist in the draining and flooding of the rice fields located around lake in the marshy area. Three channels connect the lake with the sea, their outflows are regulated by floodgates that maintain water levels in the rice fields. The lake sediments are characterized by dominant accumulation of fine materials (silt and clay), with limited sand. The sedimentation process in the lake is affected by dynamic factors such as waves, wind, and longshore drift (North-South). Tidal effects, with an

average daily fluctuation of around 15 cm, are negligible [35]. Since 1974, it was described that the lakebed underwent regularization due to the disappearance of submerged vegetation (caused by eutrophication), deep areas, primarily channels, filled with materials, while shallow areas experienced erosion. Particularly noteworthy has been the erosion along the shores of the islands. These reductions occur due to the increased erosive effect of the waves when the protective effect of the lake's submerged vegetation is lost. Various authors have estimated the lake's sedimentation rate. Sanjaume et al. [33] reported a sedimentation mean rate of 0.57 mm/yr since landfill began to the present. Instead, Carmona and Ruiz [36] suggested an accretion rate ranging between 0.8 and 1.14 mm/year with high variations depending on the lake area. The most recent studies by Marco-Barba et al. [37], using ^{137}Cs and ^{210}Pb, report slightly higher values, ranging from 4.2 to 6 mm/year in the superficial part and 1 mm/year in the deeper part (120 cm). These discrepancies may be because solid inputs are mainly received during episodes of torrential rainfall in the watershed [38]. Periods of higher flooding frequency were noted (1579-1598, 1610-1633, 1671-1695, 1770-1808, 1850-1908, 1913-1924 and 1947-1958) with peak between 1808 and 1924 [38].

Two sampling points P1 (Universal Transverse Mercator (UTM) WGS84 Coordinates 30 S: X: 727659 Y: 4358302) and P2 (UTM Coordinates: X: 727341 Y: 4355743) (Fig. 1) were selected (North and South of the lake). The Lake depth was 1.2 m at the station located in the Northern part of the lake and 1.3 m at the one located in the Southern part. However, the water layer depth varies depending on the station and weather conditions.

Sampling campaigns were carried out on April 2021, from a boat, using a sediment core sampler (57 mm inner diameter; Beeker, Eijelkamp) that preserves the sediment–water interface with an 80 cm deep water column. The sediment cores, 70 cm in length, were kept in a bucket with ice and later frozen in the laboratory. They were cut into 10 cm segments using a stainless-steel cutter, freeze-dried, and stored at − 20 ºC until analysis. The overlying water was not removed to prevent sediment oxidation. For more details on the procedures refer to the sampling procedure in 'Data in Brief'.

2.2. Sediment characterization

The ages of the different layers of the sediment cores were established through two different components: the ^{14}C-data of the organic matter present in the sediments, and the ^{14}C-data of the seashells (*Cerastoderma glaucum*) found in some of them (from 30 cm up to 70 cm depths). Samples were ^{14}C dated by Beta Analytic Inc. (Miami, USA) by accelerator mass spectrometry (AMS) [39]. For more information about AMS measurement see in 'Data in Brief' (including Quality Assurance Report of the results provided by Beta Analytic).

Total nitrogen (TN), total sulfur (TS), total carbon (TC) of the sediment cores were determined by a LECO CNS928 elemental analyzer. Inorganic carbon (IC) were measured using the Bernard calcimeter method [40]. Organic carbon (C_{org}) was calculated by difference between TC and IC amounts. The C/N ratio uses the C_{org} and TN. Granulometry and texture was determined using Bouyoucos hydrometer.

2.3. Determination of OCs

A total of 159 target contaminants including 24 PFASs, 11 OPFRs, 37 PPCPs, 71 pesticides and 16 PAHs were analyzed (Supplementary material, **Tables S1-S5**). Other reagents and chemicals are also detailed in 'Data in Brief'. Three different extraction methods for OCs using 1 g of lyophilized sediment were applied:

i) Moderately polar compounds, such as pesticides, were extracted using the citrate buffered Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method [41] (described in detail in 'Data in Brief').

ii) Polar compounds (PPCPs, PFASs and OPFRs) were extracted using the method previously reported by Carmona et al. [42] that involves Solid Liquid Extraction (SLE) with a McIlvaine-ethylenediaminetetraacetic acid (EDTA) buffer (pH = 5.5) followed by Solid Phase Extraction (SPE) (detailed information in 'Data in Brief').

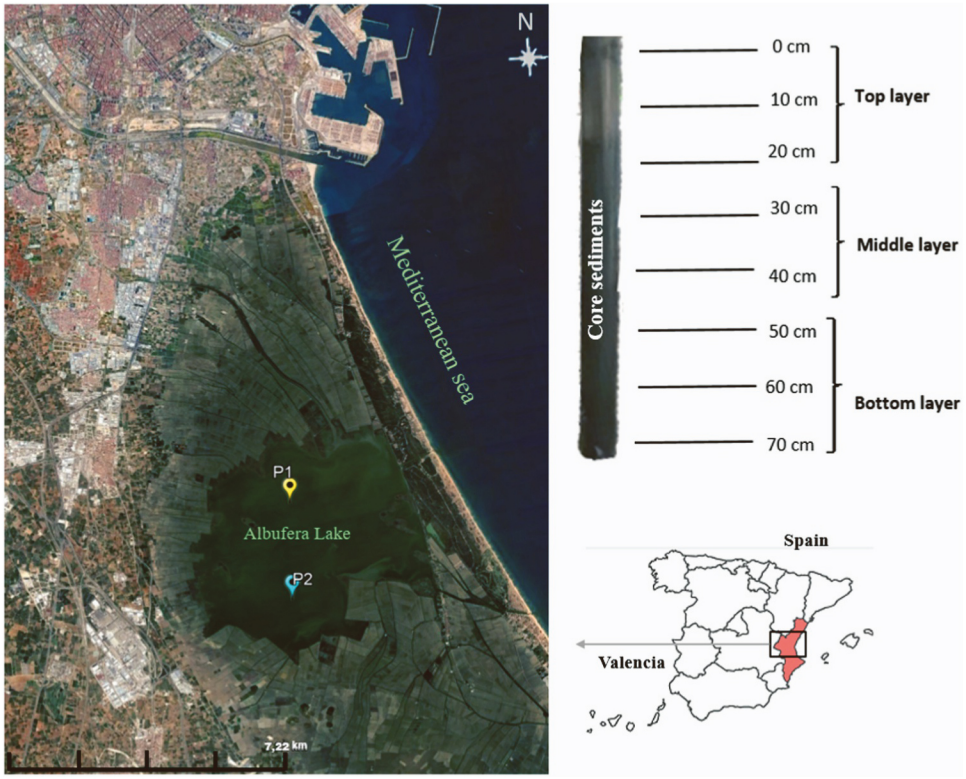


Fig. 1. Location of the sampling points in L'Albufera Lake. P1: North point (yellow) and P2: South point (blue).

iii) Non polar compounds (PAHs) were extracted according to the method of Martinez et al. [43] based on SLE with hexane–dichloromethane (1:1 v/v) and Alumina-N SPE clean-up (detailed information in 'Data in Brief').

Pesticides, PPCPs, PFASs and OPFRs were analyzed by reversed-phase liquid-chromatography (LC) separation using a Vanquish Horizon LC system (Thermo Scientific) coupled to an orbitrap Exploris 120 high-resolution mass spectrometer (Thermo Scientific) with a heated electrospray ionization (HESI) source. Further information on settings and instrument parameters are described in 'Data in Brief'. Compounds were checked manually using the vendor software TraceFinder (version 4.1, Thermo Scientific).

To enhance data evaluation, a non-target screening was conducted in the extract obtained for moderately polar compounds, employing both, positive and negative ionization mode. This involved using data-dependent analysis (DDA), focusing on peak intensity as the key parameter. The process included fragmenting the four most intense ions in each instrumental cycle. The results were analyzed using Compound Discoverer 3.2 (Thermo Fisher Scientific, Software for HRMS data treatment) implementing the workflow for environmental samples (detailed in **Fig. S1** and Table S6) and using mzCloud (On-line) as MS-library. Initially, non-target candidates were isolated through the implementation of an automated exact mass filter (applying a window of ± 5 ppm). The raw files were uploaded along with a blank sample used to filter out any interfering signal resulting from cross contamination.

PAHs were analyzed using a gas chromatography–mass spectrometry (GC–MS) JASCO Series YL6900 (Jasco, Spain). PAHs separation was achieved using a capillary column Zebron ZB-5MS (30 m × 0.25 mm i.d. with 0.25 μm film thickness) from Phenomenex (Torrance, CA, USA). GC–MS conditions are described in 'Data in Brief'.

2.4. Heavy metals (total and extractable fraction)

A broad range of HMs and metalloids (Al, As, B, Be, Bi, Cd, Co, Cr, Cu, Fe, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Si, Sr, Ti, Tl, V and Zn) were analyzed. Microwave assisted extraction was used to determine their total content according to method 3051 A of the United States Environmental Protection Agency (US EPA, 2007), but with the nitric acid and hydrochloric acid proportions (3:1) as provided by ISO 12914 (ISO, 2012). (Further information on the extraction protocols described in detail in 'Data in Brief').

Geogenic background concentrations were determined by assuming that the deepest sediment layer (60–70 cm) represents the background concentrations for HMs. The mean ± 2σ range was employed to characterize the background values for each HM, with the upper background level used in the calculations. Several indexes were used to establish the contamination degree: (i) Contamination Factor (CF) and Contamination degree (CD); (ii) Pollution Load Index (PLI) and, (iii) enrichment factor (EF). (Further information on contamination assessment calculation are described in 'Data in Brief').

Metal bioavailability was assessed by extraction with analytical grade EDTA (0.05 M at pH 7), following the procedure described in the reference material BCR®– 700 [44]. (Further information on extraction protocols are described in detail in 'Data in Brief').

Concentrations of total and extractable HMs were measured using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific® ICAP6500 DUO), except As and Cd that were quantified by an Inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies. ICPMS7900). The sediment moisture was determined by drying the sediment at 105 °C up to constant weight, and the HMs results were expressed in dry weight (dw). From these data, the Extractable/Total Ratio was calculated as an indicator of both the relative mobility of each element and their potential bioavailability.

2.5. Statistical analysis

The statistical analysis was performed using IBM SPSS version 26.0. Data weres assessed using Kolmogorov-Smirnov ($n > 50$) or Shapiro–Wilk ($n < 50$) tests, Levene's test, Mann–Whitney U (M-W) or Kruskal-Wallis (K-W) test (detailed in "Data in Brief"). Spearman Rho correlation analysis was applied since variables that did not show a normal distribution and the Spearman correlation coefficients were calculated in order to interrelate contamination concentrations in the core sediment layers with their physical (clay, silt and sand fractions) and chemical characteristics (C_{org}, IC, TN and TS contents) related to the retention of these contaminants. Also, bivariate correlation analysis was applied at the 95% and 99% significance levels between the age, depth, concentration of CECs and sediment cores characteristics to assess relationships.

3. Results and discussion

3.1. Chronology. Radiocarbon Dating Results

The samples dated from the two sediment cores have progressively older ages with core depth as shown in 'Data in Brief' Fig. 2. In the North, age of ^{14}C from the surface layer of the core (first 10 cm) (35.8%) 1474 - 1638 cal AD (476 - 312 cal BP) was relatively older than the second one (from 10–20 cm) (35.8%) 1867 - 1917 cal AD (83 - 33 cal BP). The same phenomenon was observed in the South. The lack of in-depth chronology of the sediments of L'Albufera Lake with surface layers older than the deeper ones was already described by Carmona and Ruiz [36] and López-Belzunce et al. [35]. The fluctuations in ^{14}C age in the cores could stem from various factors: (1) the input of terrestrial organic materials with older carbon into the lake (known as the old carbon effect), (2) the freshwater ^{14}C reservoir effect, or (3) the loss or redistribution of sediment in these layers. The most likely explanation is the influx of terrestrial organic materials carried by overflow and flooding episodes, as described in Section 2.1. Additionally, the lack of knowledge about the amount of sediment extracted from the lake to fill rice fields since 1850 could contribute to these discrepancies. Wind action is another reported factor that may influence dating results, particularly in the Southern zone, where it can cause the resuspension of lake sediments under certain conditions.

Conversely, Rodrigo et al. [45] dated sediment samples from L'Albufera lake with ^{210}Pb, ^{226}Ra, and ^{137}Cs, that finding ages between 1941 ± 15 at 40 cm depth and 2005 ± 1 in the uppermost layer being able to date recent sediments. Unfortunately, these authors did not used ^{14}C dating for comparison and took the samples in other parts of the lake. Marco-Barba et al. [37] dated sediment cores from the lagoon with ^{210}Pb and ^{137}Cs but their datation is not straightforward. They had to use the 1857 flooding as a mark to figure out the sediment age. It is unclear if radioactive elements could be resuspended. However, interpreting the age from radionuclides relies on the assumption of post-depositional stability within the sediment column. Foster and Charlesworth [46] found cases where this assumption is invalid due to physical mixing, bioturbation, and potential remobilization of HMs. This can lead to a discrepancy between the chronologies derived from radionuclides like ^{137}Cs and ^{210}Pb, suggesting chemical remobilization. To enhance the interpretation, the authors recommend using independent chronological markers such as pollen, diatoms, and carbonaceous particles found in the sediments.

To confirm our results on the sediment ages, the seashells found in the layers 30–40 cm, 40–50 cm, 50–60 cm, and 60–70 cm were dated in the North ('Data in Brief'). Dates of 1486 - 1786 cal AD, 1456 - 1716 cal AD, 810 - 1106 cal AD, and 768 - 1050 cal AD were obtained. Marine shells (*C. glaucum*) found in the two sediment cores suggest a time at which the lagoon had brackish conditions. This result coincides with those of Sanjaume et al. [33] who affirmed that in L'Albufera Lake, shell fragments appear from 25 cm and increase with depth, similar to our

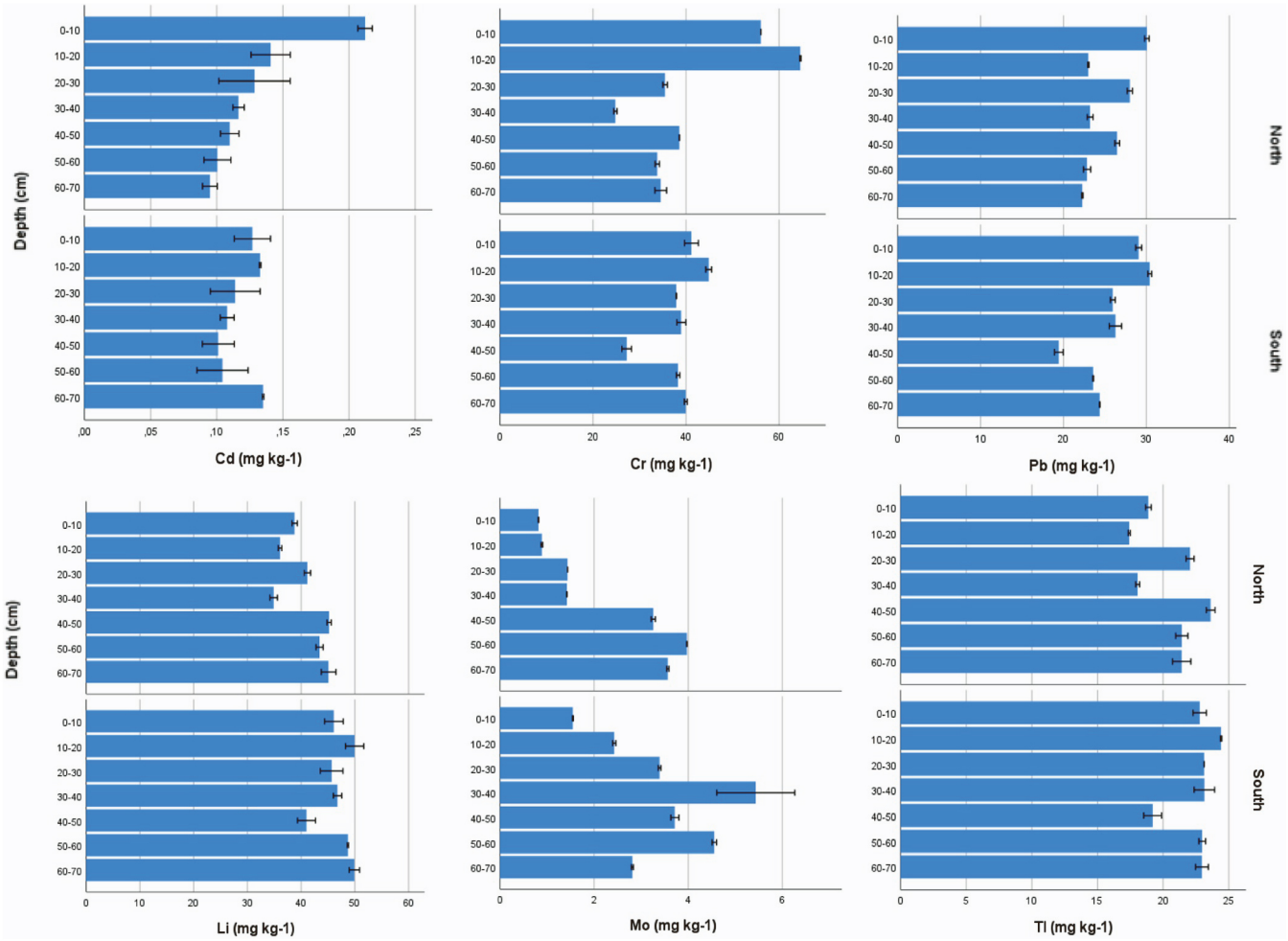


Fig. 2. Total content of Cd, Cr, Pb, Li, Mo, Tl in the different sediment layers in the Northern and Southern sampling points.

findings.

Table 1 compares historical climatic and geomorphological events from various sources with data obtained from sediments and shells in this study in order to find historical events in the lake. This comparison aims to identify historical events in the lake that could help understand sediment behavior. The comparison reveals differences in radiocarbon dating between C_{org} in the sediments and C dating from the shells in the Norther area. Only in the 50–60 cm depth layer both dating methods show similar ages (876–994 AD for the C_{org} in sediment and 810–1106 AD for C from the shells). However, in the 30–40 cm and 40–50 cm depth layers, the sediment dates to 1225–1298 AD, while the shells indicate a more recent age of 1456–1786 AD. This latter date is supported by Sanchis Ibor [19] who dates the transition of the lake's waters from salty to fresh between 1577 AD and 1761 AD.

The ^{14}C dating of organic matter in sediments, considering that it shows a terrigenous origin, can be imprecise. However, dating shells, mainly from saltwater mollusks, helps to establish the age of sediments at a depth of 30 cm to around 1456 AD. By dividing sediment layer depths by the number of years and assuming a constant sedimentation rate, a rate of 0.50 mm/year in the North, and a lower rate of 0.27 mm/year in the South were found. The differences in sedimentation rates are because the Northern area receives important sediment contributions from several ravines. Contrarily, in the South dominated by irrigation channels, the sedimentation took place in the rice fields, resulting in less sediment reaching the lake. In fact, during strong rain episodes, there is a phenomenon of "water meeting" where the water from the North (more brownish) does not mix with that from the South (more gray). Sanjaume et al. [33] already reported sedimentation rates in the range of 0.47–0.57 mm/year and noted experimental observations indicating a lower sedimentation rate than estimated. Considering the calculated sedimentation rate as well as the age of the shells in the last layer where present and making an estimation of the upper layers age, the upper sediments would correspond at 20–30 cm to 1786–1863 AD, at 10–20 cm to 1863–1949 AD, and at 0–10 cm to 1941–2021 AD. However, there is a wide margin of error, as it does not take into account sediment deposition from floods (currently reduced due to channel regulation) or sediment resuspension. In any case, the uppermost sediment layers in direct contact with the water are the ones that should reflect present day pollution, given the direct exchange between water and sediment.

3.2. Physical and chemical characterizations of sediment cores

Sediment texture, dominated by silts and clays (steady at 50% in both cores), shows an increase in sand from 0% at 20–30 cm to 10% at 40–50 cm in the North ("Data in Brief"). Conversely, silt show a decrease by half from the 10–20 cm to the 40–50 cm layer. Sand content, ranging from 4.1% to 10%, is present in certain layers (30–50 cm and 60–70 cm depth in both sediment cores). This could be associated with past flood events and sand inflow from the sea in sediment layers dated before the closure of the sand barrier, typically marked by the presence of shells. Chemical parameters (C_{org}, TN, and TS) decrease with depth ("Data in Brief", Fig. 3). C_{org} percentages range from 4.5 to 2.4 in the North and 3.2 to 1.9 in the South. TN concentration follows a similar pattern

Table 1
Historical evolution in Albufera Lake that influences in their water salinity; results of sediments and shells radiocarbon dating and main changes in sediment properties.

From	To	Reference	Fact	Sediment age by radiocarbon dating (this paper)		Shell age by radiocarbon dating (this paper)	Sediment properties
				Northern	Southern		
Late Quaternary	-	Sanjaume et al. [47]	The entire area was a marine embayment bounded seaward by a developing barrier island. **Sea water**	-	-	-	-
Roman period (218 BC-476 AD)	-	Sanchis Ibor [19]	Open water surface estimated in 30 000 ha. **Salty water**	550 AD-644 AD (60-70cm)	233-97 BC (60-70cm) 22-206 AD (50-60cm) 346-480 AD (40-50cm) 413-512 AD (30-40cm)	-	Sand (10%)
1110 ± 115 BP (725-840 AD)	Present	Sanjaume et al. [47]	Closure of the sand barrier. **Brackish lagoon**	876 AD-944 AD (50-60cm)	882-995 AD (20-30cm)	768 AD-1050 AD (60-70cm) 810 AD-1106 AD (50-60cm)	Highest Na contents (>2 g kg^{-1}) and increment in EC
1200 AD	-	Santiesteban et al. [48]	Closure of the sand barrier. **Brackish lagoon**	1225 AD-1325 AD (30-50cm)	1028-1172 AD (10-20cm)		Na concentration increases from 1.3 g kg^{-1} to 1.9 g kg^{-1} Clay also increases (62%) Sand (4.1 – 10%)
1200 AD (XIII century)		Sanchis Ibor [19]	Water management to maximise fishing by controlling the opening of the ridge				
1200 AD (XIII century)-Islamic period		Marco Segura et al. [49]	Micro-irrigation systems in the Northern area extended in feudal times and diversion of water flows from the River Turia to the lake.				
1258 AD	1273 AD	Sanchis Ibor [19]	Construction of the Júcar Royal Channel (Jaume I King)		1222-1286 AD (0-10cm)		
1400 AD	(XV century)	Sanchis Ibor [19]		1474-1638 AD (0-10cm)		1456 AD-1786 AD (30-50cm)	
1415 AD		Sanchis Ibor [19]					
1484 AD	1506 AD	Sanchis Ibor [19]					
1500 AD	(XVI century)	Sanchis Ibor [19]					
1577 AD	1761 AD	Sanchis Ibor [19]					No sand fraction
Late XVIII century	Early XIX century	Sanchis Ibor [19]	Completion of the works to extend the Júcar royal irrigation channel. Significant increase in freshwater supplies	1867-1917 AD (10-20cm)	-	Sediment cores without shells	No sand fraction
1950-1960 AD	1980 AD	Sanchis Ibor [19]	Urban and industrial expansion in the wetland environment. Dominant industries: furniture, metal and tanning. Tourist development. The drainage network becomes a collector of wastewater from these activities. Increased application of pesticides.	-	-		Highest OC, Lowest Na values No sand fraction

EC: electrical conductivity, Na: Sodium

(0.11–0.38%) in both sediment cores, while IC remains constant in depth in both sediment cores (See in 'Data in Brief' for details).

The Northern sediment core generally has higher C_{org} content, while the Southern core aligns more closely with the findings of Hernández-Crespo and Martín [32], that report Corg values ca. 3 % in surface sediment layers that decrease with deep.

The C_{org}/TN ratio is an indicator of organic matter origin, aiding in identifying sedimentary sources [50]. In the studied cores, these ratios ranged from 12.0 to 16.0 in the North and from 13.4 to 17.6 in the South ('Data in Brief'). Typically, autochthonous organic matter, rich in low molecular weight proteins and nitrogen, has a low C_{org}/TN ratio (4 – 10) indicative of algal origin [51]. Allochthonous organic matter, rich in humic material with higher molecular weight has consecuently a higher C_{org}/TN ratio (20−30). A uniform C_{org}/TN ratio in our cores suggests no rapid mineralization and good C_{org} preservation. High C_{org}/TN values in some L'Albufera Lake layers may be linked to the observation that terrigenous organic matter tends to preserve better than carbon from aquatic production [52].

Furthermore, C_{org}/TN ratio supports the influence of flood events in the contribution of sediments. In addition, the analyzed cores show an increase in sodium contents with depth (from 900 mg kg^{-1} at 10 cm to more than 2100 mg kg^{-1} in the deepest layer) ('Data in Brief')) in both Northern and Southern points. This increase in salinity with depth is indicative of the change from brackish to freshwater conditions, which supports previous sediment dating results and the finding of *C. glaucum* within the shells.

3.3. Distribution of HMs and metalloids

Cd, Cr, Cu, Pb, Si, Sr, and Zn showed a clear decrease with depth in the sedimentary column, especially in the North. However, other elements (Al, As, Co, Fe, La, Li, Mn, Ni, Ti, Tl, Rb, Sr, V) did not follow this trend and, in some cases, exhibited largely constant concentrations along the sediment profile. Fig. 2 illustrates these different behaviours for few more characteristic elements of each group (see **Fig. S3** for all of them). The assessment of the HMs inputs from anthropogenic activities using the CF and the EF, revealed marked enrichment of certain metals in the upper sediment layers (Data in Brief, Fig. 4), particularly in the North. Elements like As, Cd, Cr, Cu, Ni, Pb, Si, Sr, and Zn show higher EF values (3 to 6) in the North, indicating moderate enrichment, with Cu and Zn being the most enriched. In the South, constant EF values suggest minor or no enrichment. Co, La, Li, Mn, Rb, Ti, Tl, and V show EF values

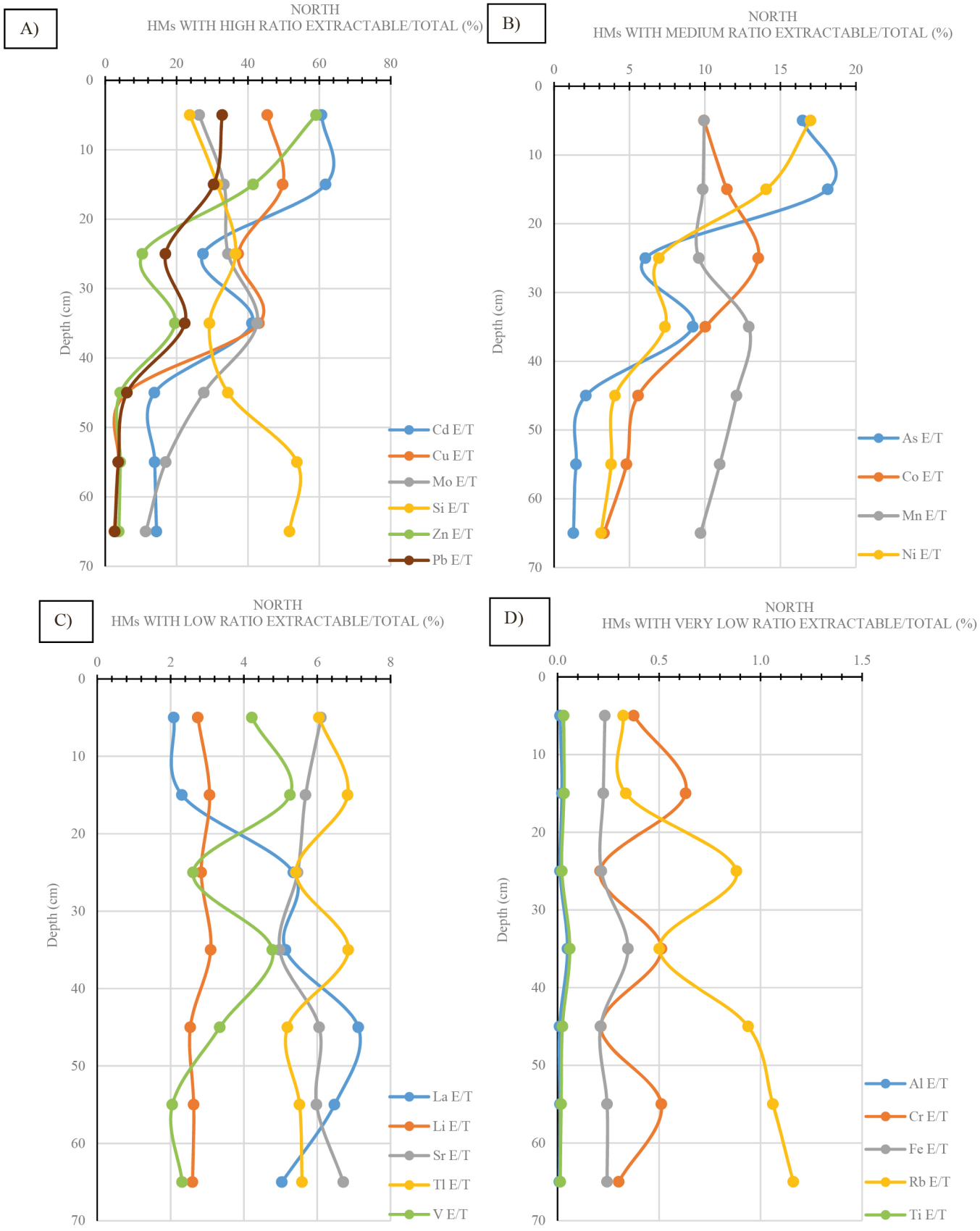


Fig. 3. EDTA-extractable content/Total content for heavy metals (HMs) and metalloids in the sediments cores at Northern sampling points in L'Albufera lake according to their ratio (A) High, (B) Medium, (C) Low and (D) Very low.

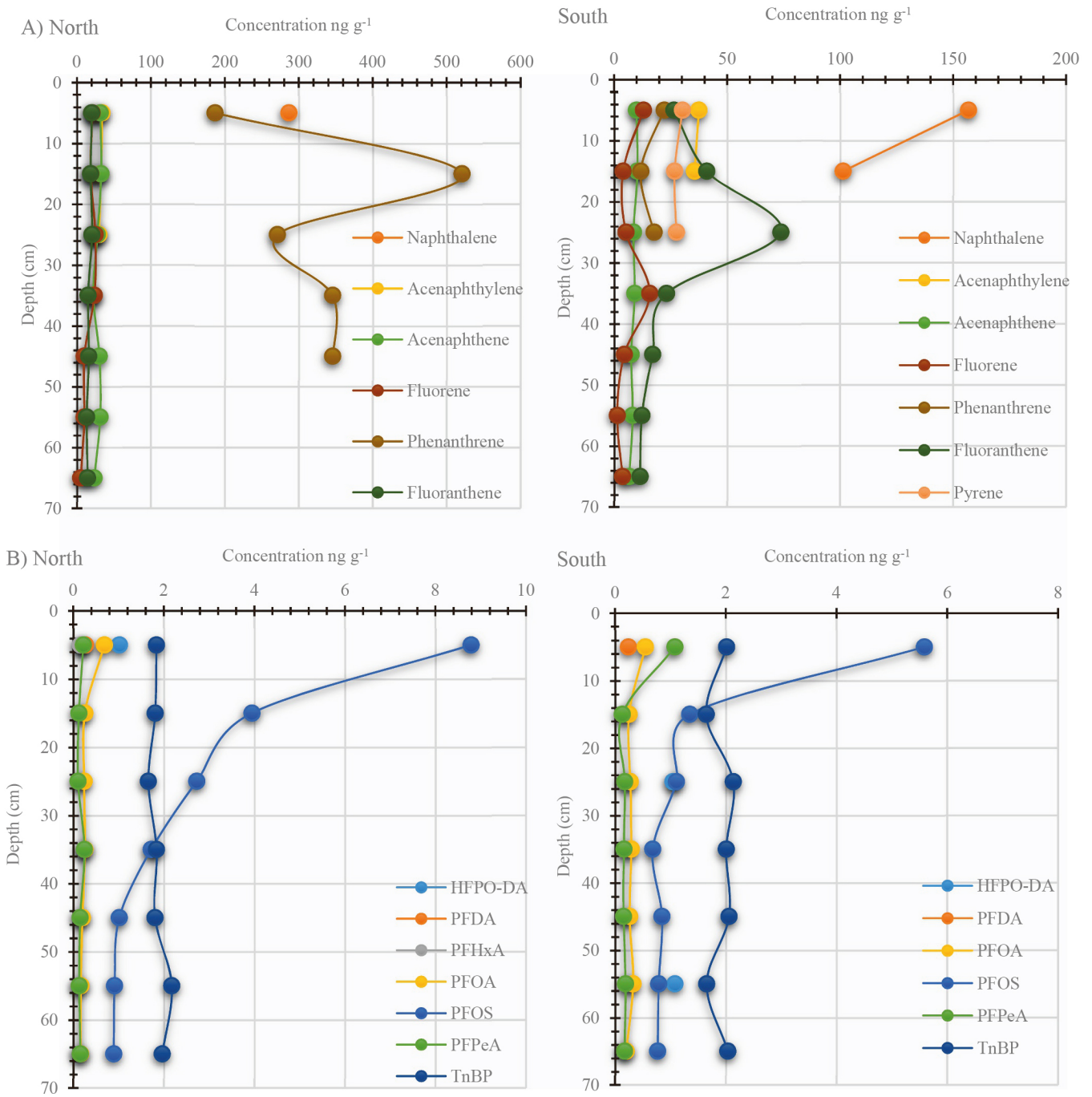


Fig. 4. Distribution of POPs along the sedimentary profile in the Northern and Southern of the lake. A) Distribution of PAHs B) Distribution of PFASs and OPFRs. Concentrations are expressed in ng g^{-1} (dw).

close to 1, indicating no significant enrichment in both North and South. The elevated human activities and pressures in the Northern land surrounding L'Albufera Lake are evident in sediment enrichment by As, Cd, Cr, Cu, Ni, Pb, and Zn. These findings align with the PLI and CD ('Data in Brief', Fig. 5), as well as with the results reported in the same lake by Hernández-Crespo and Martín et al. (2015).

The pH values of the lake sediment (between 8.02 and 8.26 for all depths in the sediment-water suspension 1:2.5) are slightly basic and IC concentration remains consistent throughout the vertical profile. This suggests that the displacement of heavy metals is unlikely [53]. Therefore, the vertical distribution of elements in the sediment column should accurately reflect the metal content during deposition events. In addition, in anaerobic conditions as those documented for L'Albura lake by Carmen Hernández-Crespo et al. [54], metal solubility is limited by sulfide formation, leading to the precipitation of metals as metallic sulfides. Electrical conductivity (EC) (sediment: water ratio 1:5) shows a slight increasing trend with depth, ranging between 1.16 dS m^{-1} (0–10 cm) and 1.55 dS m^{-1} (60–70 cm). The observed pattern aligns with that previously observed by Hernandez-Crespo et al. [32] in pore water. They found stronger salinity gradients at sampling sites located further East. Spearman correlation analysis indicates significant negative correlations between the total content of Co, La, Li, Mn, Ni, Pb, Rb, Tl, and V with calcium carbonate, while these elements show significant positive correlations with total sulfur content ('Data in Brief', **Table 5**). Organic matter, with a high metal sorption capacity, decreases with depth, making soil mineral constituents such as clay more important for

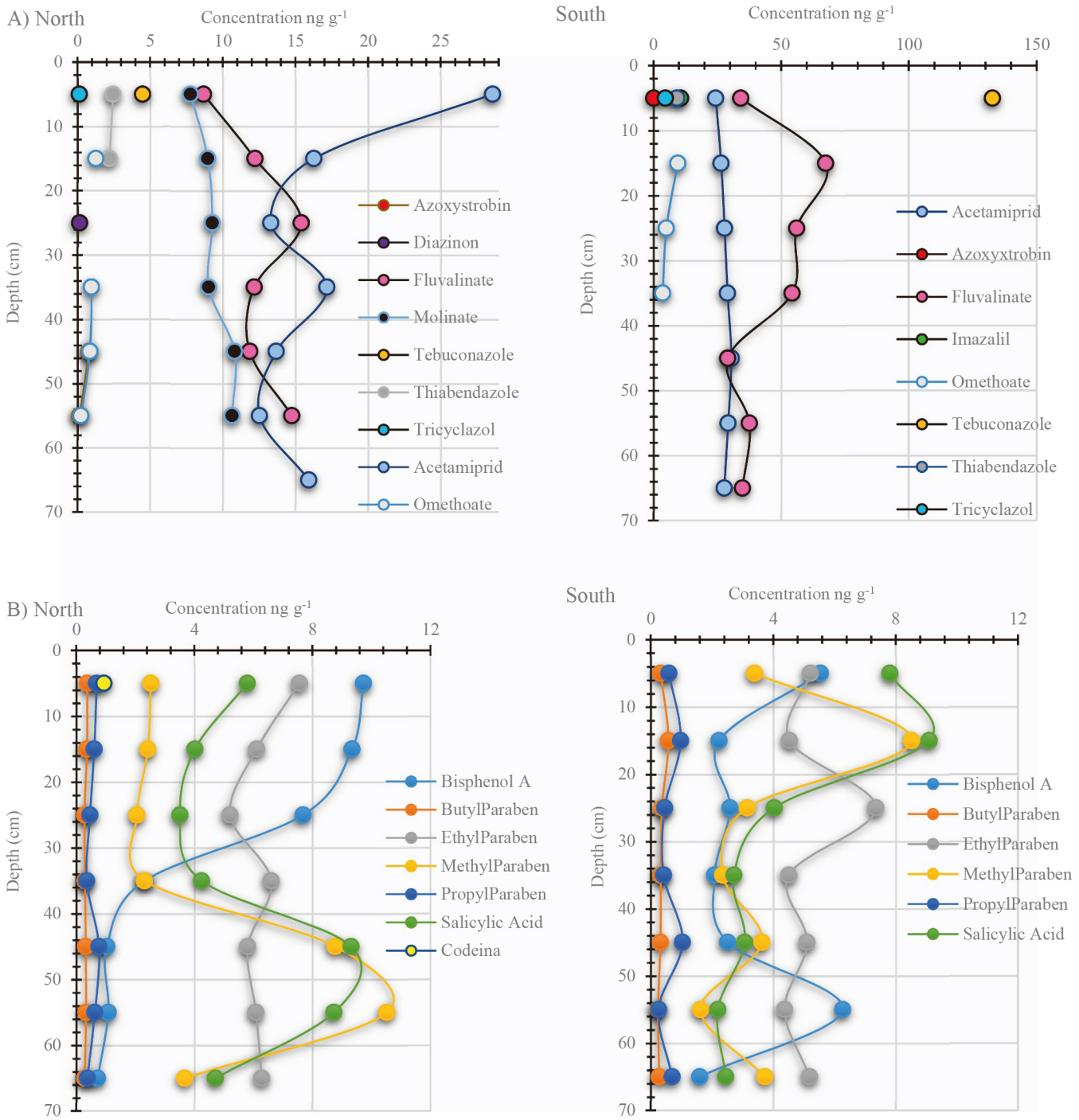


Fig. 5. Distribution of pesticides and PPCPs along the sedimentary profile in the Northern and Southern of the lake. A) Distribution of pesticides B) Distribution of PPCPs. Concentrations are expressed in ng g^{-1} (dw).

sorption. However, in our study, significant positive correlation coefficients were only observed for As and Cd with total C_{org} and for Co, La, Ti, and Tl with clay content ('Data in Brief', **Table 5**). It should be kept in mind that phenomena as the resuspension of sediments might have altered the original concentration of HMs, resulting in homogenization across different layers.

Most HMs contents are higher in the upper layer reflecting the increase of the industrial and agricultural practices in the area since the mid-20th century (even through sediments have been dated as 1474–1638 AD in the North and as 1222–1286 AD in the South). This could be attributed to the deposition of these sediments in the 1957 flood episode, which carried various solid materials of uncertain origin. However, as these sediments are in direct contact with the present-day contaminated water, the concentration of HMs reflects this situation. Most HMs show historical metal inputs and their more recent contributions since the mid-20th century due to accelerated industrial and urban development in the Valencia metropolitan area. However, the concentration of others Mo, Rb, Tl, and V seems to be higher in the deeper layer. This could be explained by the past brackish environment in L´Albufera lake that showed higher salinity in deepest layers that can solubilize these elements or also due to the increase of sulphides and anoxic conditions with depth that can scanvege them. Furthermore,

increase in the clay content (from 52 to 62%) between 30 to 50 cm depth ('Data in Brief') in the North is detected. This could be also related to the salinity increment (from 900 mg kg^{-1} at 10 cm to >2100 mg kg^{-1} in the deepest layer). This salt increment induces firstly, a clay dispersion process and subsequently, as clay fine particles in a salty media are unstable, their flocculation and movement into deeper layers [33]. This fact could have an effect on the re-mobilization of HMs in the sediment column and could explain the increment of the Extractable/Total ratio obtained, generally, at 40–50 cm depth for some elements like Cd, Cu, La, Mn, Mo, Pb, Rb, Tl and Zn.

Fig. 3 showed EDTA-extractable/total (E/T) ratio obtained for HMs in the sediment cores of the North (see the comparison North/South in Fig. S4). This ratio indicates the availability and relative mobility of metals in sediments. Given the common assumption that HMs from human activities are more reactive and potentially available to organisms than natural occurring fraction [55-57], it could be expected higher availability index in the uppermost sediment layers as a result of the point and diffuse pollution sources in this area. Results indicate clear trends in the availability of elements, with Cd (60%) ≈ Zn (59%) >Cu (45%) >Pb (33%) > followed by Mo (26%) and Si (24%) showing the highest availability in the shallowest sediment layers (0–10 cm) (Fig. 3 A). Moreover, the E/T ratio for Cd, Cu, Pb, and Zn decreases with depth, serving as a comparative index for HMs mobility and reflecting recent contamination history [58,59]. In deeper layers, HMs are less extractable because they are associated to the mineral sediment fraction, close to background concentrations. The depth profile evolution of Cd, Zn, and Cu suggests the influence of agricultural practices in the area [60], as these elements are found in phosphate fertilizers and pesticides [61]. The higher availability of Cd and Pb in the upper sediment layer could be an indicative of greater industrial activities, heavy traffic, hunting and fishing/tourist activities around L'Albufera Lake, especially in its Northern part. Conversely, the E/T ratio of Si increases in the deeper layers. One possible explanation is that the presence of diatoms (rich in Si) together with the high pH and the salinity that increases at the depth of the sediments favours its dissolution and its presence in an amorphous state (20 times more soluble in water than calcium) [62].

This is supported by the results because the EDTA-extractable Si and the Si E/T ratio show significant and positive Pearson correlation coefficients with electrical conductivity (EC1:5 0.857) and sodium concentrations (0.893), and these salinity parameters increased with depth.

As, Co, Mn, and Ni exhibit a moderate E/T ratio, ranging from 10% (Co and Mn) to 17% (As and Ni) in the top 20 cm at Northern points (Fig. 3**B**). These values decrease with depth, indicating reduced mobility. In the Southern area, these values are lower, ranging between 5% (As) and 12% (Co) in shallower sediment layers. On the other hand, a low E/T ratio ranging between 2% and 8% for La, Li, St, Tl, and V (Fig. 3**C**) is observed. Unlike other elements, La and Sr are less available in the North compared to the South. The lowest E/T ratios are obtained for Al, Cr, Fe, Rb, and Ti (Fig. 3**D**), with values less than or equal to 1%. Despite total Cr has an average concentration of 60 mg kg^{-1}, its availability, mobility, and potential risk to organisms are very low.

Biogenic organic material and silt- and clay-sized fractions, containing clay minerals, iron hydroxides, manganese oxides, and organic matter, play a key role in binding HMs in lake sediments through ion-exchange processes [46]. Spearman's test indicates positive correlations between C_{org}, TN, and the EDTA extractable fraction of As, Cd, Co, Cu, Ni, Pb, Sr, and Zn ("Data in Brief", **Table 5**). Partial correlation analysis, with C_{org} as a control variable, reveals the influence of this parameter on these metals, as indicated by the disappearance of significant coefficients.

3.4. Distribution of OCs in the core

The OCs analysed in this study have different characteristics (see **Table S1 – S5**) includes many molecules having low log Kow, high solubility of water and short half-lives. Thus, the compounds were divided into POPs including PAHs, OPFRs and PFASs and CECs consisted of pesticides and PPCPs. Thirty-one OCs were detected out of the 159 investigated. These include 10 pesticides, 7 PPCPs, 6 PFASs, 1 OPFRs, and 7 PAHs, with concentrations ranging from less than 0.11 ng g^{-1} to more than 520.0 ng g^{-1} d.w. considering both sampling stations. See results in Figs. 4–5.

The Σpesticides concentration in sediment cores showed a statistically significant difference ($p < 0.01$, M-W) between the North and South, with higher levels in the North. However, the analysis indicated that differences in ΣPFASs and ΣPPCPs concentrations between the North and South were not statistically significant ($p > 0.05$, K-W).

3.4.1. Distribution of POPs

Seven PAHs were detected in the sediment cores of L'Albufera Lake [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Acp), fluorene (Flr), phenanthrene (Phe), fluoranthene (Flt) and pyrene (Pyr)]. Nap was only detected in the upper sediment layers in the Northern area. Spatial differences in PAH presence may result from higher tourist traffic in the area due to the location of several small port that offer boat trips for the Lake. Concentration of PAHs in sediment cores ranged from 5.20 to 521.0 ng g^{-1} in the North and 1.40 to 156.8 ng g^{-1} (dw) in the South (Fig. 4A). PAHs tend to be adsorbed onto the particulate matter and stored in the sediments as they are persistent and hydrophobic [63,64]. In our study, 3–4- rings PAHs dominated the concentration of total PAHs in both sediment cores, with the presence of 2- rings PAHs (Nap). These findings align with results from Bai et al. [14], who observed a prevalence of 2–3-ring PAHs in remote Tibetan Plateau lake sediments. However, high molecular weight (5–6 rings) PAHs were not detected in either the North or South, whereas 4-ring PAHs were found in both locations.

Fig. 4A illustrated the distribution of PAHs along the sediment cores. In the North, vertical PAHs distribution showed a constant concentration along the core, with the exception of phenanthrene that was found at higher concentrations than the other PAHs up to a depth of 40 cm. The relative proximity of a traffic motorway in the North of study area may explain the presence of this PAH. In the South, the vertical distribution of PAHs indicated a consistent concentration along the core for acenaphthene and fluorene. However, fluoranthene exhibited a higher concentration between 20 and 30 cm. This PAH were already previously related to the rice straw burning [65].

PAHs concentrations in this study were compared with those in sediments from other lakes. Generally, they were higher than those reported previously for sediments from the Norwegian Arctic (highest concentration 140 ng g^{-1} (dw), excluding benz(a)anthracene) [66]. However, they were lower than concentrations in sediment cores from Lake Baxian [67] (highest concentration 8766 ng g^{-1} (dw)), western China lakes [68] (highest concentration 544.8 ng g^{-1} (dw)), and Qinghai Lake on the Tibetan Plateau [69] highest concentration 341.0 ng g^{-1} (dw). Nonetheless, the concentrations in this study were comparable to those reported in sediment from remote lakes across the Tibetan Plateau [70]. Other studies [71,72] suggested that PAHs concentration profiles in sediment cores exhibit increasing concentrations with decreasing depth, reflecting heightened human activities and industrial production.

To determine the origin of PAHs through the sediment core, various ratios have been proposed, including the Flu/(Flu+Pyr) ratio, the only one applicable in our study. A Flu/(Flu + Pyr) ratio between 0.4 and 0.5 indicates fossil fuel combustion, < 0.4 petrogens and > 0.5 grass, wood or coal combustion. According to this ratio ('Data in brief'), most of the PAHs would come from grass, wood or coal combustion except the first 10 cm of the South that would have as origin fossil fuel combustion. These results can be justified by the burning of rice straw, a common practice in the area that has recently been banned. The burning of straw in the 15000 ha of rice fields in the Albufera Natural Park emits, 1193.9 tons of very fine particles (PM2.5) annually and represents a toxicological risk for the surrounding population due to the emission of PAHs among other contaminants [65,73]. The high levels of fluorantene in the

upper 30 cm of sediment cores in the South could be an indicator of this practices since the highest level could be noted in the rice cultivation expansion period. In the sediment core taken at the North, the concentrations of C_{org} and TN were significantly correlated with PAHs concentration ($p < 0.05$), but no significant correlation was found with IC, clay, silt, sand and TS ($p > 0.05$) ('Data in Brief' **Table 6**). In the sediment core taken at the South, the concentrations of C_{org}, IC, TN and TS were significantly correlated with PAHs concentration ($p < 0.01$) ('Data in Brief' **Table 6**). Our results coincide with those reported by Bai et al. [14] which reported significantly correlated with PAHs concentration and TN. Significant correlations between PAHs and C_{org} indicate that C_{org} might be a key factor affecting the concentrations of PAHs in sediments due to their affinity for adsorption to C_{org} (high logKow values, **Table S5**). C_{org} exerts a large influence on the distribution, migration, and adsorption of PAHs in lake environments [74,75]. Bai et al. [14] reported that C_{org} in sediment cores from remote lakes from the Tibetan Plateau was significantly correlated with ∑PAHs ($p < 0.01$). However, the C_{org} concentration is almost constant in the first 40 cm, decrease progressively from 40 to 60 cm and then, in the deepest 10 cm increases again. This only correlates with the PAHs concentrations in the upper layers (see PAHs concentrations normalized to Corg in Figure S5).

In our study, acenaphthene concentration and silt are significantly correlated ($p < 0.05$) in the North. While acenaphthene concentration and C_{org}, IC, NT and TS are significantly correlated ($p < 0.01$) in the South. Furthermore, fluoranthene concentration and TN are significantly correlated ($p < 0.05$) in the South ('Data in Brief' **Table 6**).

Six PFASs were detected in the sediment cores of L'Albufera lake: GenX (HFPO-DA), perfluorodecanoic acid (PFDA), perfluorohexanoic acid (PFHxA), perfluorooctanoic acid (PFOA), sodium perfluorooctanesulfonate (PFOS) and perfluoropentanoic acid (PFPeA). PFHxA was not detected in the South while in the North it was detected in the top layer (0–10 cm). Gen X, PFDA and PFHxA were only detected in the upper layer of the sediment core in the North suggesting that the input of this PFASs was recent [76]. The concentration of PFASs in the sediment cores ranged from 0.11 to 8.79 ng g^{-1} in the North and 0.13 to 5.59 ng g^{-1} (dw) in the South. PFOS tends to show higher concentration than the other PFASs. Fig. 4B shows the concentration trends of PFASs in both sediment cores. Long-chain PFASs (C8–C12) such as PFOS, PFOA and PFDA were a proportion of 50% of total PFASs detected.

Studies have demonstrated the difference in partitioning behaviors between long-chain and short-chain PFASs in sediment particles and pore water in two sediment cores from Tokyo Bay, Japan [77]. Also, Ahrens et al. [78] suggested that the water solubility of PFASs decreased with increasing chain length. Short-chain PFASs diffused via pore water within the sediment column instead of being retained in sediment particles. Short-chain PFASs are more hydrophilic than long-chain PFASs [79]. Expectedly, shorter-chain PFASs were anticipated to be more prevalent in the water, while longer-chain ones would likely be more adsorbed to the sediment [80]. Christensen et al. [81] suggested stronger sorption of PFOS and PFDA to sediment, while PFHxS and PFBS showed intermediate or lower affinities.

PFOA was detected in sediment cores, showing consistent vertical concentration profiles ranging from 0.16 to 0.69 ng g^{-1} in the North and 0.20 to 0.55 ng g^{-1} (dw) in the South. Based on its log K_{oc} values (Table S3), it is anticipated to exhibit moderate mobility. PFOS was found at higher concentrations in upper sediment layers of both cores, with concentrations progressively decreasing in the deeper layers. Yeung et al. [13] also detected PFOS in all layers of the sediment core collected in 2006 in Lake Ontario. Mussabek et al. [82] also indicated that the concentration of PFOS was higher in the upper sediment layer decreasing progressively in the deeper sediment layers. HFPO-DA was also found in the surface layer of the cores taken at the North of the lake. This is explainable because this compound has been also recently introduced as substitute of PFOA and its input must be recent. However, in the core located at the South of the lake HFPO-DA appears at 20–30 cm and 50–60 cm depths. Al Zbedy et al. [83] already noted that certain HFPO-DA ions may leach down to lower soil depths with excessive water specially if they have a basic character. There is still little information to explain this behavior.

Our results indicate a tendency for PFASs concentrations to increase with higher C_{org} content, though not statistically significant. In surface layers where the total C_{org} content is higher, the concentrations of PFASs are also higher, specially for PFOS (PFASs concentrations normalized to Corg are shown in Fig. S5). This is consistent with Ahrens et al. [84] who showed a lower sorption capacity for sandy sediment with a low C_{org} content, whereas higher sorption capacities are found for muddy sediments with higher C_{org} content. Then, apparently, the increase of PFASs concentrations in the upper part of the core could be mainly due to a change in C_{org} content in these layers. PFOA and PFOS concentration and C_{org} content as well as PFOS concentration and TN content are significantly correlated (($p < 0.05$) and ($p < 0.01$) respectively) in the North, while in the South no significant differences were found ('Data in Brief' Table 6). The amount of C_{org} has been reported as a key factor in the sorption of PFASs to sediments [85-88].

On the other hand, only tri-n-propylphosphate (TPP) and tri-n-butyl phosphate (TnBP) were found in both sediment cores. TPP was only detected because its concentration was below the limit of quantification. This result agrees with the study of Carr et al. [89] who never detected TPP above the MDLs (0.222 and 0.060 ng g^{-1} (dw), respectively) in a sediment core from Cienfuegos Bay, Cuba, from 1990 to 2015. The concentration of OPFRs in the sediment cores ranged from 1.66 to 2.18 ng g^{-1} in the North and 1.65 to 2.14 ng g^{-1} (dw) in the South. The concentrations and vertical distributions of OPFRs in the sediment cores are shown in Fig. 4B. The apparent sedimentary concentration records of TnBP may be easily influenced by its migration downward within the sediment profile via diffusion in pore water [90]. It has a lower K_{ow} and K_{oc} than others (**Table S4**) so it is more "mobile" than other OPFRs. Other study [91] reported high concentrations of TnBP in the surface layer (0–20 cm) of a Lake sediment core.

The results shown that feasibility of sediment cores for assessing historical contamination archives is strongly depending on characters and dynamics of sediment sampling site/area. Furthermore, in this study we study mostly emerging POPs, whereas the legacy ones (e.g., legacy POPs such as PCBs) could shown a simpler and clearer trend. However, previously, Peris et al. [23] analyzed organochlorine pesticides (banned in Spain since 1978) in surface sediment of the lake. These results of Peris et al. [23] supported the difficulty to establish historical marks due to the area dynamics because small amounts of DDT mostly as their main degradation products DDE and DDD were reported indicating that DDT contamination is old but distributed in the most surface sediments. Furthermore, several sourrounding ravines and ditches are also contaminated by these coumpounds becoming a source in the episodes of heavy rain.

3.4.2. Distribution of CECs

Ten pesticides were found in the L'Albufera Lake's sediment cores: acetamiprid, azoxystrobin, diazinon, fluvalinate, imazalil, molinate, omethoate, tebuconazole, thiabendazole and tricyclazol. Imazalil was only detected in the South's top layer (0–10 cm), while diazinon and molinate were found only in the North. Concentrations ranged from 0.14 to 28.6 ng g^{-1} in the North and 0.18 to 132.8 ng g^{-1} (dw) in the South, with acetamiprid at the highest concentrations in the North and tebuconazole and fluvalinate in the South. Fig. 5A shows the pesticides distribution for the Northern and Southern part of the lake. Pesticides tend to be found at higher levels than other OCs in both sites. These results are similar to those reported by Soriano et al. [24] who also found higher concentration of pesticides, in the North and South of the lake, compared to the other of CECs studied. The main origin of these contaminants is their use in agriculture, with their primary pathways for entering the lake water being runoff and atmospheric deposition, as previously documented by Calvo et al. [21] and Pascual Aguilar et al. [92].

The vertical distribution of pesticides followed three types of patterns: (i) distributed vertically through the core at different concentrations (molinate, fluvalinate and acetamiprid); (ii) a trend to appear in the depth sediment layers and not in the upper one (omethoate); (iii) pesticides only detected in the most surface sediment layers (azoxytrobin, imazalil, tebuconazole, thiablendazole, and tricyclazol). Assuming equilibrium conditions, the distribution of CECs between sediments and pore water depends on the chemical hydrophobicity and its octanol-water partitioning coefficient (K_{ow}), the C_{org} adsorption coefficient (K_{oc}) and the organic content of the sediment particles (f_{oc}), but is independent of chemical concentration [93]. CECs with low log Kow and log Koc values exhibits low sorption affinity to organic-rich sediment particles and is usually more abundant in water [94]. Individual levels of certain pesticides (acetamiprid, molinate and fluvalinate) tend to move in-depth in both sediment cores. Molinate was only detected in the Northern part of the lake, where its highest concentration was 10.8 ng g^{-1} that appear at the lowest depth where it was detected (40–50 cm). Based on the values of partitioning coefficient, molinate is expected to show moderate sorption and mobility in the water/sediment system. In our study, molinate concentration and IC, TN and TS content are significantly correlated ($p < 0.05$) in the North ('Data in Brief', **Table 6**). For these contaminants, the most probable route to river sediments is massive surface runoff or atmospheric deposition [95,96]. Acetamiprid was detected in all core sediment layers in the Northern and Southern parts of the lake with a maximum concentration of 28.6 ng g^{-1} and 30.5 ng g^{-1} (dw), respectively. The highest concentration was found in the upper layer of the core in the North (0–10 cm) and in the third layer (20–30 cm) in the South. The presence of highest levels in the surface layers of the sediment in the North could be related to a recent application instead the concentration increasing in-depth could due to the lack of recent inputs. There is very little information on the distribution of pesticides in sediment cores. However, Matić Bujagić et al. [95] reported a similar behavior of a related pesticide (imidacloprid) that was detected in the sediment core, at concentrations up to 3.5 ng g^{-1}, reached at 60–65 cm depth. Acetamiprid concentration and TS concent are significant correlated ($p < 0.05$) also in the North.

Omethoate appear in-depth sediment layers from 10 cm up to 50 cm. The behavior of this pesticide is difficult to explain due to lack of data. It is an insecticide but it can also appear as a degradation product of dimethoate that was banned in 2020. The only fact that supports our finding is a press new denouncing that the Valencia City Council mistakenly used dimethoate to treat trees in different locations of the city of Valencia at the end of 2020 [97]. Dimethoate could arrive to the Lake through atmospheric deposition and degrade to highly mobile in sediments omethoate. In plants and in the environment, omethoate occurs as a break down product within a few days after dimethoate application.

Azoxystrobin, tebuconazole, thiabendazole, imazalil and tricyclazol detected only in the top layers of both sediment cores are classified as only moderate, slightly and a bit mobile (**Table S1**). Tebuconazole (log K_{ow} 2.7) was detected only in the top of both sediment cores with an average concentration of 4.5 and 138.8 ng g^{-1} (dw) in the Northern and Southern part of the lake, respectively. The high concentration of tebuconazole in the South can be related to the crops, as this pesticide is extensively used in the last steps of rice cultivation. Tricyclazol exhibits low sorption affinity to organic-rich sediment particles ($\log K_{ow} = 1.4$) and shows a moderate mobility. An experimental field study about rice cultivation [98] reported that tricyclazol is not really persistent in the water of rice fields possibly due to degradation or volatilization processes. Out of all detected pesticides, imazalil displays the highest Koc indicating almost complete immobilization, even though the log Kow value of 2.56 points to moderate sorption to sediments. Imazalil was only found in the South with the concentration of 10.7 ng g^{-1} (dw) in the top layer (0–10 cm). Other studies also report low concentrations of imazalil in shallow lakes' or River sediments [95,92,99].

Seven pharmaceuticals were detected in the sediment cores of L'Albufera Lake: Bisphenol A, butylparaben ethylparaben, methylparaben, propylparaben, salicylic acid and codeine. The concentration of PPCPs in the sediment cores ranged from 0.28 to 10.5 ng g^{-1} in the North and 0.24 to 9.10 ng g^{-1} (dw) in the South (Fig. 5B). The origin of these compounds could be the treated waters of several wastewater treatment plants (WWTPs) that are release to the lake to keep the ecological flow as well as the release of non-treated water of small settlements and isolated houses. Detected PPCPs displayed irregular trend in the vertical distribution throughout both sediment cores. More than 50% of the PPCPs detected belong to the paraben chemical class indicating that parabens might be the top contaminants in the studied area because of their widespread use in preservatives of pharmaceutical, personal care, and food products [100]. Codeine –the only pharmaceutical detected– was only in the upper layer of the sediment core in the North suggesting its recent input.

The concentrations of bisphenol A in the sediment cores ranged from 0.73 to 9.74 ng g^{-1} in the North and 1.60 to 6.27 ng g^{-1} (dw) in the South. In 2007, the U.S. Environmental Protection Agency (USEPA) labelled bisphenol A as a priority contaminant because in the past decades, some studies have confirmed their potentially adverse influences on human and animals with mutagenic and carcinogenic effects [101]. Bisphenol A does not hydrolyse in water because of its chemical structure and more than 50% of this compound get adsorbed in sediments [101]. Furthermore, it has a high sorption affinity in sediments and limited mobility in the water sediment/system. In our study, bisphenol A concentration is significantly correlated to TN ($p < 0.01$) and sand ($p < 0.05$) content in the North.

Ethylparaben, methylparaben and salicylic acid showed moderate/high sorption affinity for the sediment, and butylparaben and propylparaben showed high sorption affinity and limited mobility. Parabens displayed similar trend in the vertical distribution throughout in both sediment cores. Ethyl, propyl and buthylparaben showed an almost constant concentration through the sediment cores both in North and South. Ethyl paraben concentration are significantly correlated to TS ($p < 0.05$) content in the North. Instead, methylparaben and salycilic acid levels are higher at greater depths in the North. High concentrations of these parabens in deeper anoxic sediments can also be attributed to the lack of anaerobic degradability leading to persistence under anoxic conditions [102]. Coversely, in the Southern sediments, the highest parabens concentrations are found in the shallowest layers (up to 30 cm). Salicylic acid concentration is significantly correlated to TN in the South ($p < 0.05$). Given the lack of data, it is difficult to draw conclusions to explain this behavior. Methyl-, ethyl-, propyl-, and butyl-paraben are now on the EU list of potential endocrine disruptors [103]. Some studies have reported paraben concentrations in surface water, surface sediment and in wastewater treatment plants [104,105]. However, the presence of these compounds (ethylparaben and methylparaben) in sediment has been widely reported in other study carried out in the same area [25], suggesting that ionic retention in clays could be involved in the retention and accumulation of these compounds. The top layer of the studied sediment cores can be compared with the results described by Wu et al. [106], who analysed surface sediments collected from Chao Lake, China. Their results showed that methylparaben and bisphenol A were predominant among the selected PPCPs, being found in high concentrations of 5.20 and 4.82 ng g^{-1} (dw), respectively.

Codeine was detected only in the Northern part of the lake with a mean concentration of 0.95 ng g^{-1} (dw) in the top layer. When this compound is in the sediment, it has a low mobility due to its Koc value. Furthermore, codeine is affected by light and, therefore, may be susceptible to direct photolysis by sunlight. CECs distribution in sediments can be strongly influenced by the amount of organic matter being C_{org} an important medium for the adsorption, storage, and transport of CECs [14]. In this study, no significant correlations were found between C_{org} and the different CECs. While salicylic acid concentration and TN content are significantly correlated ($p < 0.05$) in the South.

3.4.3. Non-target analysis (NTA)

With the view of revealing non-target candidates out of the scope of the method used in this study, a non-target approach was developed with the aid of Compound Discoverer 3.2 (Thermo®). The important advantage that derives from the possibilities of NTA, is the identification of compounds such as metabolites of substances for which reference standards are scarce or non-existent. Data was processed using Compound Discoverer with one single workflow. ChemSpider® database search provided more hits which complements mzCloud® search. Built-in FISh in Custom Explanations was used to verify hits from ChemSpider® against MS^2 data. The selected workflow conducts untargeted environmental research. It performs retention time (RT) alignment, unknown compound detection, and compound grouping across all samples. This workflow also predicts elemental compositions for all compounds and hides chemical background (using blank samples). It identifies compounds using mzCloud® (ddMS^2 and/or DIA), ChemSpider® (exact mass or formula) and local database searches against Mass Lists (exact mass with or without RT). Compound Discoverer® produced high number of results for the raw files so they need to be filtered (**Figure S2**). During the process, blank samples were set in order to assess contamination / interferences present in the matrix or even in the instrument. The list of compounds detected with NTA are included in Table 2.

Dimethyl sebacate, galaxolidone, oleamide, and Polyethylene glycols (PEG n6) were detected in all samples. PEG n6 is a polymer and it is used in soaps and detergents, in printing as well as in the wood preservation industry and others that produce textiles, ceramics, plastics, glass, resins, paper and rubber [107]. Galaxolidone was also detected in 100% of the samples. It is an oxidation transformation product of galaxolide and it is added to personal care products [108]. Backe [109] identified galaxolidone with mzCloud® database in grab samples. 19-Norandrostenedione was only detected in surface layers of both cores and it is an anabolic androgenic steroid with improving performance-enhancing effects, but it can also be produced in situ by demethylation of other abundant steroids or from endogenous production [110].

4. Conclusions

Without wishing to dispute its potential efficacy, the distribution of contaminants in depth in the Albufera lake sediment cannot be related to the age of the C_{org} in the sediments. First, because the sediment dating process presents many uncertainties, especially due to the possible terrigenous origin of the sediments and their entrainment into the lake by torrential rains, and also to the lack of knowledge on the sediment resuspension processes that take place in this lake. This are two pillar that requires further analysis to establish potential reliable cases where sediments can be used as historical records. As a result, a direct interpretation of the sedimentary occurrence of contaminants in L'Albufera Lake into a historical use is somewhat speculative. Then, the study of the Anthropocene contamination on the environment through the sedimentation needs improved protocols to determine those cases when it could be reliable and a direct relation can be established. In this study, the in-depth related distribution of contaminants did not show a clear trend. Clearly, sediments are contaminanted since 10 pesticides, 7 PPCPs, 6 PFASs, 1 OPFRs, and 7 PAHs were detected at concentrations ranging from less than 0.11 ng g^{-1} to more than 520.0 ng g^{-1} (dw). Furthermore, HMs and metalloids were detected through the sediment core. Some of them showed an enrichment to the surface layers and others to the deepest layers. The results obtained established significant correlations between OCs concentrations and C_{org} indicate that C_{org} might be a key factor affecting the concentrations of OCs found in depth, even through the concentrations of the contaminants normalized to the Corg content do not show a different pattern. These data in combination with other physical-chemical characteristics of the sediments at each particular core depth, such as IC, TN and TS, can help to better understand the vertical deposition, transport, and degradation of organic contaminants. However, to develop a direct relationship between sediment age and contaminant concentrations, and thus elucidate the historical trend of contamination based on dated sediment core could be very difficult. There is little information on the concentration of organic contaminants, especially emerging ones in sediments, so the data obtained in the present study provides important information on the distribution and dynamics of contaminants in sediments and helps to corroborate the data presented in previous studies.

Environmental implication

Sediment cores are often considered historical contamination archives, providing insights into the rise of anthropogenic impact. However, our study in a Mediterranean coastal wetland reveals that contaminant distribution in sediments, at least in this study case, is influenced more by the contaminant's physical and chemical properties, as well as events like extreme sediment deposition and resuspension. This makes it nearly impossible to establish a direct relationship between sediment age and contaminant concentration. However, interesting information about distribution of contaminants can be obtained studying "in depth" the sediment cores.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 2
Peak area count of each compound using non-target analysis from the analysis of core samples from L'Albufera Lake.

Sampling Point	Depth (cm)	2'-Deoxyadenosine	Adenosine	Dimethyl sebacate	Dinoseb	Galaxolidone	Oleamide	PEG n6	19-Norandrostenedione	Nifenazone
North	0-10	$4.98{\cdot}10^{6}$	$2.32{\cdot}10^{6}$	$3.59{\cdot}10^{6}$	$4.54{\cdot}10^{7}$	$2.15{\cdot}10^{5}$	$1.97{\cdot}10^{6}$	$1.21{\cdot}10^{6}$	$8.09{\cdot}10^{4}$	$1.58{\cdot}10^{5}$
	10-20	$2.13{\cdot}10^{5}$	$4.69{\cdot}10^{5}$	$3.26{\cdot}10^{5}$		$1.26{\cdot}10^{4}$	$9.98{\cdot}10^{5}$	$3.59{\cdot}10^{5}$	$4.78{\cdot}10^{3}$	
	20-30	$1.78{\cdot}10^{5}$	$6.54{\cdot}10^{5}$	$1.96{\cdot}10^{5}$		$8.49{\cdot}10^{5}$	$1.03{\cdot}10^{6}$	$1.07{\cdot}10^{4}$	$7.98{\cdot}10^{4}$	
	30-40	$9.98{\cdot}10^{4}$	$9.63{\cdot}10^{4}$	$4.21{\cdot}10^{3}$		$7.89{\cdot}10^{3}$	$5.65{\cdot}10^{5}$	$3.47{\cdot}10^{4}$		
	40-50	$1.08{\cdot}10^{5}$	$1.32{\cdot}10^{5}$	$7.89{\cdot}10^{3}$		$2.36{\cdot}10^{3}$	$1.01{\cdot}10^{4}$	$8.97{\cdot}10^{3}$		
	50-60	$8.78{\cdot}10^{4}$	$4.78{\cdot}10^{4}$	$4.69{\cdot}10^{1}$		$4.26{\cdot}10^{2}$	$2.32{\cdot}10^{3}$	$6.87{\cdot}10^{3}$		
	60-70		$3.24{\cdot}10^{3}$	$1.23{\cdot}10^{2}$		$3.21{\cdot}10^{2}$	$1.59{\cdot}10^{4}$	$9.91{\cdot}10^{2}$		
South	0-10	$1.47{\cdot}10^{6}$	$8.12{\cdot}10^{6}$	$1.02{\cdot}10^{7}$	$3.65{\cdot}10^{6}$	$7.48{\cdot}10^{7}$	$9.98{\cdot}10^{6}$	$5.45{\cdot}10^{5}$	$2.56{\cdot}10^{5}$	
	10-20	$2.36{\cdot}10^{5}$	$3.69{\cdot}10^{6}$	$2.58{\cdot}10^{6}$		$2.54{\cdot}10^{6}$	$6.78{\cdot}10^{5}$	$3.89{\cdot}10^{4}$		
	20-30	$1.18{\cdot}10^{5}$	$1.54{\cdot}10^{5}$	$2.13{\cdot}10^{5}$		$7.31{\cdot}10^{5}$	$5.47{\cdot}10^{5}$	$1.14{\cdot}10^{5}$		
	30-40	$8.96{\cdot}10^{4}$		$4.87{\cdot}10^{6}$		$4.59{\cdot}10^{4}$	$8.39{\cdot}10^{3}$	$1.03{\cdot}10^{5}$		
	40-50		$2.31{\cdot}10^{2}$	$3.65{\cdot}10^{4}$		$7.89{\cdot}10^{3}$	$7.98{\cdot}10^{4}$	$9.98{\cdot}10^{4}$		
	50-60		$2.01{\cdot}10^{2}$	$2.34{\cdot}10^{3}$		$3.47{\cdot}10^{3}$	$4.48{\cdot}10^{3}$	$5.73{\cdot}10^{3}$		
	60-70			$1.32{\cdot}10^{3}$		$1.26{\cdot}10^{4}$	$1.23{\cdot}10^{2}$	$8.41{\cdot}10^{2}$		

Data availability

The authors will publish research data in the journal Data in Brief.

Acknowlegment

This work has been supported by the Grant CIPROM/2021/032 funded by the Conselleria d'Educació, Universitats i Ocupació of the Generalitat Valenciana. Y. Soriano acknowledges her pre-doctoral contract by the grant PRE2019–089042 funded by MCIN/AEI/ 10.13039/501100011033 and by "ESF Investing in your future". The instrumental used in this study were financed by the project IDFEDER-2021–083 "X-ray of pollution and the effects of the anthropocene/climate change binomial (X pollutants)" action co-financed by the EU through the operational program of the European Regional Development Fund (ERDF) of the Valencian Community 2014–2020. We also thank the director and the staff of the Office of the Natural Park of L'Albufera for their continuous advice and support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.134168.

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ARTICLE 04

SUPPLEMENTARY MATERIAL:

Exploring organic and inorganic contaminant histories in sediment cores across the anthropocene: accounting for site/area dependent factors

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Compounds	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)	MoA
Acetamiprid	135410-20-7	$C_{10}H_{11}ClN_4$	222.67	2950 (high)	0.8 (low)	132-267 (mobile moderate)	0.7	0.94	3	4.7	Neuroactive
Acetochlor	34256-82-1	$C_{14}H_{20}ClNO_2$	268.77	282 (moderate)	4.24 (high)	156 (moderately mobile)	n/a	1.67	20	40.5	Mitosis, Cell cycle
Alachlor	15972-60-8	$C_{14}H_{20}ClNO_2$	269.77	240 (moderate)	3.09 (high)	335 (moderately mobile)	0.6	0.80	39	-	Mitosis, Cell cycle
Acrinathrin (adduct)	101007-06-1	$C_{26}H_{21}F_6NO_5$	541.44	0.0022 (low)	6.3 (high)	48231 (non mobile)	n/a	-0.92	538	6.5	Unknown
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.7	35 (low)	2.70 (moderate)	100 (moderately mobile)	1.7	2.57	4.3	75	Photosynthesis inhibition
Atrazine-desethyl	6190-65-4	$C_6H_{10}ClN_5$	187.63	2700 (high)	1.51 (low)	110 (moderately mobile)	-	3.24	-	-	Unknown
Atrazine-desisopropyl	1007-28-9	$C_5H_8ClN_5$	173.60	980 (high)	1.15 (low)	130 (moderately mobile)	-	-	-	-	Unknown
Azinphos-ethyl	2642-71-9	$C_{12}H_{16}N_3O_3PS_2$	345.4	4.5 (low)	3.18 (high)	1500 (slightly mobile)	n/a	1.40	101	50	Unknown
Azinphos-methyl	86-50-0	$C_{10}PN_3H_{12}S_2O_3$	317.3	28 (low)	2.96 (moderate)	1112 (slightly mobile)	5.0	1.42	40	10	Unknown
Azoxystrobin	131860-33-8	$C_{22}H_{17}N_3O_5$	403.4	6.7 (low)	2.5 (low)	207 to 594 (slightly mobile)	n/a	3.10	Low risk	6.1	Respiration inhibition
Bensulfuron methyl	83055-99-6	$C_{16}H_{18}N_4O_7S$	410.4	67 (moderate)	0.79 (low)	409 (mobile moderate)	5.2	0.91	1.6	18.5	Unknown
Bentazone	25057-89-0	$C_{10}H_{12}N_2O_3S_1$	240.3	7112 (high)	-0.46 (low)	55.3 (mobile)	3.5	1.95	21	80	Photosynthesis inhibition
Bifenthrin	82657-04-3	$C_{23}H_{22}ClF_3O_2$	422.88	0.001 (low)	6.6 (high)	236610 (non mobile)	n/a	-2.66	1703	8	Unknown
Buprofezin	69327-76-0	$C_{16}H_{23}N_3OS$	305.44	0.637 (low)	4.5 (high)	5363 (non mobile)	n/a	1.21	509	16.8	Chitin biosynthesis inhibition

Compounds	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)	MoA
Carbendazim	10605-21-7	$C_9H_9N_3O_2$	191.21	8 (low)	1.48 (low)	225 (mobile moderate)	4.2	2.21	25	7.9	Mitosis, Cell cycle
Carbofuran	1563-66-2	$C_{12}H_{15}NO_3$	221.26	322 (moderate)	1.8 (low)	86.5 (moderately mobile)	n/a	2.36	12	6.1	Neuroactive
Carbofuran-3-hydroxy	16655-82-6	$C_{12}H_{15}NO_4$	237.25	6207 (high)	1.45 (low)	682 (slightly mobile)	-	-0.53	-	-	Unknown
Chlorfenvinphos	470-90-6	$C_{12}H_{14}Cl_3O_4P$	359.6	145 (moderate)	3.80 (high)	680 (slightly mobile)	n/a	1.72	250	7	Neuroactive
Chlorpyrifos	5598-13-0	$C_9H_{11}Cl_3NO_3PS$	350.6	1.05 (low)	4.70 (high)	5509 (non mobile)	n/a	0.58	1374	5	Neuroactive
Chlothianidin	210880-92-5	$C_6N_5H_8SO_2Cl$	249.8	340 (moderate)	0.90 (low)	123 (moderately mobile)	11.1	3.74	3ξ	40.3	Unknown
Coumaphos	56-72-4	$C_{14}H_{16}ClO_5PS$	362.8	1.5 (low)	4.13 (high)	-	-	-	-	-	Unknown
Cyhalofop-butyl	122008-85-9	$C_{16}H_{12}FNO_4$	357.38	0.44 (Low)	3.32 (high)	5247 (non mobile)	n/a	-0.69	7.5	0.15	Unknown
Cyhalothrin (adduct)	91465-08-6	$C_{23}H_{19}ClF_3NO_3$	449.85	0.005 (low)	5.5 (high)	283707 (non mobile)	n/a	-2.09	4982	0.24	Unknown
Diazinon	333-41-5	$C_{12}H_{21}N_2O_3PS$	304.35	60 (moderate)	3.69 (high)	609 (some mobile)	2.6	1.51	500	4.3	Neuroactive
Dichlofenthion	97-17-6	$C_{10}H_{13}Cl_2O_3PS$	315.15	0.245 (low)	5.14 (high)	18 (mobile)	-	2.14	3000	-	Unknown
Difenoconazole	119446-68-3	$C_{19}H_{17}Cl_2N_3O_3$	406.26	15.0 (low)	4.36 (high)	3760 (slightly mobile)	1.1	0.83	330	3	Sterol biosynthesis inhibition
Dimethoate	60-51-5	$C_5H_{12}NO_3PS_2$	229.3	25900 (high)	0.75 (low)	2 (mobile)	n/a	2.18	8	12.6	Neuroactive
Diuron	330-54-1	$C_9H_{10}Cl_2N_2O$	233.09	25 (low)	2.87 (moderate)	813 (bit mobile)	n/a	2.65	9.45	8.8	Photosynthesis inhibition
DMA	95-68-1	$C_8H_{11}N$	121.18	-	-	-	4.9	-	-	-	Unknown
DMF	68-12-2	C_3H_7NO	73.09	-	-	-	-0.3	-	-	-	Unknown
DMPF	33089-74-6	$C_{10}H_{14}N_2$	162.23	-	-	-	-	-	-	-	Unknown
Ethion	563-12-2	$C_9H_{22}O_4P_2S_4$	384.48	2 (low)	5.07 (high)	10000 (Not mobile)	-	-	586	-	Neuroactive
Etofenprox	80844-07-1	$C_{25}H_{28}O_3$	376.49	0.0225(low)	6.9 (high)	17757	n/a	-0.30	-	5.7	Unknown

Compounds	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)	MoA
Fenitrothion	122-14-5	$C_9H_{12}NO_5PS$	277.2	19 (low)	3.32 (high)	2000 (slightly mobile)	n/a	0.48	29	1.1	Neuroactive
Fenthion	55-38-9	$C_{10}H_{15}O_3PS_2$	278.3	4.2 (low)	4.84 (high)	1500 (slightly mobile)	n/a	1.26	154	22	Neuroactive
Fenthion-sulfone	3761-42-0	$C_{10}H_{15}O_5PS_2$	310.3[β]	190.4[β]	2.05[β] (low)	235 (moderately mobile)	n/a	-	-	n/a	Unknown
Fenthion-sulfoxide	3761-41-9	$C_{10}H_{15}O_4PS_2$	294.3[β]	3.72[β] (low)	1.92[β] (low)	183 (moderately mobile)	n/a	-	-	n/a	Neuroactive
Fipronil	120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$	437.15	3.78 (low)	3.75 (high)	727 (slightly mobile)	n/a	2.06	321	54	Neuroactive
Flumethrin	69770-45-2	$C_{28}H_{22}Cl_2F_NO_3$	509.09	-	-	-	-	-	-	-	Unknown
Fluvalinate	69409-94-5	$C_{26}H_{22}ClF_3N_2O_3$	502.91	0.002 (low)	3.85 (high)	-	-	-	-	-	Unknown
Hexythiazox	78587-05-0	$C_{17}H_{21}ClN_2O_2S$	352.88	0.1 (low)	2.67 (low)	9455 (non mobile)	n/a	0.03	1100	11.5	Unknown
Imazalil	35554-44-0	$C_{14}H_{14}Cl_2N_2O$	297.18	184 (moderate)	2.56 (low)	4753 (Non mobile)	6.5	0.26	56.3	7.8	Sterol biosynthesis inhibition
Imazamox	114311-32-9	$C_{15}H_{19}N_3O_4$	305.34	626000 (high)	5.36 (high)	11.6 (Very mobile)	2.3	3.59	0.1	132	Protein biosynthesis inhibition
Imidacloprid	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	610 (high)	0.57 (low)	225 (mobile moderate)	n/a	3.69	0.61	30	Neuroactive
Isoproturon	34123-59-6	$C_{12}H_{18}N_2O$	206.3	70.2 (moderate)	2.5 (low)	251[β]	n/a	2.61	177	40	Photosynthesis inhibition
Malathion	121-75-5	$C_{10}H_{19}O_6PS_2$	330.4	148 (moderate)	2.75 (moderate)	1800 (Slightly mobile)	n/a	0.00	103	0.4	Neuroactive
MCPA	94-74-6	$C_9H_9ClO_3$	200.62	29390 (very high)	-0.81 (low)	74 (mobile)	3.7	2.98	1	13.5	Synthetic Auxin
Methiocarb	2032-65-7	$C_{11}H_{15}NO_2S$	225.3	27 (low)	3.18 (high)	660 (slightly mobile)	n/a	1.82	75	1.6	Neuroactive
Metolachlor	51218-45-2	$C_{15}H_{22}ClNO_2$	283.8	530 (high)	3.4 (high)	120 (moderately mobile)	n/a	2.36	68.8	88	Mitosis, Cell cycle
Molinate	2212-67-1	$C_9H_{17}NOS$	187.3	1100 (high)	2.86 (moderate)	190 (moderately mobile)	n/a	1.89	72	4	Lipid metabolism

Compounds	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)	MoA
Omethoate	1113-02-6	$C_5H_{12}NO_4PS$	213.2	500000 (high)	-0.9 (low)	41.3 (mobile)	-	2.73	75	-	Neuroactive
Parathion-ethyl	56-38-2	$C_{10}H_{14}NO_5PS$	291.27	12.4 (low)	3.83 (high)	7660 (non mobile)	-	1.52	40	3.5	Unknown
Parathion-methyl	298-00-0	$C_8H_{10}NO_5PS$	263.21	55 (moderate)	3 (moderate)	240 (moderately mobile)	-	1.35	71	15	Neuroactive
Prochloraz	67747-09-5	$C_{15}H_{16}Cl_3N_3O_2$	376.7	26.5 (low)	3.5 (high)	500 (bit mobile)	3.8	1.55	371	2.0	Sterol biosynthesis inhibition
Propanil	709-98-8	$C_9H_9Cl_2NOT$	218.08	95 (moderate)	2.29 (low)	152 (mobile moderate)	19.1	-0.51	111	1.2	Photosynthesis inhibition
Propazine/Terbutylazine	139-40-2	$C_9H_{16}ClN_5$	229.71	8.6 (low)	3.95 (high)	154 (moderately mobile)	1.7	3.86	62	77	Photosynthesis inhibition
Propiconazole	60207-90-1	$C_{15}H_{17}Cl_2N_3O_2$	342.22	150 (moderate)	3.72 (high)	1086 (bit mobile)	1.1	1.58	116	6	Sterol biosynthesis inhibition
Pyriproxyfen	95737-68-1	$C_{20}H_{19}NO_3$	321.37	0.37 (low)	5.37 (high)	21175 (non mobile)	6.9	-0.20	1379	1.6	Endocrine
Simazine/tebutylazine	122-34-9	$C_7H_{12}ClN_5$	201.7	5 (low)	2.30 (low)	130 (moderately mobile)	1.6	2.20	221	46	Photosynthesis inhibition
Spinetoram	935545-74-7	$C_{42}H_{69}NO_{10}$	748.0	29.0 (low)	4.2 (high)	22836 (non mobile)	7.7	0.27	114	5.1	Unknown
Spinosyn A	131929-60-7	$C_{41}H_{65}NO_{10}$	731,46	-	-	-	-	-	-	-	Unknown
Spinosyn D	131929-63-0	$C_{42}H_{67}NO_{10}$	745.47	-	-	-	-	-	-	-	Unknown
Tebuconazole	107534-96-3	$C_{16}H_{22}ClN_3O$	307.82	36 (low)	3.7 (high)	769 (bit mobile)	5.0	1.86	78	42.6	Sterol biosynthesis inhibition
Terbumeton	33693-04-8	$C_{10}H1_9N_5O$	225.29	130 (moderate)	3.04 (high)	295 (mobile moderate)	-	3.79	-	-	Photosynthesis inhibition
Terbumeton-desethyl	30125-64-5	$C_8H_{15}N_5O$	197.24	-	-	-	-	-	-	-	Unknown
Terbuthylazine-2-hydroxy	66753-07-9	$C_9H_{17}N_5O$	211.33	7.19 (low)	-	187 (moderate mobile)	-	4.75	-	-	Unknown
Terbutryn	886-50-0	$C_{10}H_{19}N_5S$	241.36	25 (baja)	3.66 (high)	2432 (bit mobile)	4.3	2.21	72.4	27	Photosynthesis inhibition

Compounds	CAS Number	Formula	MW	Solubility in water at 20 °C (mg L^{-1})	Log K_{ow} 20 °C	K_{oc} (ml g^{-1})	pk_a	GUS	BCF	DT_{50} (Days)	MoA
Thiabendazole	148-79-8	$C_{10}H_7N_3S$	201.25	30 (baja)	2.39 (low)	3983 (bit mobile)	4.7	1.94	96.5	1.6	Respiration inhibition
Thiamethoxam	153719-23-4	$C_8H_{10}ClN_5O_3S$	291.7	4100 (high)	-0.13 (low)	56.2 (mobile)	n/a	3.58	3[ξ]	30.6	Neuroactive
Tolclofos-methyl	57018-04-9	$C_9H_{11}Cl_2O_3PS$	301.13	0.708 (low)	3.8 (high)	3028 (slightly mobile)	n/a	0.77	670	1.25	Unknown
Tricyclazole	41814-78-2	$C_9H_7N_3S$	189.24	596 (high)	1.4 (low)	169 (moderate mobile)	n/a	3.89	3.1	92	Unknown

MW: Molecular Weight (g mol^{-1}), K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, k_a: Acidity Constant, GUS: Groundwater Ubiquity Score, BCF: Bioconcentration Factor, DT_{50}: Dissipation Half-Life, MoA: Mode of Action

Table S2. Characteristics of the PPCPs analysed in the present study

Compounds	CAS number	Chemical composition	MW	Solubility in water at 25ºC (mg L^{-1})	Log K_{ow} 20ºC	K_{oc}	pka	MoA
Acetaminophen	103-90-2	$C_8H_9NO_2$	151.16	14.00	0.46	-	9.38	Antiinflammatory
Acetylsalicylic acid	50-78-2	$C_9H_8O_4$	180.16	4.6	1.19	100	3.5	Neuroactive
Alprazolam	28981-97-7	$C_{17}H_{13}ClN_4$	308.76	13.1	2.12	$9.8X10^4$	18.30	Antibiotic
Amoxicillin	26787-78-0	$C_{16}H_{19}N_3O_5S$	365.40	3.43×10^3	0.9	100	2.8/7.2	Beta Blocker
Atenolol	29122-68-7	$C_{14}H_{22}N_2O_3$	266.30	13300	0.16	-	9.60	Sterol biosynthesis inhibition
Atorvastatin	134523-00-5	$C_{33}H_{35}FN_2O_5$	558.64	1.12×10^{-3}	6.36	400	4.30	Lipid metabolism
Bezafibrate	41859-67-0	$C_{19}H_{20}ClNO_4$	361.82	-	3.99	-	3.83	Endocrine
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	228.29	300	3.32	251-2886	9.60	Antibiotic
Butylparaben	94-26-8	$C_{11}H_{14}O_3$	194.227	2.07×10^2	3.57	520	8.47	Neuroactive
Caffeine	58-08-2	$C_8H_{10}N_4O_2$	194.19	2.16×10^4	-0.07	741-7762	10.40	Ion channel modulation
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.27	18	2.45	520	13.9	Nucleic acid biosynthesis
Chloramphenicol	56-75-7	$C_{11}H_{12}Cl_2N_2O_5$	323.13	2500	0.92	1150	7.49	Synthetic Auxi
Clofibric acid	882-09-7	$C_{10}H_{11}ClO_3$	214.65	-	2.84	-	3.18	Neuroactive
Codeine	76-57-3	$C_{18}H_{21}NO_3$	299.36	-	1.19	700	8.21	Antiinflammatory
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	2.37	4.51	245	4.15	Angiotensin Receptor or Enzyme
Enalapril	75847-73-3	$C_{20}H_{28}N_2O_5$	376.45	1.64×10^4	0.07	350	2.97	Unknown
Ethylparaben	5026-62-0	$C_9H_{10}O_3$	166.17	8.85×10^2	2.47	119-209	8.34	Unknown

Etoricoxib	202409-33-4	$C_{18}H_{15}ClN_2O_2S$	358.84		2.91	-	19.69	Unknown
Flufenamic acid	530-78-9	$C_{14}H_{10}F_3NO_2$	281.23	9.09	5.25	-	3.88	Ion channel modulation
Furosemide	54-31-9	$C_{12}H_{11}ClN_2O_5S$	330.75	73.1 (30ºC)	2.03	110	3.90	Antiinflammatory
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.29	21	3.97	3.400	4.91	Antiinflammatory
Indomethacin	53-86-1	$C_{19}H_{16}ClNO_4$	357.79	0.937	4.27	1300	4.50	Neuroactive
Lorazepam	846-49-1	$C_{15}H_{10}Cl_2N_2O_2$	321.20	80	2.40	-	13.00	Signal transduction
Metformin	657-24-9	$C_4H_{11}N_5$	129.16	1.06×10^6	-2.64	12-19	12.4	Unknown
Methylparaben	99-76-3	$C_8H_8O_3$	152.15	2.50×10^3	1.96	87	8.40	Antiinflammatory
Naproxen	26159-34-2	$C_{14}H_{14}O_3$	230.26	15.9	3.18	330	4.15	-
Norfloxacin	70458-96-7	$C_{16}H_{18}FN_3O_3$	319.33	280	-1.0	61.000	6.22/8.51	Nucleic acid biosynthesis
Ofloxacin	82419-36-1	$C_{18}H_{20}N_3FO_4$	361.37	1.08×10^4	-0.4	44.143	6.05/8.22	Unknown
Omeprazole	73590-58-6	$C_{17}H_{19}N_3O_3S$	345.40	82.3	2.23	-	9.29	Endocrine
Propylparaben	94-13-3	$C_{10}H_{12}O_3$	180.20	5.00×10^2	3.04	290	8.05	Antiinflammatory
Salicylic acid	69-72-7	$C_7H_6O_3$	138.12	2.240	2.26	404	2.97	Unknown
Simvastatin	79902-63-9	$C_{25}H_{38}O_5$	418.56	3.0×10^{-2} (T not specified)	4.68	940	14.91	Unknown
Thiamphenicol	15318-45-3	$C_{12}H_{15}Cl_2NO_5S$	356.22	-	-0.33	-	7.65	Neuroactive
Tramadol	27203-92-5	$C_{16}H_{25}NO_2$	263.38	1151	1.34	616	9.41	Lipid metabolism
Triclocarban	101-20-2	$C_{13}H_9Cl_3N_2O$	315.58	0.11 (20ºC)	4.90	12.000-71.687	12.70	Lipid metabolism
Triclosan	3380-34-5	$C_{12}H_7Cl_3O_2$	289.54	10 (20ºC)	4.66	3500-20.000	7.68	Vitamin K pathway
Warfarin	81-81-2	$C_{19}H_{16}O_4$	308.33	17 (20ºC)	2.33	30.5-912	5.08	Unknown

MW: molecular weight (g mol^{-1}), K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, k_a: Acidity Constant, MoA: Mode of Action

Table S3. Characteristics of the PFASs analysed in the present study

Compounds	**Abbr**	**CAS number**	**Chemical composition**	**Carbon chain length**	**MW (g mol^{-1})**	**Solubility in water at 20ºC (mg L^{-1})**	**Log K_{ow} 20ºC**	**Log K_{oc}**	**Log BCF**	**MoA**
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	83329-89-9	$C_{10}F_{20}ClSO_4K$	10	670.69	-	-	-	-	Unknown
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	73606-19-6	$C_8F_{16}ClSO_4K$	8	532.58	-	-	-	-	Unknown
2-(Perfluorooctyl)ethanoic acid	FOEA	27854-31-5	$C_{10}H_3F_{17}O_2$	10	478.10	-	-	-	-	Unknown
2H-Perfluoro-2-decenoic acid	FOUEA	70887-84-2	$C_{10}H_2F_{16}O_2$	10	458.10	-	-	-	-	Unknown
2,3,3,3-Tetrafluoruro-2-(1,1,2,2,3,3,3-heptafluoropropoxy) (13C3) propanoic acid	HFPO-DA	13252-13-6	$C_6HF_{11}O_3$	6	330.05	-	-	-	-	Unknown

Sodium 4,8-dioxa-3H-perfluorononanoate	NaDONA	2250081-67-3	$C_7HF_{12}O_4Na$	7	400.05	9.369	3.56	-	2.509	Unknown
Perfluorobutanoic acid	PFBA	375-22-4	C_3F_7COOH	4	214.04	1373	2.14	-	1.173	Unknown
Perfluorodecanoic acid	PFDA	335-76-2	$C_9F_{19}COOH$	10	514.08	0.008043	6.15	-	4.137	Unknown
Perfluorododecanoic acid	PFDoDA	307-55-1	$C_{12}HF_{23}O_2$	12	614.10	-	-	-	-	Lipid metabolism
Sodium perfluorodecanesulfonate	PFDS	335-77-3	$C_{10}HF_{21}SO_3$	10	600.15	0.001678	5.83	-	3.949	Unknown
Perfluoroheptanoic acid	PFHpA	375-85-9	$C_6F_{13}COOH$	7	364.06	3.647	4.15	1.52-2.82	3.049	Unknown
Sodium perfluoroheptanesulfonate	PFHpS	375-92-8	$C_7HF_{15}SO_3$	7	450.12	0.8058	3.82		2.706	Unknown
Perfluorohexanoic acid	PFHxA	307-24-4	$C_5F_{11}COOH$	6	314.05	27.12	3.48	1.63-2-35	2.448	Unknown
Perfluorohexadecanoic acid	PFHxDA	67905-19-5	$C_{15}F_{31}COOH$	16	814.13	-	-	-	-	Unknown
Potassium perfluorohexanesulfonate	PFHxS	82382-12-5	$C_6HF_{13}SO_3$	5	400.12	6.174	3.16	-	2.112	Unknown
Perfluorononanoic acid	PFNA	375-95-1	$C_8F_{17}COOH$	9	464.08	0.06258	5.48	$1.2X10^5$	3.961	Unknown
Perfluorononanesulfonic acid	PFNS	68259-12-1	$C_9HF_{19}O_3S$	9	550.14	0.01326	5.16	2.40-4.70	3.663	Lipid metabolism
Perfluorooctanoic acid	PFOA	335-67-1	$C_7F_{15}COOH$	8	414.07	0.4813	4.81	1.92-2.59	3.574	-
Perfluorooctadecanoic acid	PFODA	16517-11-6	$C_{17}F_{35}COOH$	18	914.10	-	-	-	-	Lipid metabolism
Sodium perfluorooctanesulfonate	PFOS	4021-47-0	$C_8HF_{17}SO_3$	8	500.13	0.1039	4.49	-	3.234	Unknown
Perfluoropentanoic acid	PFPeA	2706-90-3	C_4F_9COOH	5	264.05	196.5	2.81	-	1.812	Unknown
Perfluorotetradecanoic acid	PFTeDA	376-06-7	$C_{13}F_{27}COOH$	14	714.11	1.62E-06	8.83	-		Unknown
Perfluorotridecanoic acid	PFTrDA	72629-94-8	$C_{12}F_{25}COOH$	13	664.11	1.62E-05	8.16	-	3.381	Unknown
Perfluoroundecanoic acid	PFUnDA	2058-94-8	$C_{11}HF_{21}O_2$	11	564.09	5.64E-07	6.82	-	4.040	Unknown

Abbr, abbreviation; MW: molecular weight (g mol^{-1}); K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, BCF: Bioconcentration Factor, MoA: Mode of Action

Table S4. Characteristics of the OPFRs analysed in the present study.

Compounds	**Abbr**	**CAS number**	**Formula**	**MW**	**Solubility in water at 25ºC (mg L^{-1})**	**Log K_{ow} 20ºC**	**Log K_{oc} (ml g^{-1})**	**BCF**	**Vapor pressure at 25 °C (Pa) ***	**MoA**
Cresyl diphenyl phosphate	CDP	26444-49-5	$C_{19}H_{17}O_4P$	340.31	Insoluble in water	5.25	3.60	-	-	Unknown
Tris(2-Butoxyethyl) phosphate	TBEP	78-51-3	$C_{18}H_{39}O_7P$	398.47	1.2 x 10^3	3.65	4.38	1.08 x 10^3	1.6×10^{-4}	Unknown
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$	285.49	7.08 x 10^3	1.44	2.48	-	8.20	Neuroactive
Tris(2-chloroisopropyl) phosphate	TCIPP	13674-84-5	$C_9H_{18}Cl_3O_4P$	327.56	1.6 x 10^3	2.59	3.11	-	7.5×10^{-3}	Unknown
Tris(2,3-dibromopropyl) phosphate	TDBPP	126-72-7	$C_9H_{15}Br_6O_4P$	697.61	8 (24ºC)	4.29	3.40	-	-	Unknown

Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	13674-87-8	$C_9H_{15}Cl_6O_4P$	430.90	1.50	3.80	3.96	-	4.0×10^{-5}	Unknown
Tris-(2-ethylhexyl) phosphate	TEHP	78-42-2	$C_{24}H_{51}O_4P$	434.64	0.60	9.49	6.87	-	-	Unknown
Tris(methylphenyl) phosphate	TMPP	1330-78-5	$C_{21}H_{21}O_4P$	368.37	0.10	6.34	-	-	-	Unknown
Tributyl phosphate	TnBP	126-73-8	$C_{12}H_{27}O_4P$	266.32	280	4	3.28	1.03×10^3	1.5×10^{-1}	Unknown
Triphenyl phosphate	TPhP	115-86-6	$C_{18}H_{15}O_4P$	326.29	1.90	4.59	3.72	-	1.5×10^{-3}	Neuroactive
Tri-n-propylphosphate	TPP (TPrP)	513-08-6	$C_9H_{21}O_4P$	224.24	6450	1.87	2.83	-	3.20	Unknown

*Abbr, abbreviation; MW, molecular weight (g mol^{-1}), K_{ow}: Octanol-Water Partition Coefficient, K_{oc}: Organic Carbon Adsorption Coefficient, BCF: Bioconcentration Factor, MoA: Mode of Action, * calculated by Estimation Programs Interface Suite (EPI) WEB 4.1 software by U.S. EPA, 2013.*

Table S5. Characteristics of the PAHs analysed in the present study

Compounds	**Abbr**	**CAS number**	**Formula**	**Rings**	**MW**	**BP**	**MP**	**Log K_{ow}**	**MoA**
Naphthalene	Nap	91-20-3	$C_{10}H_8$	2	128	209	80.0	3.37	unknown
Acenaphthylene	Acy	208-96-8	$C_{12}H_8$	3	152	290	124	4	unknown
Acenaphthene	Acp	83-32-9	$C_{12}H_{10}$	3	154	252	108	3.92	unknown
Fluorene	Flr	86-73-7	$C_{13}H_{10}$	3	166	295	117	4.18	unknown
Phenanthrene	Phe	85-01-8	$C_{14}H_{10}$	3	178	326	136	4.57	unknown
Anthracene	Ant	120-12-7	$C_{14}H_{10}$	3	178	326	136	4.54	unknown
Fluoranthene	Flt	206-44-0	$C_{15}H_{10}$	4	202	369	166	5.22	Mitosis, Cell cycle
Pyrene	Pyr	129-00-0	$C_{16}H_{10}$	4	202	369	166	5.18	Carcinogenic
Benzo[a]anthracene	BaA	56-55-3	$C_{18}H_{12}$	4	228	400	177	5.91	unknown
Chrysene	Chr	218-01-9	$C_{18}H_{12}$	4	228	400	177	5.86	unknown
Benzo[b]fluoranthene	BbF	205-99-2	$C_{20}H_{12}$	5	252	461	209	5.8	unknown
Benzo[k]fluoranthene	BkF	207-08-9	$C_{20}H_{12}$	5	252	430	194	6	unknown
Benzo[a]pyrene	BaP	50-32-8	$C_{20}H_{12}$	5	252	461	209	6.04	unknown
Indenol[1,2,3-cd]pyrene	IcdP	193-39-5	$C_{22}H_{12}$	6	276	498	233	6.5	unknown
Dibenz[a,h]anthracene	DahA	53-70-3	$C_{22}H_{14}$	6	278	487	218	6.75	unknown
Benzo[g,h,i]perylene	BghiP	191-24-2	$C_{22}H_{12}$	6	276	467	218	6.5	unknown

Abbr: abbreviation; MW: molecular weight (g mol^{-1}); BP: boiling point (°C); MP: melting point (°C); K_{ow}: Octanol-Water Partition Coefficient, MoA: Mode of Action

Table S6. Parameters set in the Compound Discoverer workflow for the non-target analysis

Node	**Select Spectra**
Spectrum Properties Filter	
Lower RT Limit	0
Upper RT Limit	0
Min. Precursor Mass	100Da
Max. Precursor Mass	5000Da
Scan Event Filters	
Polarity Mode	(not specified)
Node	**Align Retention Time**
General Settings	
Alignment Model	Adaptive Curve
Maximum Shift [min]	0.2
Mass Tolerance [ppm]	5
Node	**Detect Compounds**
General Settings	
Mass Tolerance [ppm]	5
Min. Peak Intensity	1000000
Min. # Scans per Peak:	5
Node	**Group Compounds**
Compound Consolidation	
Mass Tolerance [ppm]	5
RT Tolerance [min]	0.1
Fragment Data Selection	
Preferred Ions	[M+H]+1; [M+NH4] +1; [M-H]-1
Node	**Calculate Mass Defect**
Mass Defect	
Fractional Mass	False
Standard Mass Defect	False
Relative Mass Defect	False
Kendrick Mass Defect	True
Kendrick Formula	
Formula 1	C2 F4
Formula 2	C2 F3 O
Formula 3	C2 H4
Formula 4	C3 H6
Formula 5	C8 H8
Node	**Search mzCloud**

General Settings	
Compound Class	All
Precursor Mass Tolerance	10 ppm
FT Fragment Mass Tolerance	10 ppm
IT Fragment Mass Tolerance	0.4 Da
Library	Autoprocessed; Reference
DDA Search	
Identity search	Cosine
Match Activation Type	True
Match Activation Energy	Match with Tolerance
Activation Energy Tolerance	20
Apply Intensity Threshold	True
Similarity Search	None
Match Factor Threshold	30
DIA Search	
Use DIA Scans for Search	True
Max. Isolation Width [Da]	500
Match Activation Type	False
Match Activation Energy	Any
Activation Energy Tolerance	100
Apply Intensity Threshold	True
Match Factor Threshold	20
Node	**Search Mass List**
Search Settings	
Mass Lists	EFS HRAM Compound Database.masslist
Use Retention Time	True
RT Tolerance [min]	0.5
Mass Tolerance [ppm]	5
Node	**Apply Spectral Distance**
Pattern Matching	
Mass Tolerance [ppm]	5
Intensity Tolerance [%]	30
Intensity Threshold	0.1
S/N Threshold	3
Use Dynamic Recalibration	True
Node	**Apply mzLogic**
Search Settings	
Max. #Compounds	0
Max. # mzCloud Similarity Results to consider per Compound	10
Match Factor Threshold	30
Node	**Fill Gaps**

General Settings	
Mass Tolerance [ppm]	5
S/N Threshold	1.5
Use Real Peak Detection	True
Node	**Mark Background**
General Settings	
Max. Sample/Blank	5
Max. Blank/Sample	0
Hide Backround	True
Node	Predict Compositions
Prediction Settings	
Mass Tolerance [ppm]	5
Min. Elements Counts	C H
Max. Elements Counts	C90 H190 Br3 Cl18 F18 N10 O18 P3 S5
Min. RDBE	0
Max. RDBE	40
Min. H/C	0.1
Max. H/C	3.5
Max. # Candidates	10
Pattern Matching	
Intensity Tolerance [%]	30
Intensity Threshold [%}	0.1
S/N Threshold	3
Use Dynamic Recalibration	True
Fragments Matching	
Use Fragments Matching	True
Mass Tolerance [ppm]	5
S/N Threshold	3
Node	**Search ChemSpider**
Search Settings	
Database(s)	ACToR (Aggregated Computational Toxicology Resource); DrugBank; EAWAG Biocatalysis/ Biodegradation Database; EPA DSSTox; EPA Toxcast; FDA UNII-NLM;
Search Mode	By Formula or Mass
Mass Tolerance	5
Max. # of results per compound	20
Max. # of Predicted Compositions to be searched per Compound	3
Node	**Assign Compound Annotations**
General Settings	

Mass Tolerance	5
Data Sourses	
Data Sourse #1	mzCloud Search
Data Sourse #2	mzVault Search
Data Sourse #3	MassList Search
Data Sourse #4	Predicted Compositions
Data Sourse #5	ChemSpider Search
Data Sourse #6	(not specified)
Data Sourse #7	(not specified)
Scoring Rules	
Use mz Logic	True
Use spectral Distance	True
Sfit Threshold	20
Sfit Range	20

Figure S1. Workflow "Environmental w Stats Unknown ID w Online and Local Database Searches" in Compound Discoverer software

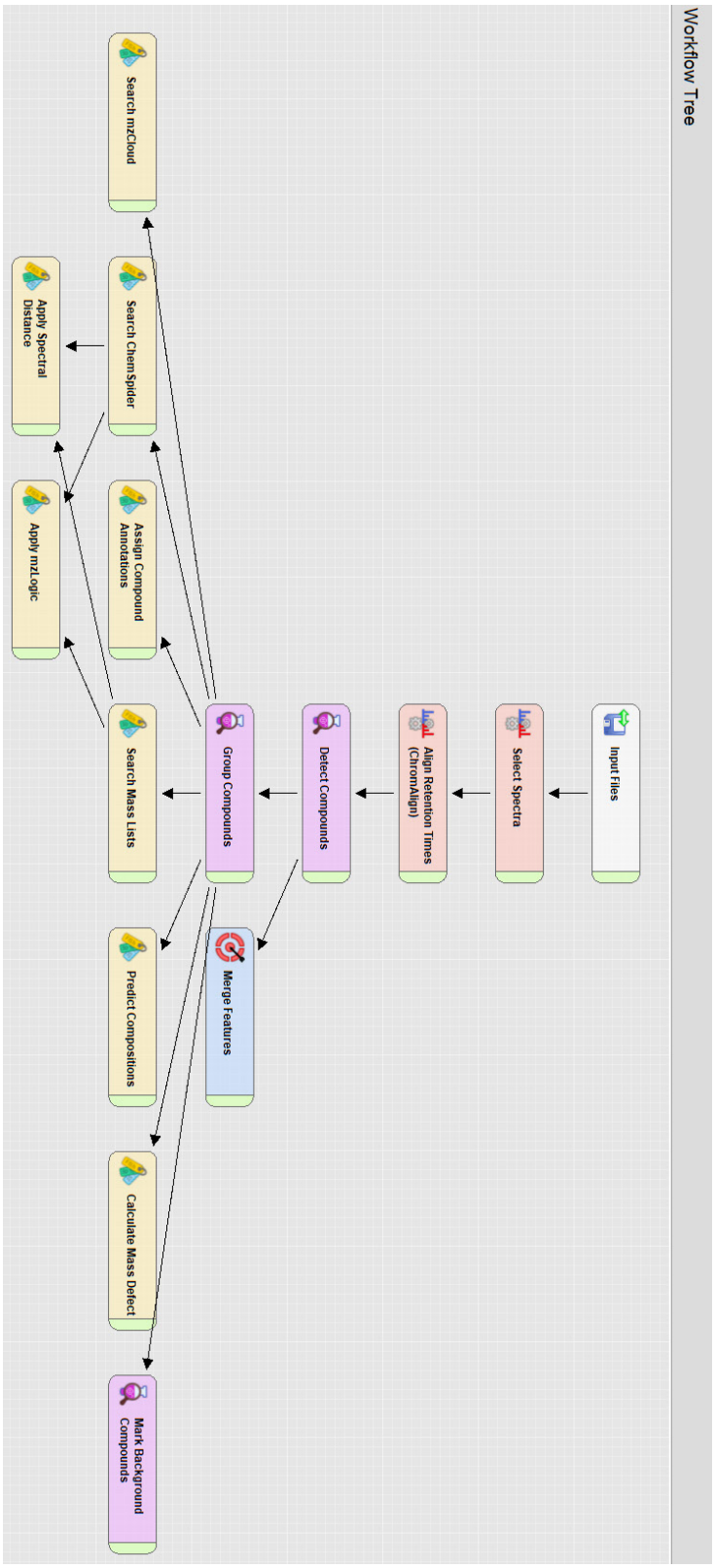


Figure S2. Filters used in Compound Discoverer software

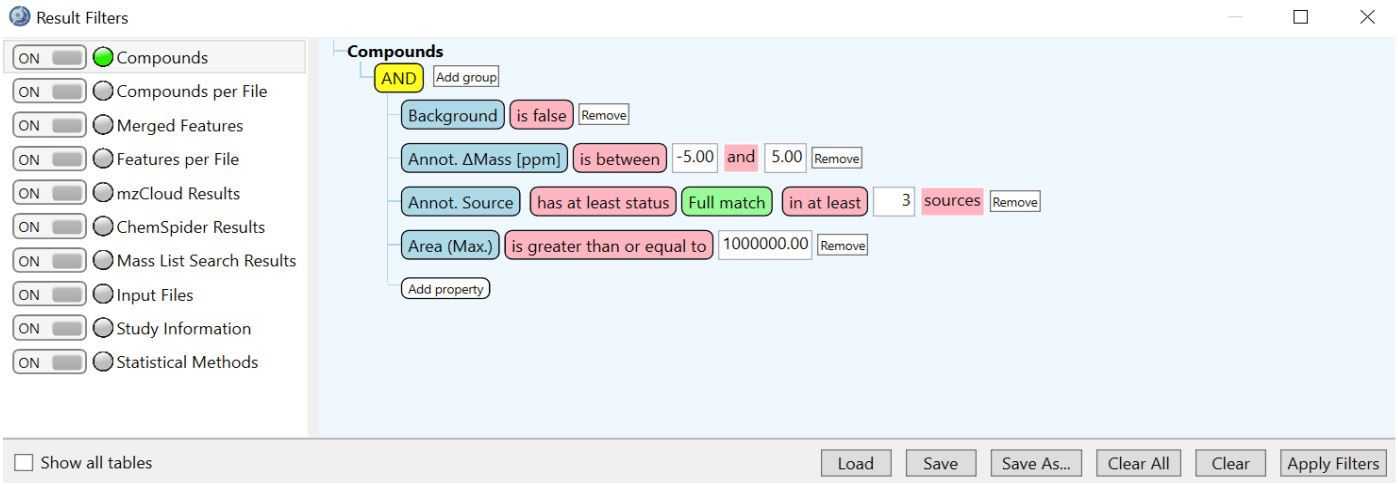
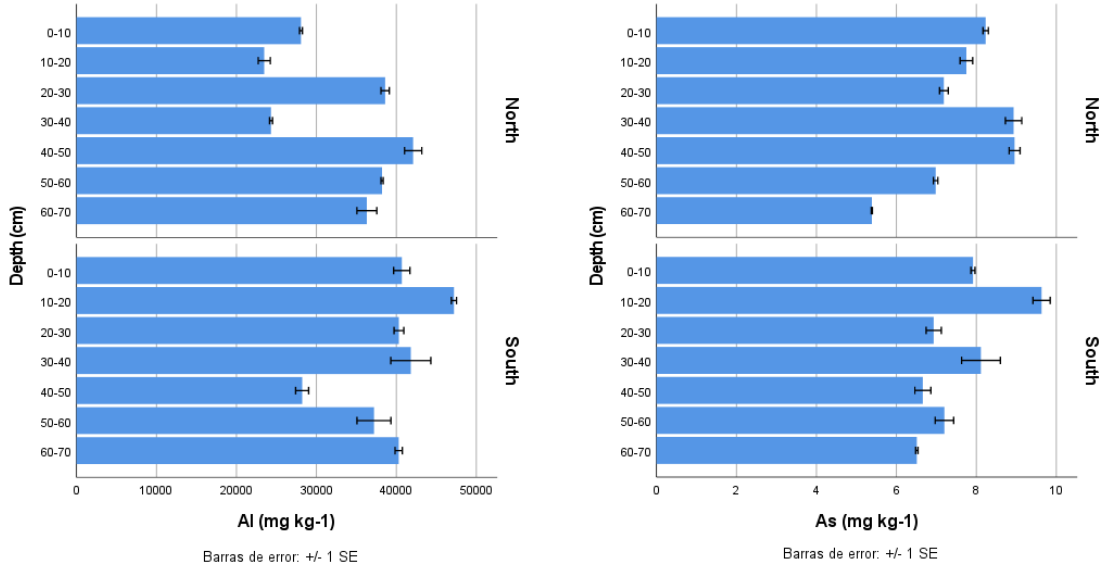
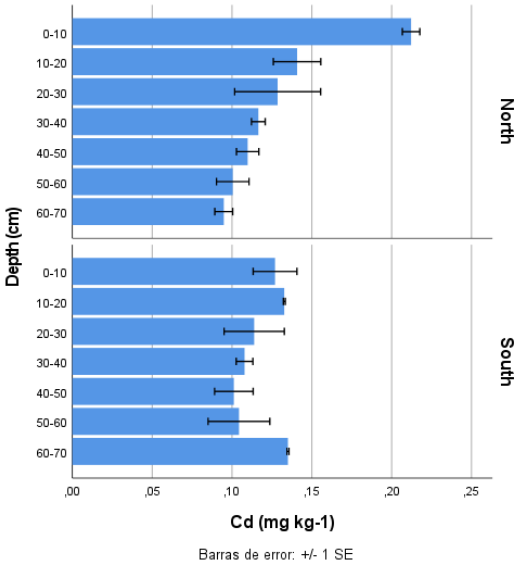
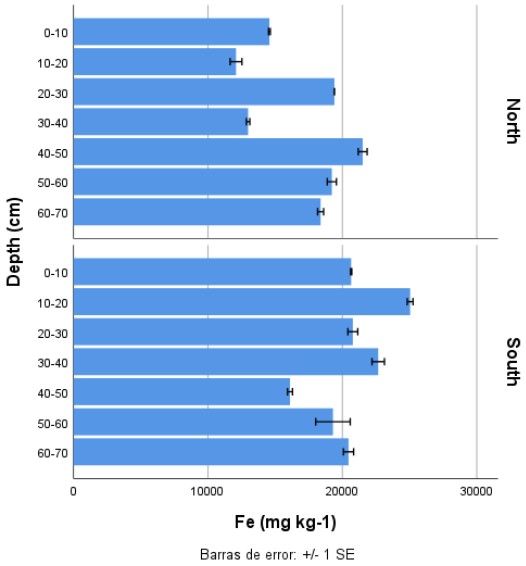
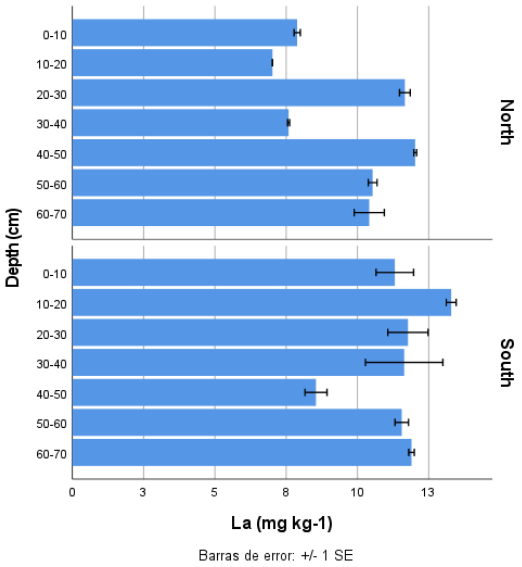


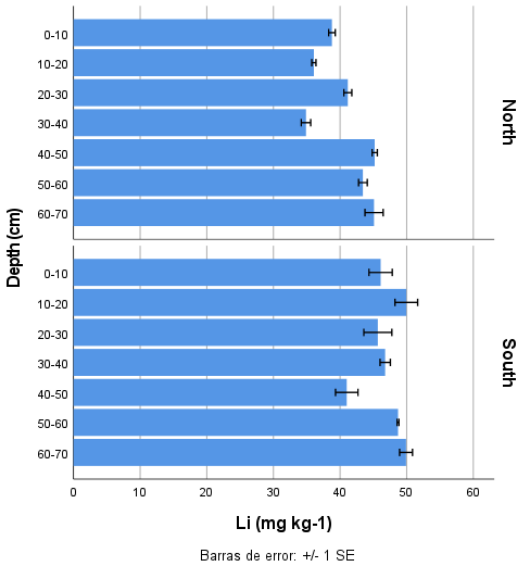
Figure S3. Total metal content in the different sediment layers in the Northern and Southern sampling points.

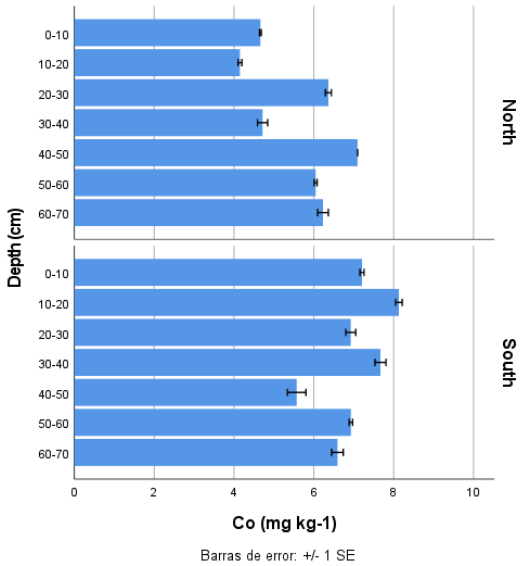


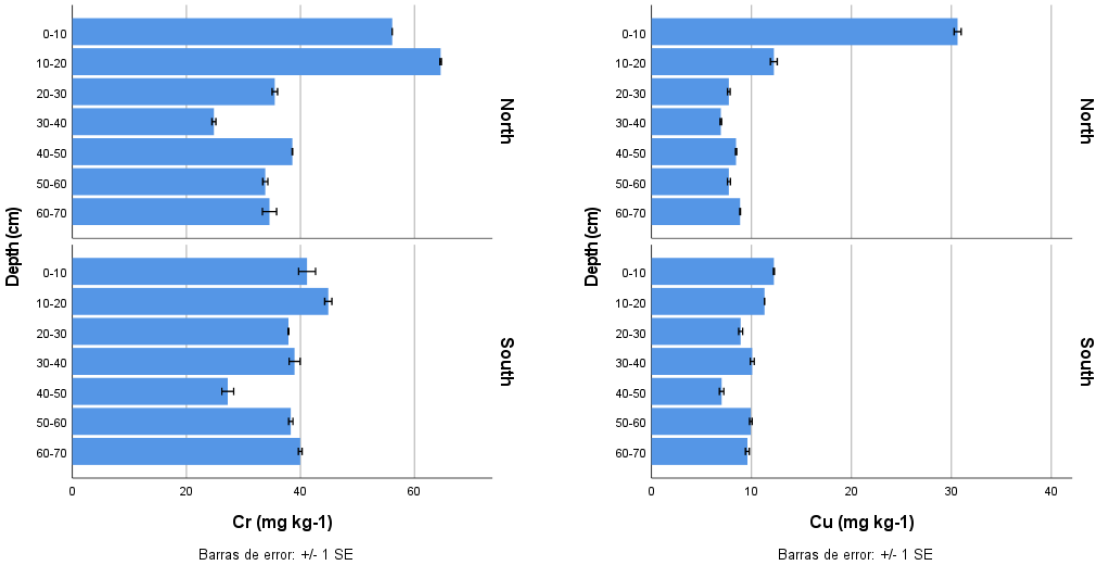

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
,00
,05
,10
,15
,20
,25
Cd (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
10000
20000
30000
Fe (mg kg-1)
Barras de error: +/- 1 SE

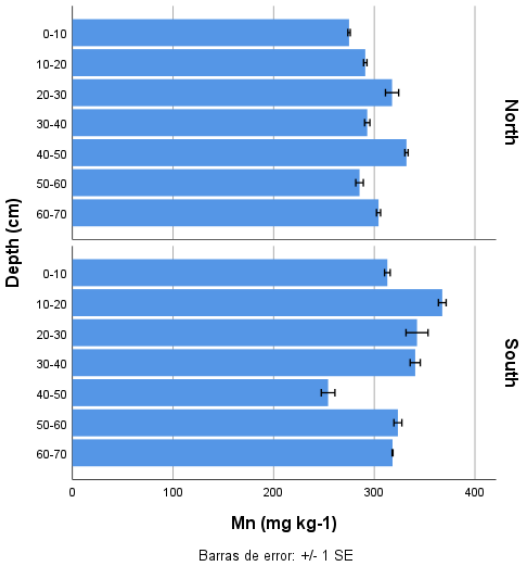

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
3
5
8
10
13
La (mg kg-1)
Barras de error: +/- 1 SE

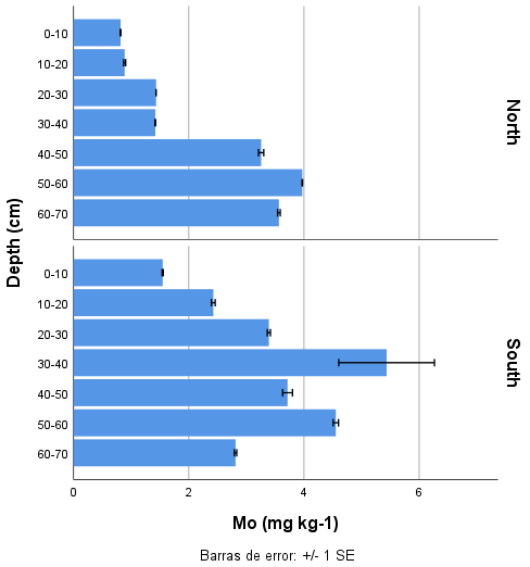

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
10
20
30
40
50
60
Li (mg kg-1)
Barras de error: +/- 1 SE

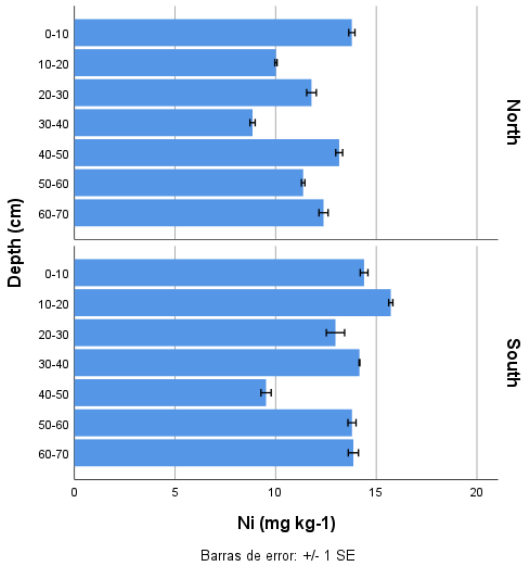

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
2
4
6
8
10
Co (mg kg-1)
Barras de error: +/- 1 SE

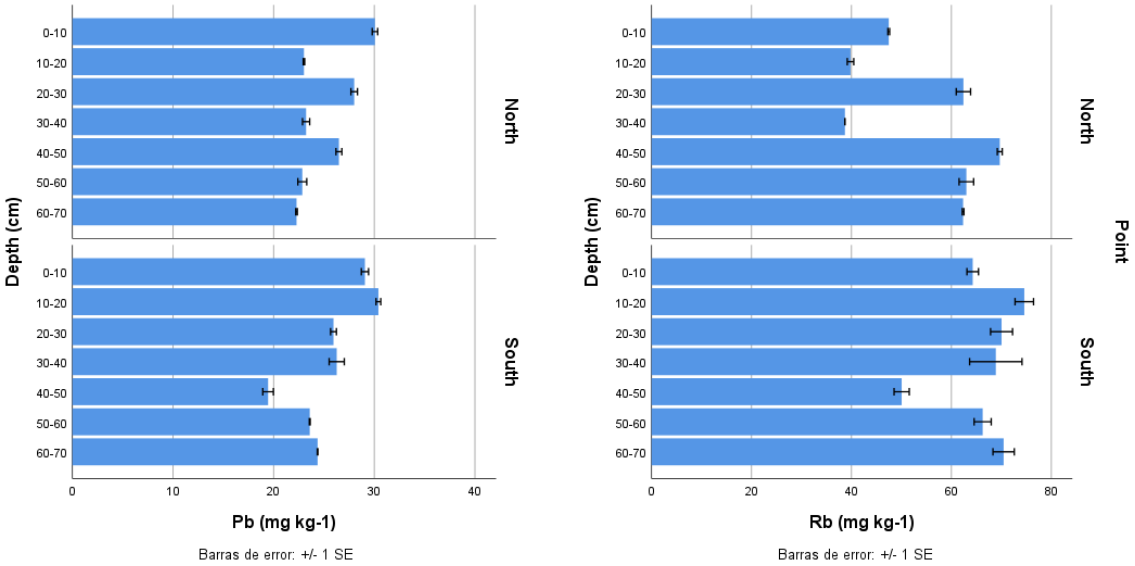

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
20
40
60
Cr (mg kg-1)
Barras de error: +/- 1 SE

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
10
20
30
40
Cu (mg kg-1)
Barras de error: +/- 1 SE

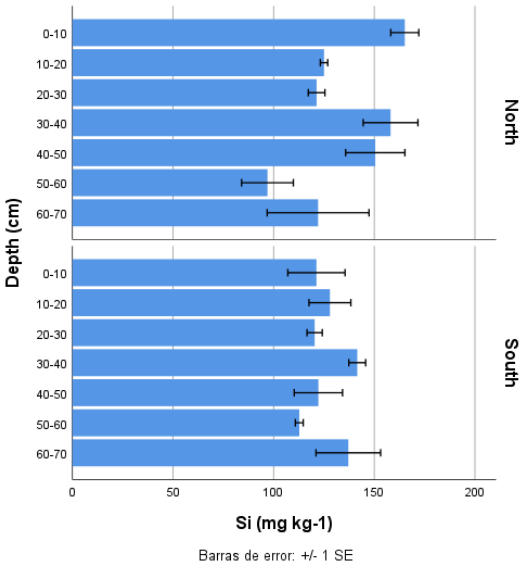

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
100
200
300
400
Mn (mg kg-1)
Barras de error: +/- 1 SE

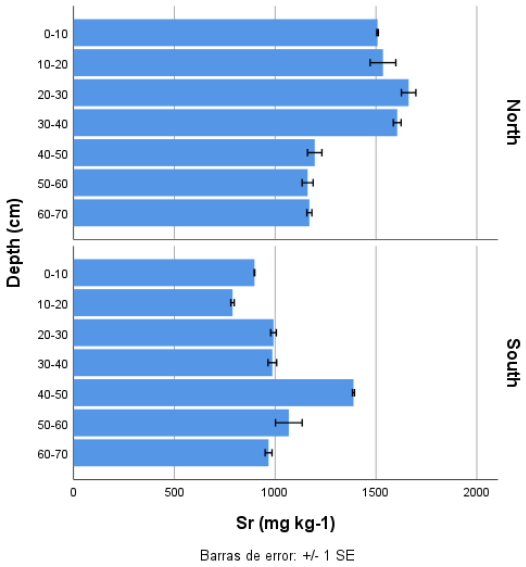

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
2
4
6
Mo (mg kg-1)
Barras de error: +/- 1 SE

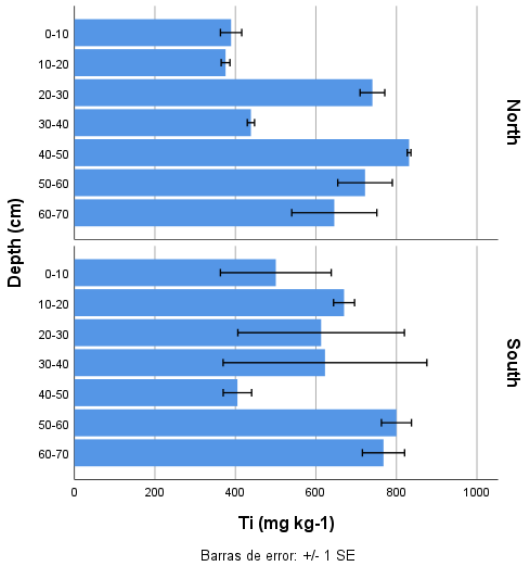

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
5
10
15
20
Ni (mg kg-1)
Barras de error: +/- 1 SE

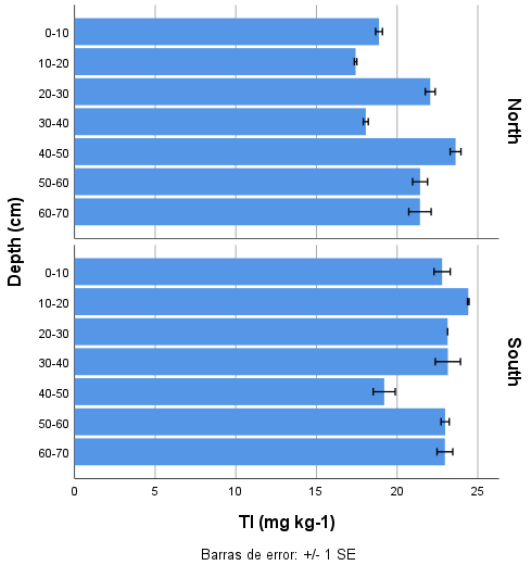

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
10
20
30
40
Pb (mg kg-1)
Barras de error: +/- 1 SE

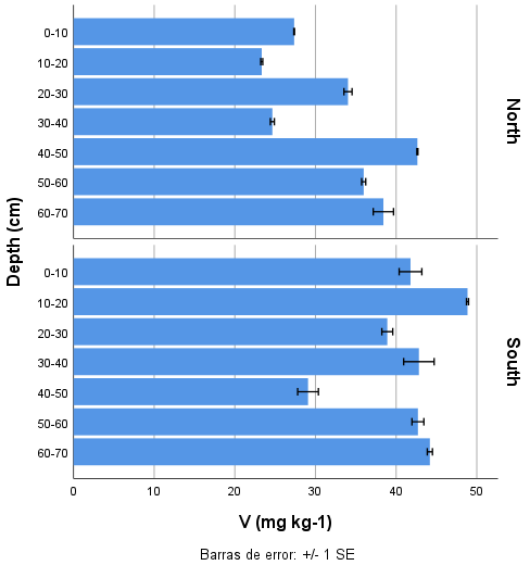
Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
Point
0
20
40
60
80
Rb (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
50
100
150
200
Si (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
500
1000
1500
2000
Sr (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
200
400
600
800
1000
Ti (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
5
10
15
20
25
Tl (mg kg-1)
Barras de error: +/- 1 SE


Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
0
10
20
30
40
50
V (mg kg-1)
Barras de error: +/- 1 SE

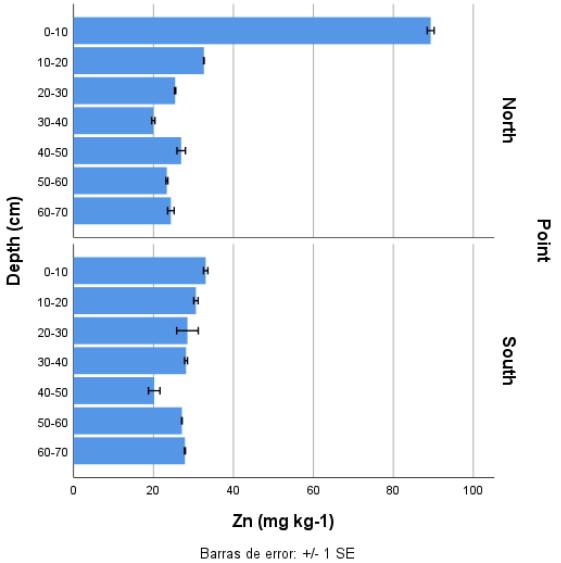
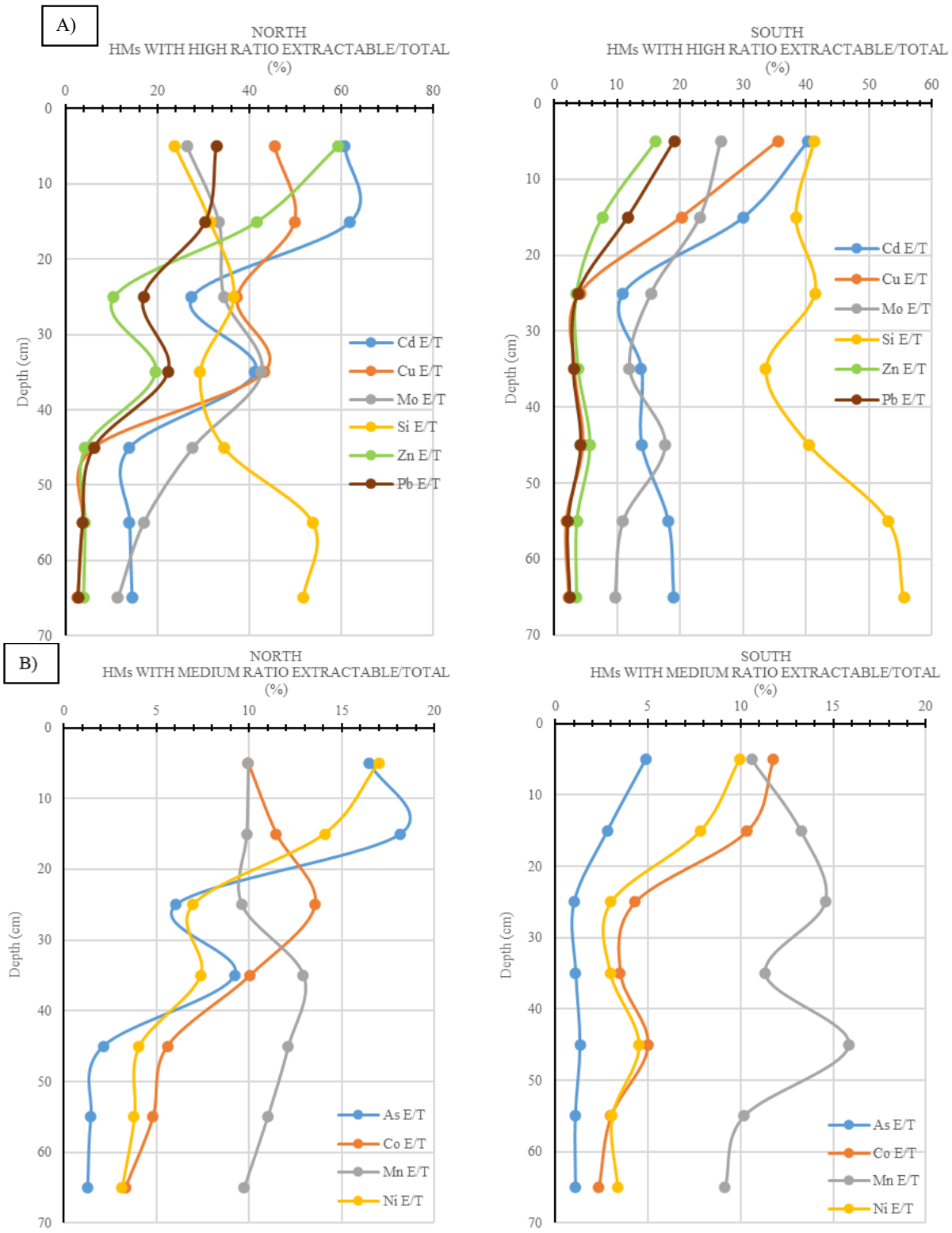
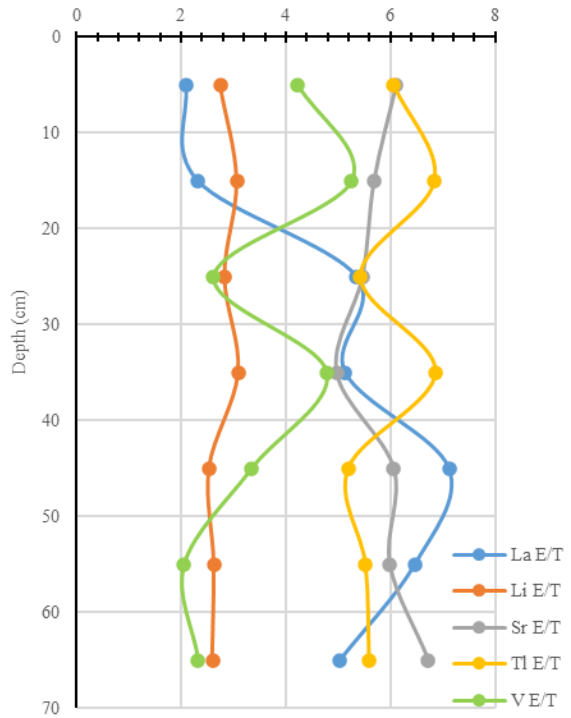
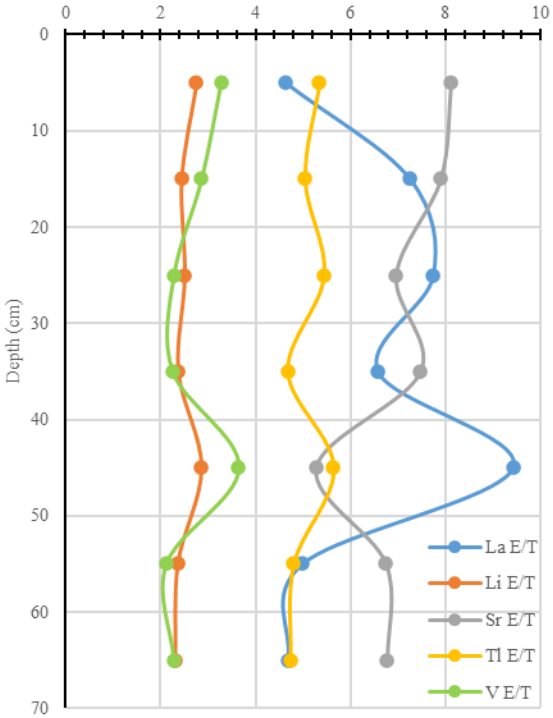

Depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
North
South
Point
0
20
40
60
80
100
Zn (mg kg-1)
Barras de error: +/- 1 SE

Figure S4. EDTA-extractable content/Total content for heavy metals (HMs) and metalloids in the sediments cores at nothern and southern sampling points in L´Albufera lake according to their ratio (A) High, (B) Medium, (C) Low and (D) very low.

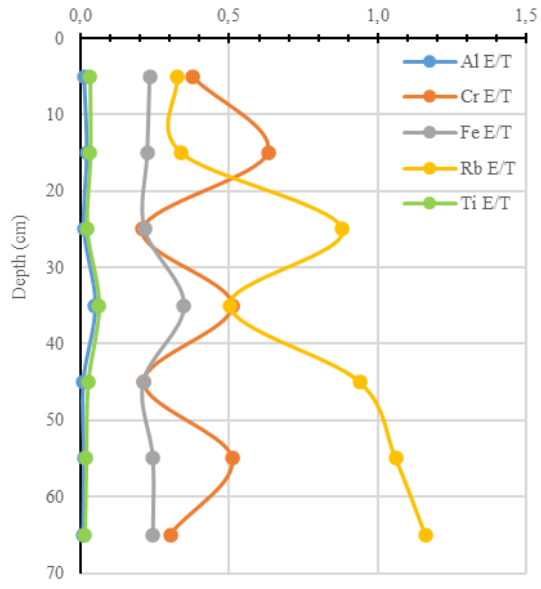


C)


NORTH
HMs WITH LOW RATIO EXTRACTABLE/TOTAL (%)
Depth (cm)
La E/T
Li E/T
Sr E/T
Tl E/T
V E/T


SOUTH
HMs WITH LOW RATIO EXTRACTABLE/TOTAL (%)
Depth (cm)
La E/T
Li E/T
Sr E/T
Tl E/T
V E/T

D)


NORTH
HMs WITH VERY LOW RATIO EXTRACTABLE/TOTAL (%)
Depth (cm)
Al E/T
Cr E/T
Fe E/T
Rb E/T
Ti E/T

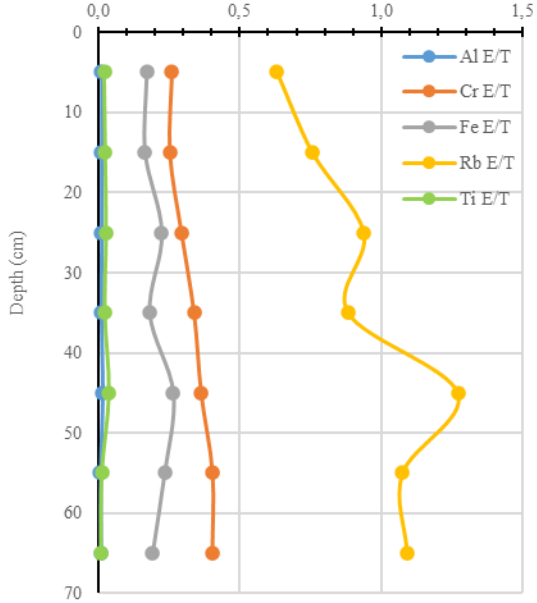
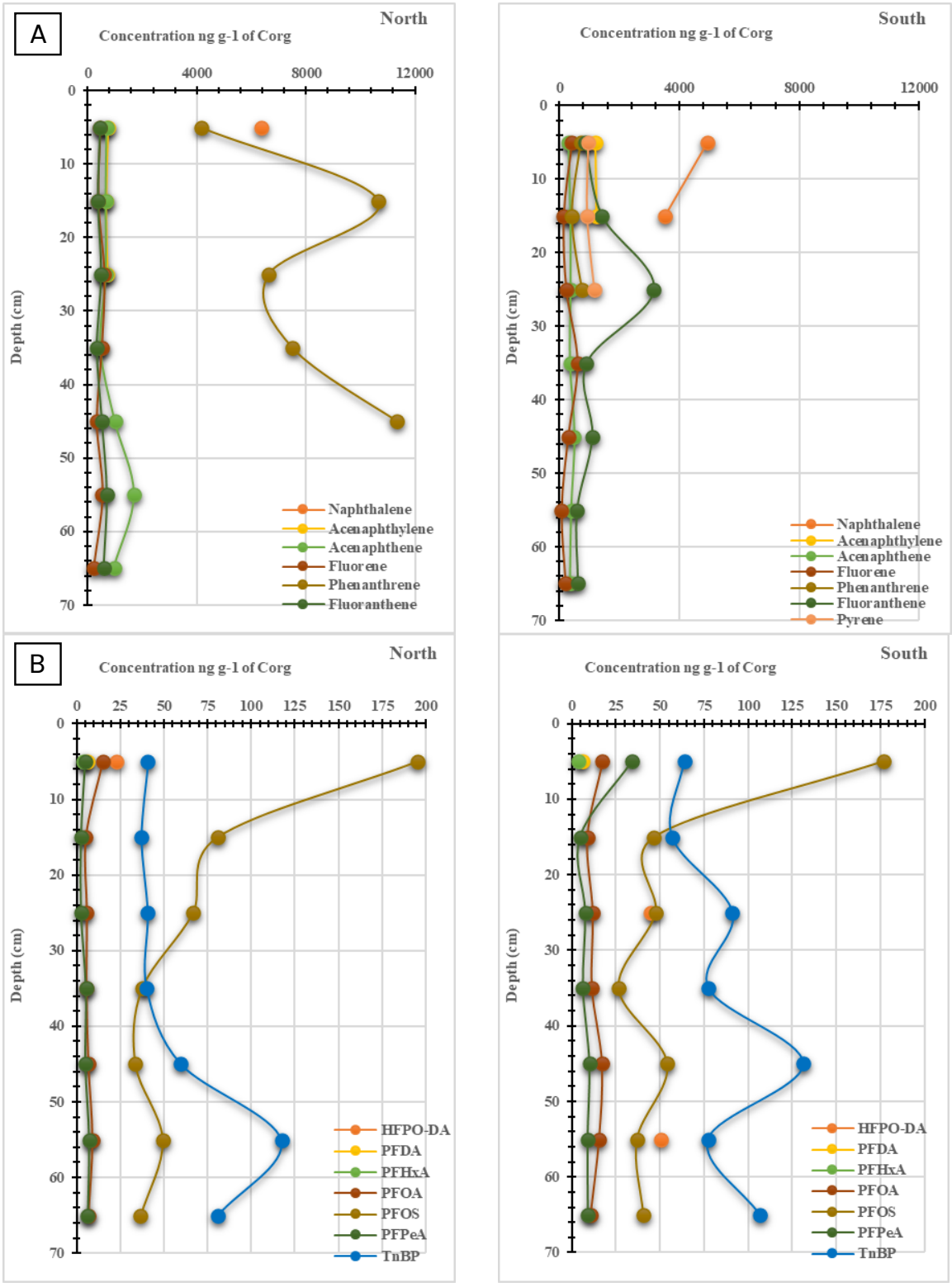

SOUTH
HMs WITH VERY LOW RATIO EXTRACTABLE/TOTAL (%)
Depth (cm)
Al E/T
Cr E/T
Fe E/T
Rb E/T
Ti E/T

Figure S5. Distribution of POPs normalized to the Corg content along the sedimentary profile in the northern and southern parts of the lake. A) PAHs B) PFASs and OPFRs. Concentrations are expressed in ng g-1 TOC.



ARTICLE 05

Trace elements and legacy and emerging organic contaminants concentrations datasets in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): association with "in-deep" sediment characteristics and risk assessment to the aquatic biota

Data in Brief 54 (2024) 110464

Contents lists available at ScienceDirect

Data in Brief

journal homepage: www.elsevier.com/locate/dib

Data Article

Trace elements and legacy and emerging organic contaminants concentrations datasets in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment characteristics and risk assessment to the aquatic biota

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ARTICLE INFO

Article history:
Received 8 April 2024
Revised 18 April 2024
Accepted 18 April 2024
Available online 3 May 2024

Dataset link: Dataset on trace elements and legacy and emerging organic contaminants concentrations in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment chara (Original data)

Keywords:
Mediterranean coastal wetland
Metal ad metalloids
Contaminants of emerging concern
Mode of action

ABSTRACT

The chronological information provided by sediment cores about the beginning and evolution of anthropogenic contaminants is crucial for understanding the influence of humans on the environment. The dataset provides information about the vertical distribution of heavy metals (HMs), metalloids and various organic contaminants (OCs) including contemporary contaminants of emerging concern (CECs), such as pharmaceuticals and personal care products (PPCPs) and pesticides; as well as persistent organic contaminants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFASs), organophosphorus flame retardants (OPFRs) in sediment cores of two different sampling areas (North and South) of L'Albufera lake. Additional information about the ^{14}C-data of the organic matter present

DOI of original article: 10.1016/j.jhazmat.2024.134168
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https://doi.org/10.1016/j.dib.2024.110464
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in the different layers of the sediment cores, and the ^{14}C-data of the seashells found in some of them are shown. The dataset includes physico-chemical analyses of sediment characteristics at the different selected depth levels such as Organic Carbon (C_{org}), Inorganic Carbon (IC), Total Nitrogen (TN), Total Sulphur (TS) and texture. Furthermore, ecological risk assessment of these contaminants in surface sediment layers is performed to ascertain is potential toxicity. These data supplement the findings presented and considered in the research article "**Exploring Organic and Inorganic Contaminant Histories in Sediment Cores Across the Anthropocene: Accounting for Site/Area Dependent Factors"**. Therefore, these data altogether are useful for researchers seeking to assess long-term impact of contamination.

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Specifications Table

Subject	Contamination
Specific subject area	Heavy metals and metalloids and organic contaminants in sediments cores in Mediterranean coastal wetlands
Type of data	Table, Chart, Graph, Figure Raw, Analyzed, Filtered
Data collection	The data were collected for six sediment cores. Three of the cores are from the Northern zone at the coordinates indicated as site 1 and the other 3 from the Southern zone at the coordinates indicated as site 2. Each sediment core, approximately 70 cm in depth, was frozen and cut into 10 cm portions. The following parameters were determined for each portion: sediment age, shells age, texture, organic carbon (C_{org}), inorganic carbon (IC), total nitrogen (TN), total sulphur (TS), heavy metals (HMs) and metalloids, polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFASs), organophosphorus flame retardants (OPFRs), pesticides and pharmaceutical and personal care products (PPCPs).
Data source location	Institution: *University of Valencia, Research Center on Desertification (CIDE)* *City/Town/Region: Moncada, Community of Valencia* *Country: Spain* Latitude and longitude (and GPS coordinates, if possible) for collected samples/data: Site 1: 39°20′39.10″N 0°21′29.60″W Site 2: 39°19′16.50″N 0°21′46.00″W
Data accessibility	Repository name: Mendeley Data identification number: *(or DOI or persistent identifier)*: 10.17632/n9p7xkp3vc.1 Direct URL to data: https://data.mendeley.com/datasets/n9p7xkp3vc/1
Related research article	[1] **Exploring Organic and Inorganic Contaminant Histories in Sediment Cores Across the Anthropocene: Accounting for Site/Area Dependent Factors** Soriano, Y.; Gimeno-García, E.; Campo, J.; Hernández-Crespo, C.; Andreu Pérez, V.; Picó, Y. J. Hazard. Mat. https://www.sciencedirect.com/science/article/pii/S0304389424007477

1. Value of the Data

- The dataset comprises the first detailed open access record of the vertical distribution of organic contaminants (OCs) and heavy metals (HMs) and metalloids within sediment cores extracted from L'Albufera Lake.
- This data is useful to understand the distribution of contaminants 'in-depth' in the Southern and Northern areas of the lake as well as be able to correlate the concentrations of organic and inorganic contaminants with the sediment's properties of LÁlbufera Lake.

- This data will help researchers on planning for further research studies within this area or even within similar areas and for comparison studies (temporal and spatial).
- Data can assist researchers, policy makers, and stakeholders to better understand the dynamics of these area including sediment resuspension and support researches about removal, transport and fate of these contaminants to improve future management plans, and help to evaluate the effectiveness of current and future legislative tools.

2. Background

This dataset supports a related research article with show the occurrence of heavy metals (HMs) and metalloids, polycyclic aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFASs), organophosphorus flame retardants (OPFRs), pesticides and pharmaceuticals and personal care products (PPCPs) in dated sediment cores from L'Albufera Lake (Valencia, Spain). This assessment involves several innovative aspects of environmental interest: dating L'Albufera Lake sediments and characterizing their physicochemical attributes; and identifying their potential sources of OCs in a natural coastal wetland. This is one of the most comprehensive studies on characterization the vertical distribution patterns of a diverse range of contaminants within sediment cores extracted from L'Albufera Lake (Valencia, Spain).

3. Data Description

This paper presents a dataset associated with the study of sediment cores obtained from two different points of the L'Albufera Lake (Valencia, Spain) to establish the history of OCs and HMs deposition in the area. These two points were located at the North (39°20′39.10″N 0°21′29.60″W) and South (39°19′16.50″N 0°21′46.00″W) of the Lake. For detailed information regarding the sampling procedure, please refer to Fig. 1.

The sediment cores were transported to the laboratory, frozen and cut in pieces of 10 cm. For each of these sediment pieces of each core the following parameters were established:

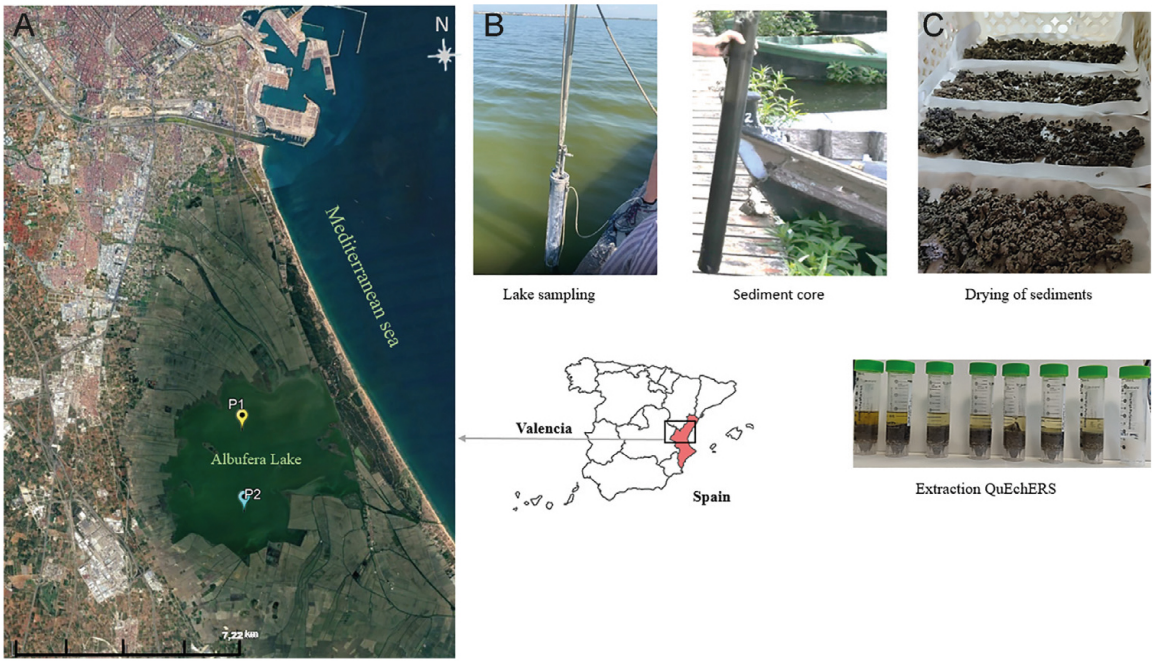


Fig. 1. Overview of the sampling procedure. a) Study area and sampling locations b) Sampling c) Extraction protocol.

Table 1
Folder structure from Mendeley data link.

File path	File description
Folder: REPORT OF RADIOCARBON DATING ANALYSES	Numerical result of dating ^{14}C of sediments cores and of the shells found at the lower layers. Two .pdf files one for sediments and the other for shells
Age and characteristics raw data	Excel file that contains raw data on sediment age and sediment characteristics
Heavy Metals in CORES_All data and Indexes	Excel files that contains raw data on average total HMs in sediment cores, background concentration of HMs, total HMs contamination degree (CD) and Contamination factor (CF) indexes, total HMs enrich factor, total HMs Pollution Load Index (PLI), HMs extractable with ethylenediaminetetraacetic acid (EDTA), ratio HMs Extractable/Total
Organic contaminants in sediment cores.	Excel file that contains raw data of pesticides, PPCPs, PFASs, OPFRs, PAHs as well as risk assessment in sediments.

The age was establishing by ^{14}C dating of both, sediments and shell found in the deepest layers. Furthermore, several sediment characteristics, such as, Organic Carbon (C_{org}), Inorganic Carbon (IC), Total Nitrogen (TN), Total Sulphur (TS) and granulometry and texture of all layers of both sediment cores were analyzed. Data on the concentration of heavy metals (HMs) and other metalloids, Polycyclic Aromatic Hydrocarbons (PAHs), pesticides, Pharmaceuticals and Personal Care products (PPCPs), Perfluoroalkyl substances (PFASs) and Organophosphorus Flame Retardants (OPFRs) in different sediments deeps were obtained. The collected data were saved and stored in the Mendeley databased, comprising one folder and three raw data Excel files. The folder titled "REPORT OF RADIOCARBON DATIN ANALYSIS" contained resulted .pdf files with results of the dating of the C_{org} in sediments and seashells. For a comprehensive overview of the folder structure, please refer to Table 1.

Furthermore, within the main text the following Figures and Tables summarizing most important information are provided:

- Fig. 2 is an overview of the ^{14}Cdating of sediment cores North and South and shells in the North (minimum (min) and maximum (max))
- Fig. 3 is the summary of the distribution in-depth of C_{org}, TN and TS.
- Table 2 shows the upper limits of the background concentrations (BUL), calculated as the mean+2σ and expressed in mg kg^{-1} dry weight.
- Fig. 4 illustrates the enrichment factors (ER) of the heavy metal (HMs) and metalloids.

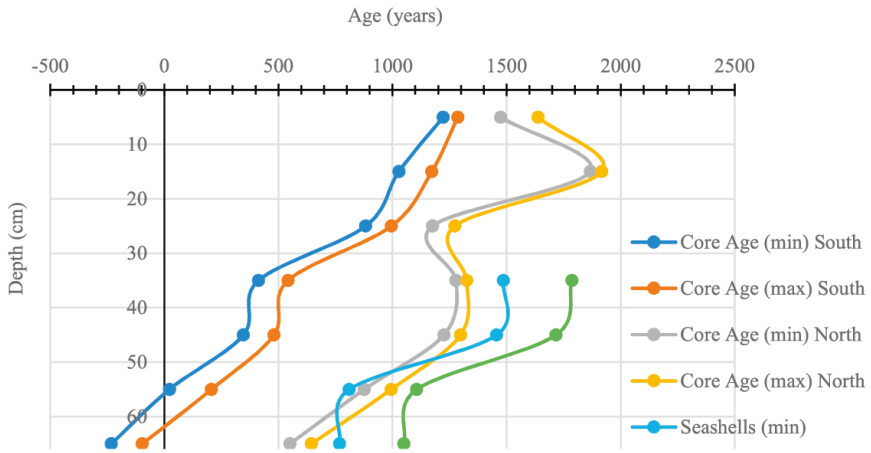


Fig. 2. Relationship between the depths and calibrated ages in the North and South sediment cores and in Seashells in the North.

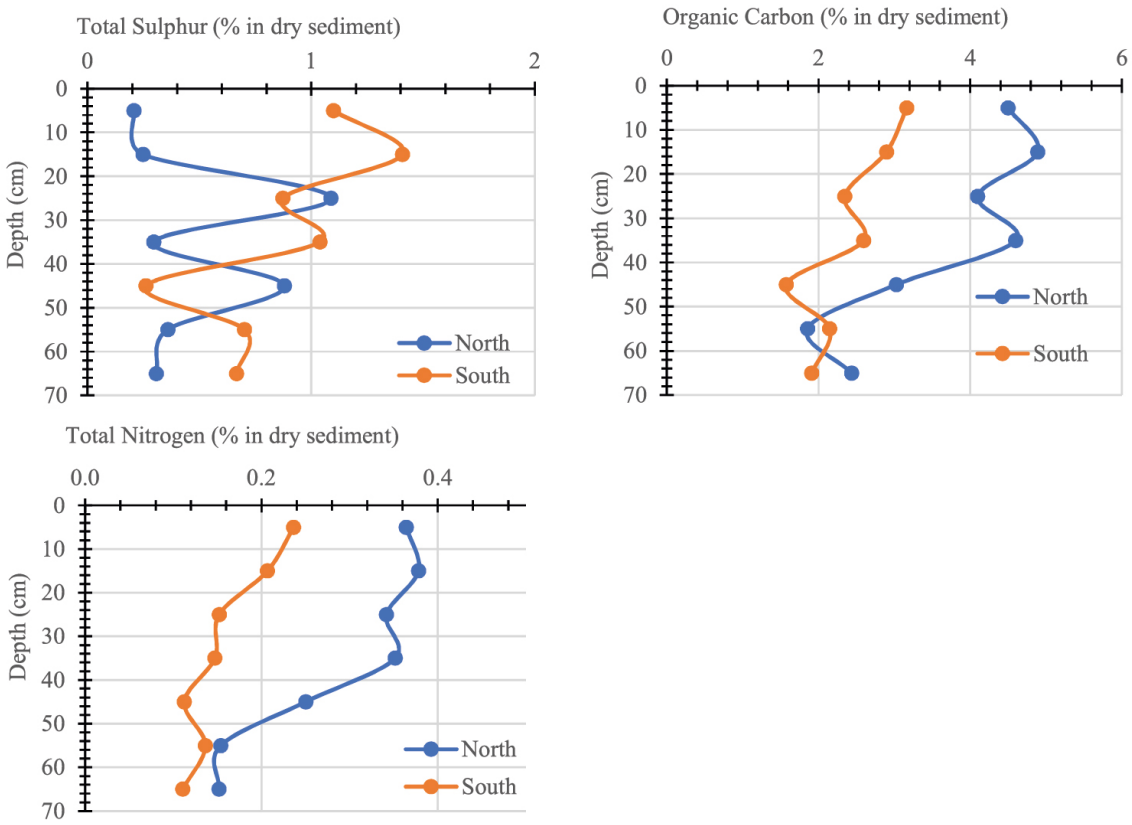


Fig. 3. Organic Carbon, Total Nitrogen and Total Sulphur, expressed in% in dry sediment, at different sampling sites.

- Tables 3 and 4 present the mean concentrations of organic contaminants at the different depth both, Northern and Southern sampling points.
- Table 5 and 6 show the spearman correlations for heavy metals (HMs) and metalloids as well as for the organic contaminants found at both, Northern and Southern sampling points.
- Fig. 5 exemplifies the contaminant load index (PLI) and the contamination degree (DC) in depth both in the North and in the South.
- Fig. 6 provides information on the compounds found and their mode of action
- Tables 7 and 8 summarize the PNEC values

Although Environmental Quality Standards for sediments have not yet been adopted in Spain, the values proposed in other countries as Sediment Quality Guidelines (SQG) have been used for comparison in the case of As, Cd, Cr, Cu, Pb and Zn. For the other studied elements, there are not established SQG yet.

In our study (see Table 2), BUL of As (6.01 mg kg^{-1}) and Cr (39.5 mg kg^{-1}) are higher than the established by the Canadian interim sediment quality guidelines (ISQG). Moreover, total Arsenic values in all sediment layers exceed the ISQG of 5.9 mg kg^{-1} for all depths and they approach to the US EPA value in the 10–20 cm depth at the Southern point around the threshold effect concentration (TEC) of 9.8 mg kg-1. For total Cr, both in the North (up to 20 cm) and in the South (up to 40 cm), the Threshold Effect Level (TEL) (37.3 mg kg^{-1}) is exceeded. However, none of the other elements studied exceed the thresholds and the Probable Effect Concentration (PEC) values.

The processes controlling HMs and metalloids scavenging and post-depositional stability in lakes, which include currents and wave action, post-depositional bioturbation, and possible HMs and metalloids release to interstitial water (which in turn will be controlled by changes in Electric Conductivity (EC) and pH), will significantly affect the preservation of the HMs and metalloids record within the sediment column [3]. Especially, the biogenic organic material and the

Table 2
Upper limits of heavy metals (HMs) and metalloids background concentrations (BUL) from the deepest sediment layer (60–70 cm) at North and South sampling points in LÁlbufera Lake and comparison to values obtained by [2] (H-C-M) in the same lake.

Element	Background concentrations of HMs (mg kg^{-1} except Al, Fe, in%)				
	BUL North	BUL South	BUL average	BUL average H-C-M [2]	BUL H-C-M [2]
Depth	60–70 cm	60–70 cm	60–70 cm	24–54 cm	20–50 cm
Al	3.98	4.16	4.07	5.07	–
As	5.43	6.59	6.01	9.80	–
Cd	0.11	0.14	0.12	0.15	0.38
Co	6.61	7.01	6.81	8.48	–
Cr	38.10	40.89	39.50	45.77	–
Cu	8.97	10.14	9.55	10.53	28.80
Fe	1.90	2.15	2.03	2.59	2.20
La	11.92	12.17	12.05	14.49	–
Li	48.96	52.66	50.81	51.26	–
Mn	309.93	319.35	314.64	380.06	345.70
Mo	3.63	2.87	3.25	6.09	–
Ni	13.02	14.58	13.80	15.83	25.90
Pb	22.49	24.46	23.47	30.86	25.50
Rb	62.83	76.50	69.66	85.11	–
Si	193.66	182.49	188.07	173.53	–
Sr	1204.65	1015.58	1110.11	1870.65	–
Ti	944.64	916.24	930.44	1032.12	–
Tl	23.38	24.34	23.86	26.10	–
V	41.98	45.09	43.54	49.71	–
Zn	26.66	28.19	27.43	32.74	88.60

BUL: calculated as the mean+2σ.
BUL are compared with background levels proposed by [2] for LÁlbufera Lake. Concentrations of Fe and Mn are similar in both studies, but however, the concentrations of Cd, Cu, Ni, Pb and Zn are lower in the present study. The discrepancy between values could be attributed to the differences in sampling depth. While in our study, the sediment layer considered for calculating the background values is 60–70 cm and, in the other study it is between 24 and 54 cm. Moreover, of the three points taking by [2], two of them are closer to the lake shore and in areas of higher sediment inputs, but in our study, the points are located more towards the center of the lake.

silt- and clay-sized fractions of sediments, play a dominant role in binding HMs into lake sediments. As these fractions include clay minerals, iron hydroxides, manganese oxides, and organic matter, ion-exchange processes between the positively charged HMs and metalloids and negatively charged surfaces are likely to occur [3].

Spearman's test (Table 5) showed significant and positive correlation coefficients between C_{org} and TN and, these are also correlated to ethylenediaminetetraacetic acid (EDTA) extractable fraction of As, Cd, Co, Cu, Ni, Pb, Sr and Zn. The partial correlation analysis with C_{org} as control variable revealed that those HMs and metalloids are influenced by this parameter because the above-mentioned significant coefficients disappeared.

Significant correlations between OCs concentrations and C_{org}, IC, TN and TS content indicate that these parameters might be a key factor affecting the concentrations of OCs in both sediment cores. Spearman's test (Table 6) for OCs showed significant and positive correlation coefficients between parameters such as C_{org}, IC, TN and TS and different organic compounds.

According the potential risk factor calculations for individual elements, only for Cd in the 0–10 cm layer at the Northern point present a moderate potential risk factor status (Er=51.4). Considering the different elements included in this index, all the RI values obtained are lower than 150, thus the potential ecological risk status of the analyzed sediments is low.

In Fig. 6 is represented the mode of action information for detected compounds and the number of analyzed versus detected target compounds per use group category. In addition, an environmental risk assessment of the possible negative environmental impacts from these substances in ecosystems was carried out using the ecological Risk Quotient (RQ).

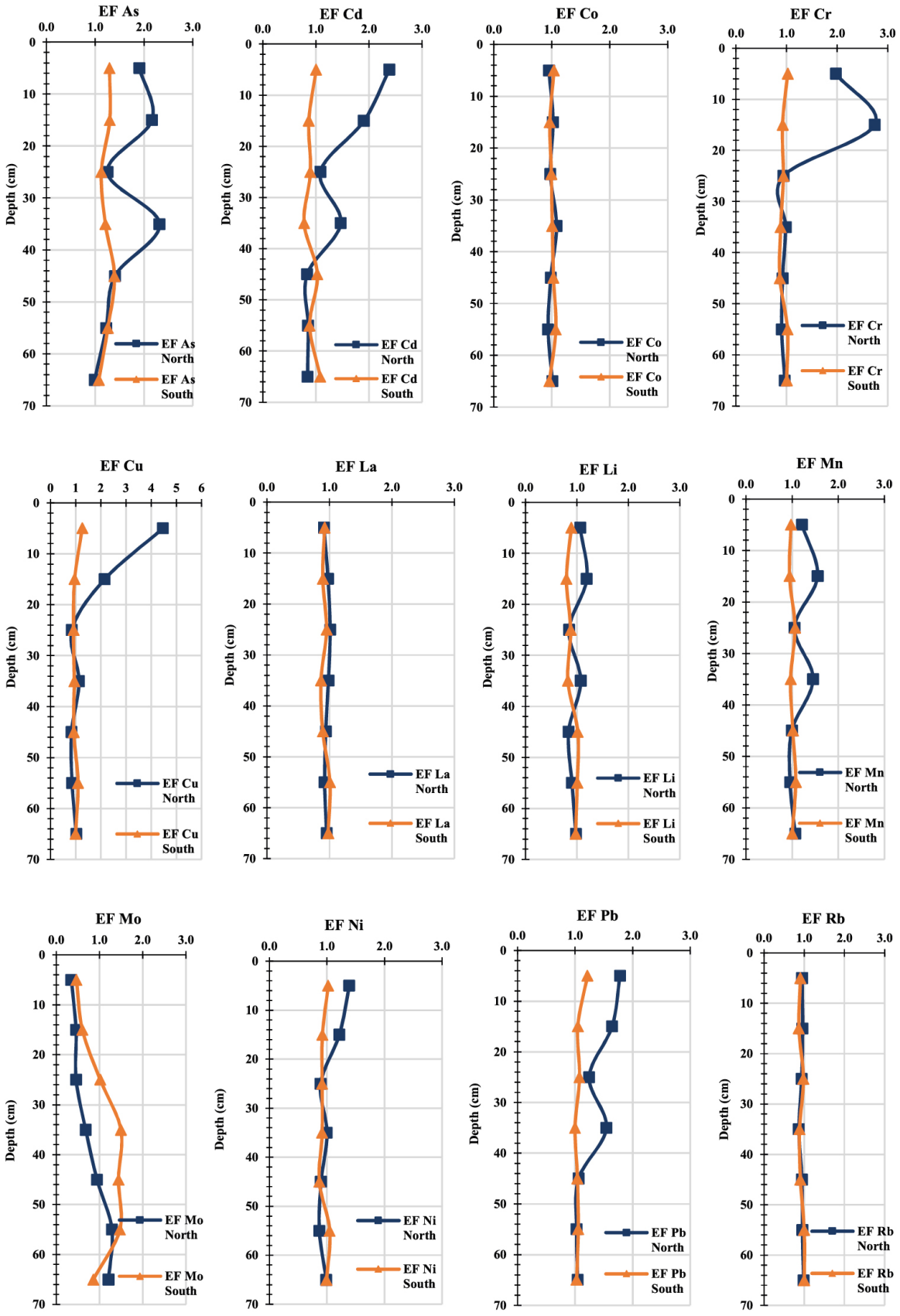


Fig. 4. Enrichment Factor (EF) in the vertical profiles at Northern and Southern sampling points in L'Albufera Lake. EF ranking class: EF ≤ 1: no enrichment; 1 ≤ EF ≤ 3: minor enrichment; 3 ≤ EF ≤ 5: moderately enrichment; 5 ≤ EF ≤ 10: moderately severe enrichment.

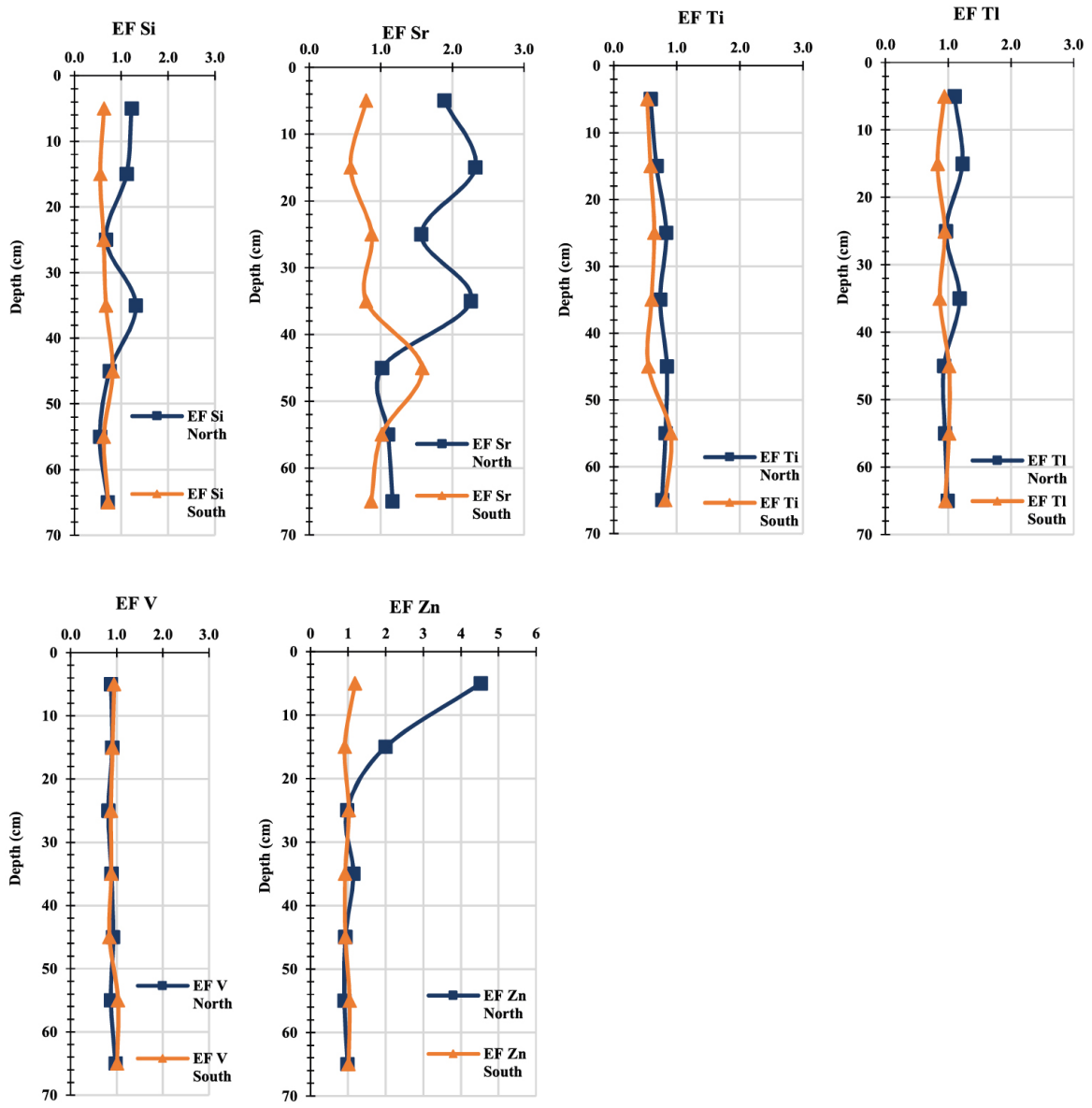


Fig. 4. Continued

The detection frequencies were 19 % PPCPs, 13 % pesticides, 25 % PFASs, 9 % OPFRs and 38 % PAHs in the North. While the detection frequencies were 16 % PPCPs, 11 % pesticides, 21 % PFASs, 9 % OPFRs and 44 % PAHs in the South. In addition, a classification of the compounds was made based on their mode of action according to the conceptual understanding of chemicals presented in [4]. In our study, 77 of the 150 detected compounds (51 %) could be assigned to at least one specific Mode Of Action (MoA) (Fig. 6,A) (The specific MOAs were indicated in supplementary material, Table S1-S4 [1]). The list contains 19 specific MoAs (Fig. 6) where the most prominent category was neuroactive (24) followed by compounds acting on the lipid metabolism (7), and Sterol biosynthesis inhibition antibiotics (6).

$RQ_{Sediment}$ between 0.01 and 0.1 are considered as low ecological risk, between 0.1 and 1.0 as medium ecological risk, and above 1.0 as high ecological risk [5]. The environmental risk assessment for the North the lake indicates that this CECs they have no ecological risk while in the South may pose a medium ecological risk (Tables 7 and 8).

Table 3
Mean concentrations ± SD (standard deviation) (ng g^{-1} dry weight) of detected OCs in sediment core from Northern part in the lake of the natural park of LÁlbufera ($n = 3$).

Compound	Concentration (ng g^{-1}) ± SD								
	Sediment Depth (cm)								
Pesticides	**0–10**	**10–20**	**20–30**	**30–40**	**40–50**	**50–60**	**60–70**	**LOD**	**LOQ**
Acetamiprid	28.6 ± 0.82	16.3 ± 0.95	13.3 ± 0.95	17.2 ± 0.29	13.7 ± 0.54	12.5 ± 0.68	15.9 ± 0.99	0.03	0.10
Azoxyxtrobin	nd	nd	nd	nd	0.81±0.18	0.16±0.01	nd	0.03	0.10
Diazinon	nd	nd	0.16±0.05	nd	nd	nd	nd	0.03	0.10
Fluvalinate	8.68 ± 3.17	12.2 ± 2.78	15.4 ± 4.04	12.2 ± 3.99	11.9 ± 3.91	14.8 ± 2.37	nd	0.34	1.00
Imazalil	nd	nd	nd	nd	nd	nd	nd	0.25	0.75
Molinate	7.78 ± 0.07	8.96 ± 0.71	9.29 ± 0.66	9.04 ± 0.64	10.81 ± 0.95	10.6 ± 1.48	nd	0.42	1.25
Omethoate		1.28 ± 0.60	nd	0.97 ± 0.10	0.86 ± 0.11	0.24 ± 0.05	nd	0.25	0.75
Tebuconazole	4.49 ± 0.58	nd	nd	nd	nd	nd	nd	0.33	1.00
Thiabendazole	2.46 ± 0.31	2.21 ± 0.47	nd	nd	nd	nd	nd	0.33	1.00
Tricyclazol	0.14 ± 0.02	nd	nd	nd	nd	nd	nd	0.04	0.12
PPCPs									
Bisphenol A	9.74 ± 1.29	9.34 ± 0.90	7.69 ± 1.96	2.33 ± 0.28	1.04 ± 0.64	1.09 ± 0.77	0.73 ± 0.31	0.07	0.21
ButylParaben	0.38 ± 0.13	0.36 ± 0.15	0.28 ± 0.06	0.30 ± 0.08	0.32 ± 0.15	0.34 ± 0.09	0.29 ± 0.17	0.03	0.10
Codeina	0.95 ± 0.53	nd	nd	nd	nd	nd	nd	0.15	0.45
EthylParaben	7.56 ± 1.16	6.12 ± 2.06	5.22 ± 1.78	6.61 ± 0.81	5.81 ± 0.23	6.09 ± 2.07	6.29 ± 1.00	0.25	0.75
MethylParaben	2.53 ± 0.76	2.43 ± 0.29	2.06 ± 0.63	2.32 ± 0.28	8.78 ± 0.62	10.5 ± 0.87	3.68 ± 0.32	0.25	0.75
PropylParaben	0.69 ± 0.10	0.61 ± 0.02	0.47 ± 0.07	0.36 ± 0.05	0.77 ± 0.11	0.63 ± 0.09	0.38 ± 0.09	0.04	0.12
Salicylic Acid	5.80 ± 1.05	4.02 ± 1.14	3.52 ± 0.68	4.25 ± 1.02	9.31 ± 1.57	8.73 ± 0.57	4.72 ± 1.12	0.42	1.25
PFASs									
HFPO-DA	1.02 ± 0.39	nd	nd	nd	nd	nd	nd	0.25	0.75
PFDA	0.27 ± 0.03	nd	nd	nd	nd	nd	nd	0.04	0.12
PFHxA	0.16 ± 0.08	nd	nd	nd	nd	nd	nd	0.03	0.10
PFOA	0.69 ± 0.04	0.26 ± 0.02	0.24 ± 0.05	0.26 ± 0.03	0.20 ± 0.02	0.17 ± 0.03	0.16 ± 0.02	0.03	0.10
PFOS	8.79 ± 0.29	3.95 ± 0.54	2.73 ± 0.74	1.72 ± 1.02	1.02 ± 1.16	0.91 ± 1.23	0.89 ± 1.01	0.03	0.10
PFPeA	0.22 ± 0.16	0.13 ± 0.02	0.11 ± 0.01	0.25 ± 0.04	0.15 ± 0.01	0.13 ± 0.03	0.16 ± 0.01	0.03	0.10
PFRs									
TnBP	1.84 ± 0.79	1.81 ± 0.79	1.66 ± 0.67	1.84 ± 0.43	1.81 ± 0.64	2.18 ± 0.74	1.97 ± 0.47	0.25	0.75
PAHs									
Naphthalene	286.8 ± 51.2	nd	nd	nd	nd	nd	nd		
Acenaphthylene	33.9 ± 5.36	32.42 ± 2.82	29.7 ± 4.03	nd	nd	nd	nd		
Acenaphthene	31.68 ± 3.18	32.69 ± 2.29	27.70 ± 1.78	22.12 ± 0.68	30.36 ± 0.44	31.37 ± 1.10	23.37 ± 2.91		
Fluorene	20.70 ± 2.07	18.70 ± 3.86	24.77 ± 0.94	23.52 ± 1.63	9.89 ± 1.49	9.92 ± 1.42	5.20 ± 0.52		
Phenanthrene	186.9 ± 0.99	521.4 ± 4.00	271.5 ± 2.47	345.3 ± 46.5	343.2 ± 12.9	nd	nd		
Fluoranthene	20.44 ± 2.28	18.36 ± 3.00	20.32 ± 3.00	15.21 ± 0.99	15.91 ± 0.46	13.30 ± 0.93	14.32 ± 1.04		
Pyrene	nd	nd	nd	nd	nd	nd	nd		

Table 4
Mean concentrations ± SD (standard deviation) (ng g^{-1} dry weight) of detected OCs in sediment core from Southern part in the lake of the natural park of LÁlbufera ($n = 3$).

Compound	Concentration (ng g^{-1}) ± SD						
	Sediment Depth (cm)						
Pesticides	0–10	10–20	20–30	**30–40**	40–50	**50–60**	60–70
Acetamiprid	27.7 ± 1.3	29.3 ± 4.62	30.5 ± 2.02	29.0 ± 1.41	27.9 ± 0.36	26.5 ± 2.93	24.4 ± 6.71
Azoxyxtrobin	0.18±0.01	nd	nd	nd	nd	nd	Nd
Diazinon	nd	nd	nd	nd	nd	nd	Nd
Fluvalinate	34.2 ± 4.20	67.5 ± 2.51	56.1 ± 13.5	54.4 ± 19.9	29.1 ± 9.42	37.6 ± 3.78	34.9 ± 15.1
Imazalil	10.6 ± 1.07	nd	nd	nd	nd	nd	Nd
Molinate	nd	nd	nd	nd	nd	nd	Nd
Omethoate	nd	9.61 ± 1.10	5.12 ± 0.24	3.68 ± 0.08	nd	nd	Nd
Tebuconazole	132.8 ± 18.10	nd	nd	nd	nd	nd	Nd
Thiabendazole	9.22 ± 0.32	nd	nd	nd	nd	nd	Nd
Tricyclazol	4.75 ± 0.97	nd	nd	nd	nd	nd	Nd
PPCPs							
ButylParaben	0.33 ± 0.08	0.57 ± 0.37	0.36 ± 0.07	0.33 ± 0.11	0.32 ± 0.11	0.24 ± 0.05	0.28 ± 0.16
PropylParaben	0.60 ± 0.07	0.98 ± 0.30	0.46 ± 0.08	0.42 ± 0.11	1.04 ± 0.25	0.26 ± 0.13	0.70 ± 0.13
MethylParaben	3.39 ± 0.11	8.53 ± 2.27	3.16 ± 0.89	2.35 ± 0.64	3.63 ± 0.47	1.63 ± 0.66	3.73 ± 0.42
EthylParaben	5.22 ± 0.71	4.54 ± 1.09	7.36 ± 4.35	4.51 ± 1.02	5.11 ± 0.05	4.37 ± 1.12	5.19 ± 0.63
Bisphenol A	5.55 ± 0.98	2.24 ± 0.91	2.59 ± 0.32	2.09 ± 0.66	2.51 ± 0.85	6.27 ± 1.57	1.60 ± 0.20
Salicylic Acid	7.81 ± 0.83	9.10 ± 1.04	4.04 ± 0.72	2.72 ± 0.31	3.07 ± 0.11	2.19 ± 0.19	2.45 ± 0.19
PFASs							
HFPO-DA	nd	nd	1.05 ± 0.26	nd	nd	1.08 ± 0.15	Nd
PFDA	0.24 ± 0.06	nd	nd	nd	nd	nd	Nd
PFHxA	nd	nd	nd	nd	nd	nd	Nd
PFOA	0.55 ± 0.09	0.26 ± 0.10	0.28 ± 0.10	0.29 ± 0.11	0.27 ± 0.13	0.33 ± 0.29	0.20 ± 0.14
PFOS	5.59 ± 0.71	1.35 ± 0.74	1.11 ± 0.74	0.68 ± 0.82	0.85 ± 1.12	0.79 ± 1.10	0.77 ± 1.10
PFPeA	1.08 ± 0.35	0.13 ± 0.01	0.18 ± 0.05	0.16 ± 0.05	0.16 ± 0.01	0.19 ± 0.01	0.17 ± 0.01
PFRs							
TnBP	2.02 ± 0.79	1.65 ± 0.51	2.14 ± 0.69	2.01 ± 0.14	2.06 ± 0.46	1.66 ± 0.19	2.04 ± 0.24
PAHs							
Naphthalene	156.04 ± 11.49	101.45 ± 6.24	nd	nd	nd	nd	Nd
Acenaphthylene	37.55 ± 1.96	35.52 ± 0.90	nd	nd		nd	Nd
Acenaphthene	9.73 ± 0.23	10.60 ± 0.44	8.70 ± 0.44	9.17 ± 0.29	7.68 ± 0.51	8.33 ± 0.30	6.71 ± 0.18
Fluorene	13.13 ± 0.24	3.99 ± 0.11	5.27 ± 0.30	15.60 ± 0.17	4.56 ± 0.18	1.39 ± 0.18	3.77 ± 0.11
Phenanthrene	22.28 ± 1.24	11.84 ± 0.72	17.67 ± 0.37	nd	nd	nd	Nd
Fluoranthene	26.50 ± 0.27	40.92 ± 0.74	73.75 ± 0.27	23.27 ± 0.11	17.06 ± 0.51	12.37 ± 0.39	11.56 ± 0.11
Pyrene	30.32 ± 0.96	26.52 ± 1.01	27.45 ± 2.00	nd	nd	nd	Nd

Table 5
Spearman correlation coefficients between A) total heavy metal and metalloids concentrations B) EDTA-extractable heavy metal and metalloids concentrations and some physical and chemical sediment properties.

a) Total HMs and metalloids	C_{org} (%)	IC (%)	TN (%)	TS (%)	Clay (%)	Silt (%)	Sand (%)
As	0.618*	NS	0.587*	NS	NS	NS	NS
Cd	0.631*	NS	0.538*	NS	NS	NS	NS
Co	NS	−0.916**	NS	0.908**	0.811*	−0.775*	NS
Cr	NS	NS	NS	NS	NS	NS	NS
Cu	NS	NS	NS	NS	NS	NS	NS
La	NS	−0.815**	NS	0.798**	0.775*	NS	NS
Li	NS	−0.824**	−0.613*	0.710**	NS	NS	NS
Mn	NS	−0.846**	NS	0.785**	NS	−0.775*	NS
Mo	−0.807**	NS	−0.798**	NS	NS	NS	NS
Ni	NS	−0.807**	NS	0.653*	NS	NS	NS
Pb	NS	−0.644*	NS	0.600*	NS	NS	NS
Rb	NS	−0.846**	NS	0.727**	NS	NS	NS
Si	NS	NS	NS	NS	NS	NS	NS
Sr	NS	0.785**	0.552*	−0.582*	NS	NS	NS
Ti	NS	NS	NS	NS	0.865*	NS	NS
Tl	NS	−0.855**	NS	0.820**	0.775*	NS	NS
V	NS	−0.829**	−0.596*	0.723**	NS	NS	NS
Zn	NS	NS	NS	NS	NS	NS	NS
b) HM extractable and metalloids							
As	.829**	NS	.873**	NS	NS	NS	NS
Cd	.758**	NS	.657*	NS	NS	NS	NS
Co	.727**	NS	.802**	NS	NS	NS	NS
Cr	NS	NS	NS	NS	−0.811*	.793*	NS
Cu	.855**	NS	.873**	NS	NS	NS	NS
La	NS	−0.538*	NS	.604*	.793*	NS	NS
Li	NS	NS	NS	.569*	NS	NS	NS
Mn	NS	NS	NS	NS	.829*	−0.847*	NS
Mo	NS	NS	NS	NS	.793*	NS	NS
Ni	.688**	NS	.727**	NS	NS	NS	NS
Pb	.811**	NS	.899**	NS	NS	NS	NS
Rb	−0.833**	NS	−0.820**	NS	NS	NS	NS
Si	−0.714**	NS	−0.714**	NS	NS	NS	NS
Sr	.644*	NS	.587*	NS	NS	NS	NS
Ti	NS	NS	NS	NS	.775*	NS	NS
Tl	NS	NS	NS	NS	NS	−0.847*	.777*
V	NS	NS	NS	NS	NS	NS	NS
Zn	.815**	NS	.802**	NS	NS	NS	NS

NS: not significant; *: significant at $p < 0.05$; **: significant at $p < 0.01$.

4. Experimental Design, Materials and Methods

4.1. AMS ^{14}C dating and sediment characteristics

The Accelerator Mass Spectrometry (AMS) measurement is performed on graphite produced by the reduction of a carbon dioxide (CO_2) sample over cobalt catalysis [6,7]. CO_2 is obtained from the combustion of the sample at more than 800 °C in an atmosphere with 100 % oxygen. The CO_2 is first dried with methanol (MeOH) [8] (dry ice) and collected in liquid nitrogen for its subsequent graphitization reaction. Identical reaction is performed according to reference standards, our in-house quality assurance samples, and background samples that ensure systematic chemical reactions. The analytical result ("BP" or "pMC") is obtained by measuring the C^{14}/C^{13} ratio of the sample relative to C^{14}/C^{13} in oxalic acid II (NIST-4990C) in one of the many own particle accelerators and using a SNICS ion source. The AMS dating result is corrected as a function of total fractionation using the $\delta^{13}C$ value of the machined graphite.

Conventional radiocarbon ages have been corrected to account for fractionation effects and calibration was performed using 2020 calibration databases. Results cited are accredited by

Table 6
Spearman correlation coefficients between of the concentration of OCs and some physical and chemical sediment properties.

Compounds	North							South						
	C_{org} (%)	IC (%)	TN (%)	TS (%)	Clay (%)	Silt (%)	Sand (%)	C_{org} (%)	IC (%)	TN (%)	TS (%)	Clay (%)	Silt (%)	Sand (%)
Acetamiprid	NS	NS	NS	−0.857*	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Azoxystrobin	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Diazinon	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Fluvalinate	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Imazalil	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Molinate	NS	−886*	−0.886*	.829*	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Omethoate	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Tebuconazole	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Thiabendazole	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Tricyclazol	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Bisphenol A	NS	NS	.893**	NS	NS	NS	−0.797*	NS	NS	NS	NS	NS	NS	NS
ButylParaben	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
EthylParaben	NS	NS	NS	−893**	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
MethylParaben	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PropylParaben	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Salicylic Acid	NS	NS	NS	NS	NS	NS	NS	NS	NS	.786*	NS	NS	NS	NS
Codeine	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Naphthalene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Acenaphthylene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Acenaphthene	NS	NS	NS	NS	NS	.775*	NS	.929**	−893**	.929**	.964**	NS	NS	NS
Fluorene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Phenanthrene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Fluoranthene	NS	NS	NS	NS	NS	NS	NS	NS	NS	.821*	NS	NS	NS	NS
Pyrene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
HFPO-DA	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PFDA	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PFHxA	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PFOA	.857*	NS	.964**	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PFOS	.786*	NS	.929**	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PFPeA	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
TnBP	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

NS: not significant; *: significant at $p < 0.05$; **: significant at $p < 0.01$.

ISO/IEC 17025:2017 standards, PJLA Accreditation #59423 for testing purposes. Conventional Radiocarbon Ages and sigmas were rounded to the nearest 10 years in accordance with the conventions established by the 1977 International Radiocarbon Conference. When accounting statistics generate sigmas of less than +/- 30 years, a conservative result of +/− 30 BP. The cited $^{\delta 13}C$ values were measured separately on an IRMS (Isotope Ratio Mass Spectrometer). They are NOT $^{\delta 13}C$ values obtained in an AMS which would include fractionation effects derived from natural, Chemical, and AMS-induced sources. The “Conventional Radiocarbon Age” was calculated using the half-life established by Libby (5568 years), corrected for total isotopic fractionation and used for calendar calibration where applicable. Age is rounded to the nearest 10 years and is expressed as radiocarbon years before the present (BP), the “present” being = AD 1950. Results greater than the modern reference are expressed as “percent modern carbon” (PMC for its acronym in English). The modern reference standard was 95 % of the NIST 14C log SRM-4990C (oxalic acid). Errors cited are 1 sigma count statistics. Calculated sigmas less than 30 BP from the Conventional Radiocarbon Age are rounded conservatively to 30. The $^{\delta 13}C$ values are for the material itself (not the d13C value obtained by AMS). The $^{\delta 13}C$ and $^{\delta 15}C$ values are relative to the VPDB standard.

Sediment characteristics were established in the laboratory using standard procedures. The total nitrogen (TN), total Sulphur (TS), total carbon (TC) of the sediment cores were determined using a LECO CNS928. Carbonates were measured using the Bernard calcimeter method (MAPA, 1994) and grain size distribution was measured using Bouyoucos hydrometer (Bouyoucos, 1962). The physical-chemical parameters of the sediment samples and the grainsize distribution (i.e. percent silt, clay and sand).

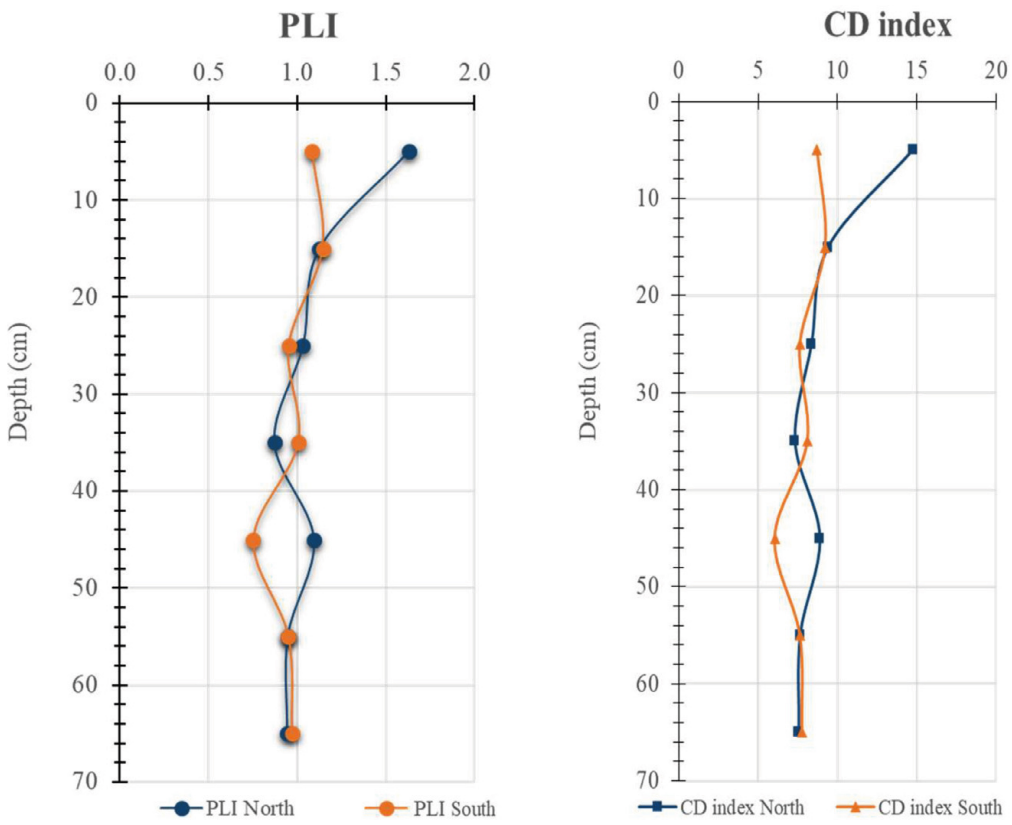


Fig. 5. Left side: Contamination Load Index (PLI): PLI >1 indicates that the site is polluted, PLI ≤ 1 indicates no contamination [10]. Right side: Contamination Degree (CD) classify the contamination status in: CD<6 low; 6< CD<12 moderate; 12<CD<24 considerable; CD>24 very high [9]. Both indexes are calculated including eight elements (As, Cd, CO, Cr, Cu, Ni, Pb and Zn).

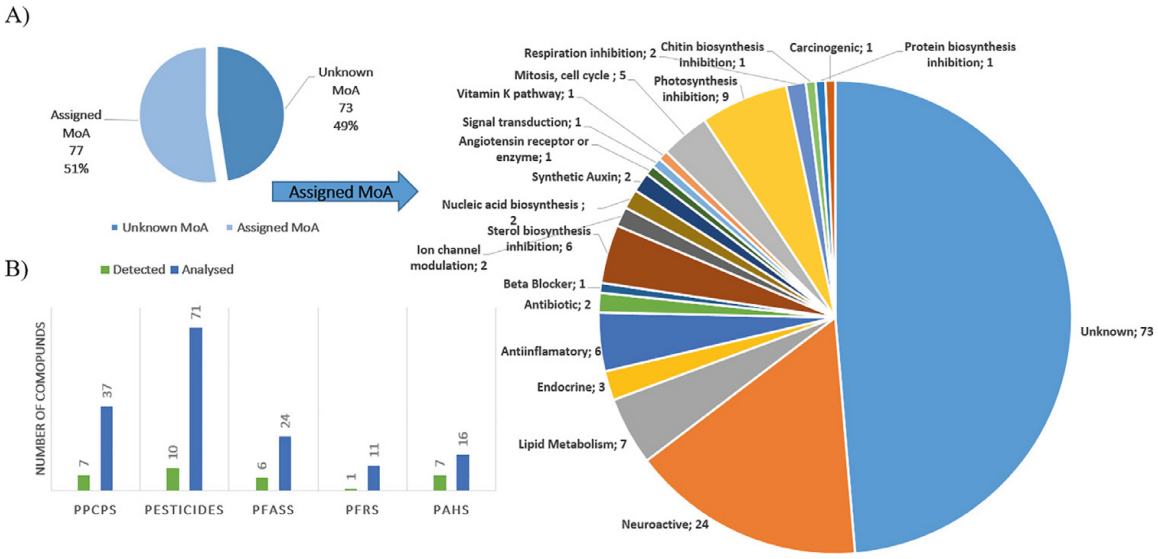


Fig. 6. A) Mode of action information for detected compounds. Left: fraction of assigned and unknown MOAs. Right: pie-chart MOA information of the detected target compounds. B) Quantitative LC-HRMS screening results. Left: number of analysed (blue colored bar) versus detected (green colored bar) target compounds per use group category. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)

Table 7
$PNEC_{sediment}$ values calculated in the most superficial layer of the sediment core in the North.

Compounds	MEC $\mu g \cdot kg^{-1}$	$PNEC_{fresh\ water}$ $\mu g \cdot L^{-1}$	k_p no units	$PNEC_{sediment}$ $\mu g \cdot kg^{-1}$	$RQ_{sediment}$ no units
Acetamiprid	28.581	0.024	20.1	386.3	$7.40 \cdot 10^{-2}$
Azoxystrobin	–	0.200	1008.3	161,328.7	–
Diazinon	–	0.010	6362.0	50,895.8	–
Fluvalinate	8.679	0.003	33,388,091.7	88,144,562.0	$9.85 \cdot 10^{-8}$
Imazalil	–	0.870	21,066.5	14,662,257.3	–
Molinate	7.780	3.800	5171.2	15,720,457.5	$4.95 \cdot 10^{-7}$
Omethoate	–	0.004	0.6	1.9	–
Tebuconazole	4.485	0.240	15,980.5	3,068,264.7	$1.46 \cdot 10^{-6}$
Thiabendazole	2.455	1.200	941.0	903,364.1	$2.72 \cdot 10^{-6}$
Tricyclazole	0.136	0.470	80.1	30,114.8	$4.53 \cdot 10^{-6}$
Bisphenol A	9.735	0.240	6661.8	1,279,065.6	$7.61 \cdot 10^{-6}$
ButylParaben	0.376	5.060	11,846.5	47,954,801.9	$7.85 \cdot 10^{-6}$
Codeine	0.946	7.190	49.4	284,060.3	$3.33 \cdot 10^{-6}$
EthylParaben	7.564	13.300	941.0	10,012,285.5	$7.55 \cdot 10^{-7}$
MethylParaben	2.530	5.000	290.8	1,163,192.5	$2.18 \cdot 10^{-7}$
PropylParaben	0.690	12.300	3496.2	34,402,238.0	$2.00 \cdot 10^{-8}$
Salicylic Acid	5.800	18.000	580.2	8,355,146.9	$6.94 \cdot 10^{-7}$
HFPO-DA	1.020	–	31,885.4	0.0	–
PFDA	0.272	0.170	10,083,042.5	1,371,293,778.1	$1.98 \cdot 10^{-10}$
PFHxA	0.161	140.000	9629.2	1,078,473,851.7	$1.49 \cdot 10^{-10}$
PFOA	0.690	0.180	205,869.3	29,645,179.8	$2.33 \cdot 10^{-8}$
PFOS	8.787	0.002	98,535.2	157,656.4	$5.57 \cdot 10^{-5}$
PFPeA	0.222	3.910	8009.2	25,052,919.4	$8.87 \cdot 10^{-9}$
TnBP	1.838	37.000	21,066.5	623,567,264.9	$2.95 \cdot 10^{-9}$
Naphthalene	286.834	–	7474.7	0.0	–
Acenaphthylene	33.900	0.530	31,885.4	13,519,401.1	$2.51 \cdot 10^{-6}$
Acenaphthene	31.680	3.700	26,521.1	78,502,467.6	$4.04 \cdot 10^{-7}$
Fluorene	20.700	0.250	48,260.5	9,652,095.1	$2.14 \cdot 10^{-6}$
Phenanthrene	186.903	–	118,465.4	0.0	–
Fluoranthene	20.100	0.006	529,165.6	2,666,994.6	$7.54E \cdot 10^{-6}$
Pyrene	–	0.028	482,604.8	10,810,346.5	–
$RQ_{sediment} = \sum MEC/\ PNECsediment$					$7.41 \cdot 10^{-2}$

4.2. Reagents and chemicals

HPLC grade MeOH ≥ 99.8 % purity was purchased from VWR Chemicals® (Radnor, PA, USA) and ammonium formate (NH_4HCO_2), formic acid (CH_2O_2), ammonium fluoride (NH_4F) and acetone (CH_3COCH_3) were purchased from Alfa Aesar (Karlsruhe, Germany). Acetonitrile (ACN) ≥ 99.9 % purity was from Merck (Darmstadt, Germany). High purity water was obtained using a Milli-Q water purification system (Millipore, Milford, MA, USA). Citric acid, Na_2HPO_4 and EDTA were purchased from Alfa Aesar (Karlsruhe, Germany). Octadecylsilica (C18) and primary-secondaryamine (PSA) were purchased from Análisis Vínicos (Tomelloso, Spain). Magnesium sulfate ($MgSO_4$) and sodium sesquihydrate citrate [$HOC(COOH)\ (CH_2COONa)_2\ 1.5\ H_2O$] from Alfa Aesar (Karlsruhe, Germany) and sodium chloride (NaCl) and trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$) from Prolabovwr (Leuven, Belgium). Strata-X-33 µm polymeric reversed phase (200 mg/6 mL) were from Phenomenex (Torrance, CA, USA). The 1.5 mL amber glass vials with stoppers 99 mm + Septum Sil /PTFE used to inject the samples were from Análisis Vínicos S.L. (Tomelloso, Spain) and the 250 µL polypropylene inserts were from Agilent Technologies (Santa Clara, CA, United States). Nylon 0.22 µm filters were purchased from Membrane Solutions (Plano, TX, USA). Polypropylene/polyethylene syringes were manufactured by BRAUN and distributed by Scharlab S.L. (Barcelona, Spain). For the solid phase extraction (SPE) Phenomenex Strata-X-33 µm Polymeric Reversed Phase (200 mg/6 mL) cartridges and a vacuum manifold Supelco Visiprep 57030- U (Sigma-Aldrich, St. Louis, Missouri, USA) were used. The 15 mL and 50 mL polypropylene centrifuge Falcon tubes were from VWR International Eurolab (Barcelona,

Table 8
$PNEC_{sediment}$ values calculated in the most superficial layer of the sediment core in the South.

Compounds	MEC $\mu g \cdot kg^{-1}$	$PNEC_{freshwater}$ $\mu g \cdot L^{-1}$	k_p no units	$PNEC_{sediment}$ $\mu g \cdot kg^{-1}$	$RQ_{sediment}$ no units
Acetamiprid	27.736	0.024	14.1	271.2	$1.02 \cdot 10^{-1}$
Azoxystrobin	0.179	0.200	708.1	113,288.6	$1.58 \cdot 10^{-6}$
Diazinon	–	0.010	4467.5	35,740.1	–
Fluvalinate	34.224	0.003	23,445,859.9	61,897,070.2	$5.53 \cdot 10^{-7}$
Imazalil	10.649	0.870	14,793.3	10,296,162.9	$1.03 \cdot 10^{-6}$
Molinate	–	3.800	3631.3	11,039,254.6	–
Omethoate	–	0.004	0.4	1.3	–
Tebuconazole	132.760	0.240	11,221.9	2,154,603.7	$6.16 \cdot 10^{-5}$
Thiabendazole	9.223	1.200	660.8	634,362.3	$1.45 \cdot 10^{-5}$
Tricyclazole	4.753	0.470	56.2	21,147.3	$2.25 \cdot 10^{-4}$
Bisphenol A	5.547	0.240	4678.1	898,188.3	$6.18 \cdot 10^{-6}$
ButylParaben	0.328	5.060	8318.9	33,674,927.5	$9.75 \cdot 10^{-9}$
Codeina	–	7.190	34.7	199,473.4	–
EthylParaben	5.221	13.300	660.8	7,030,849.4	$7.43 \cdot 10^{-7}$
MethylParaben	3.394	5.000	204.2	816,819.6	$4.16 \cdot 10^{-6}$
PropylParaben	0.595	12.300	2455.1	24,158,016.0	$2.46 \cdot 10^{-8}$
Salicylic Acid	7.815	18.000	407.4	5,867,169.8	$1.33 \cdot 10^{-6}$
HFPO-DA	–	–	22,390.6	–	–
PFDA	0.244	0.170	7,080,536.5	962,952,964.2	$2.53 \cdot 10^{-10}$
PFHxA	–	140.000	6761.9	757,328,304.7	–
PFOA	0.550	0.180	144,566.0	20,817,504.1	$2.64 \cdot 10^{-8}$
PFOS	5.589	0.002	69,193.6	110,709.8	$5.05 \cdot 10^{-5}$
PFPeA	1.081	3.910	5624.3	17,592,716.7	$6.15 \cdot 10^{-8}$
TnBP	2.015	37.000	14,793.3	437,882,790.5	$4.60 \cdot 10^{-9}$
Naphthalene	156.800	–	5248.9	–	–
Acenaphthylene	37.500	0.530	22,390.6	9,493,623.9	$3.95 \cdot 10^{-6}$
Acenaphthene	9.870	3.700	18,623.7	55,126,177.2	$1.79 \cdot 10^{-7}$
Fluorene	13.007	0.250	33,889.6	6,777,915.7	$1.92 \cdot 10^{-6}$
Phenanthrene	22.170	–	83,189.1	–	–
Fluoranthene	26.451	0.006	371,591.838	1,872,822.863	$1.41 \cdot 10^{-5}$
Pyrene	30.240	0.028	338,895.784	7,591,265.560	$3.98 \cdot 10^{-6}$
$RQ_{sediment} = \sum MEC / PNECsediment$					$1.03 \cdot 10^{-1}$

Spain). Sediment samples were lyophilized using a Sentry 2.0 lyophilizer from VirTis SP Scientific manufacturer (Gardiner, NY, USA). The sampler combined sample concentrator model SBH-CONC/1 and heating plate model SBH130D/3 were provided by (Stuart®UK).

4.3. Samples extraction

4.3.1. Sediment extraction for moderately polar compounds

1 g of sediment lyophilized was weighed into a 50 mL Falcon tube and moistened with 7.5 mL of water. Then, 10 mL of ACN were added. The contents were vigorously shaken by hand for 1 min. A mixture of 6 g $MgSO_4$, 1.5 g NaCl, 1.5 g $C_6H_5Na_3O_7 \cdot 2\ H_2O$, and 0.75 g [HOC(COOH)$(CH_2COONa)_2$ and 1.5 H_2O] were added. Subsequently, the tube was vigorously shaken again for 3 min, followed by vortexing for 1 min and centrifugation at 2465 rcf for 5 min.

An aliquot of 1 mL of the supernatant was transferred to a 15 mL centrifuge tube containing 50 mg PSA, 150 mg MgSO4, and 50 mg of C18 and the tube was vigorously shaken again for 1 min. Then vortexed for 1 min followed by centrifugation for 5 min at 2465 rcf. The cleaned extract was transferred into a screw cap vial. Filter the supernatant with a 0.45 µm PTFE / 0.22 µm filter.

4.3.2. Sediment extraction for polar compounds

1 g lyophilized sample with 5 mL of Milli-Q water, 5 mL of MeOH, 5 mL Mcllvaine – EDTA buffer (100 mL citric acid 0.1 M, 62.5 mLNa_2HPO_4 0.2 M and 6.05 g EDTA-2Na, pH 4) and 50 µL of a labeled internal standards mix at a concentration of 1 µg mL^{-1} was spiked into each sample were mixed, vortexed for 5 min, sonicated for 10 min followed by centrifugation for 5 min at 2465 rcf. The supernatant was collected and made up to 200 mL with Milli-Q water and sonicated for 10 min. Then vortexed for 1 min followed by centrifugation for 5 min at 2465 rcf. Cartridges of stationary phases were used: Phenomenex Strata-X (33 µm, polymeric reversed phase, 200 mg/6 mL). All samples were passed through cartridges by use of a vacuum. These cartridges were activated before the passage of the sample with 6 mL of MeOH, 6 mL of Milli-Q water, and 200 mL of water with supernatant was passed through the cartridges under vacuum at 400 mba h^{-1} Pa^{-1} (flow rate: 10 mL min^{-1}). The cartridges were then washed with 6 mL of Milli-Q and dried for 15 min. The analytes were eluted with 6 mL of MeOH and 3 mL of MeOH–dichloromethane (50:50 v/v) and collected in a 15 mL plastic Falcon tube of polypropylene. Extracts were evaporated to dryness under a gentle stream of nitrogen at 40°C. The residue was redissolved in 500 µL with water-MeOH (70:30, v/v) vortexed for 1 min and sonicated for 3 min. The extract was added to a 1.5 mL glass vial with a 250 µL polypropylene insert, using a Nylon filter (0.22 µm pore size and 4 mm diameter) coupled to a disposable polypropylene/polyethylene syringe and stored for PPCPs, PFASs and OPFRs analysis. Extracts were stored at −20 °C until injection.

4.3.3. Sediment extraction for polycyclic aromatic hydrocarbons (PAHs)

1 g of sediment previously lyophilized was placed into a 15 mL Falcon tube containing 6 mL hexane–dichloromethane (1:1 v/v) and 50 µL of labeled internal standards mix at a concentration of 1 µg mL^{-1} was spiked into each sample. The tube was then subjected to ultrasonic bath treatment for 10 min. Afterwards, the solution was centrifuged during 5 min at 2500 rpm. These two last steps were repeated three times. The sonicated extracts were evaporated in a rotary evaporator to almost to dryness (0.5 mL approximately) for further clean up. In both cases the extracts were purified following a clean-up procedure using solid-phase extraction cartridges of neutral alumina. Briefly, Alumina-N SPE (Supelclean™ LC-Alumina-N SPE Tube bed wt. 2 g, volume 6 mL) were preconditioned with 2 mL hexane. A sample of 0.5 mL was passed through the cartridges without vacuum and elute with 100 mL of hexane followed by 20 mL of hexane dichloromethane (2:1 v/v) concentrate to 250 µL. Then 250 µL of the extract was added to a 1.5 mL LC vial. Extracts were stored at −20°C until injection.

4.3.4. Sediment extraction for total content of heavy metals (HMs) and metalloids

Sediment samples (fraction < 0.125 mm Ø) were homogenized in an agate mortar, and then 0.5 g ± 0.05 digested by HCl-HNO3 (3:1) in Teflon beakers using a Millestone® Ethos D PLUS microwave digester by ramping to 200 °C in 20 min and holding for 15 min at 200 °C. Samples were digested by duplicate. The digested products were then placed into a 50 mL tube and centrifuged for 5 min at 3500 rpm (HEAREUS® Megafuge 1.0 centrifuge). The supernatant was then transferred to a 25 mL volumetric flask and made up to the mark using ultrapure water. The extracts obtained were stored at 4 °C, until HM measurement.

4.3.5. Sediment extraction for heavy metal and metalloids available fraction

Metal bioavailability was assessed by extraction with analytical grade EDTA that has been found to be the reagent that best correlates the extractable fraction of an element in the sediment with the amount that living organisms can adsorb under normal conditions and provides more information about its bioavailability. A solution of 0.05 M EDTA at pH 7 was used following the procedure described in the reference material BCR®-700. Subsequently, 3 g ± 0.05 of pulverized soil was weighed with an agate mortar, then placed in a 50 mL centrifuge tube and 30 mL of EDTA was added. Tubes were shaken for 90 min at 180 rpm on the P SELECTA® Rotabit horizontal shaker, and then centrifuged for 10 min at 3500 rpm in the HEAREUS® Megafuge 1.0 centrifuge. The resulting supernatant was transferred to 30 mL polyethylene tubes,

prior filtering the solution with ALBET® paper filters of 2–4 µm pore Ø, and stored at 4 °C until HM quantification. Concentrations of pseudo total and extractable fractions of HM were measured using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific® ICAP6500 DUO). The detection limits of the analytical procedure were 0.01 mg L^{-1}.

Data quality was ensured by digesting and measuring blanks and the standard reference materials BCR®-143R and BCR®-700 for the total and extractable fractions, respectively. The accuracy, expressed as a recovery of the reference material was between 91 and 120 % for the studied elements. Concentration of elements in procedural blanks were undetected. The proportion of the EDTA-extractable fraction relative to the total concentration of the metal and metalloids is used as an indicator of the quantity of metal and metalloids available for organisms and as an index of relative mobility since the toxicity of trace elements depends not only on their total concentration, but also on their mobility and reactivity with other components of the ecosystem (Solano, 2005).

The results of the quantification of the total content of the 25 HMs and metalloids studied (hereafter referred to as metals) indicate that all the elements analyzed can be correctly quantified by ICP-OES, except Bi, Cd and Sb, which show concentrations below the detection this technique. Due to its interest, total Cd has been measured by ICP-MS. Regarding the EDTA extractable heavy metal fraction (corresponding to the bioavailable fraction), all elements have been quantified by ICP-OES, except for As (in some samples), Be, Bi, B, Bd, Cd, Sb and Se. Of these elements, As and Cd were measured by ICP-MS. Therefore, only the results of 20 elements are presented in this work (Al, As, Cd, Co, Cr, Cu, Fe, La, Li, Mn, Mo, Ni, Pb, Rb, Si, Sr, Ti, Tl, V and Zn).

Pesticides, PPCPs, PFASs and OPFRs were analyzed using reversed-phase liquid-chromatography (LC) separation on a Thermo Ultimate 3000 LC. PAHs were analyzed using a gas chromatography–mass spectrometry (GC–MS) JASCO Series YL6900. Further information on settings and instrument parameters are described in Tables 9 and 10.

4.4. Statistical analysis

IBM SPSS version 26.0 was used for statistical analysis. Normality of the data was assessed with Kolmogorov–Smirnov ($n > 50$) or Shapiro–Wilk ($n < 50$) tests, and Levene's test checked homogeneity of variances. Due to non-normality, Mann–Whitney U (M–W) or Kruskal–Wallis (K–W) tests were employed for parametric analysis. Significance was set at $p < 0.05$. Spearman Rho correlation analysis explored relationships between pollutant concentrations and physical/chemical characteristics of sediment layers. Bivariate correlation analysis at 95 % and 99 % significance levels evaluated connections between age, depth, CECs concentration, and sediment core characteristics.

4.5. Ecological risk assessment of OCs and HMs

4.5.1. Contamination factor (CF) and contamination degree (CD)

CF evaluates the enrichment in metals and metalloids in relation to the background concentrations of each metal and metalloids in sediments using the following equation.

$$CF = \frac{C_{metal}}{C_{background}} \quad (1)$$

where, C_{metal} is the concentration of each metal and metalloids in the sediment sample, and $C_{background}$ is the uncontaminated background level of the metal and metalloids [9].

While CF is calculated for individual elements. CD provides an overall assessment in the sediment contamination of the study sites [9]. CD is calculated using the following equation.

$$CD = \sum_{i}^{n} CF \quad (2)$$

Table 9
Instrumental characteristics used for PAHs determination.

GC Conditions	
Analytical column	Capillary column Zebron ZB-5MS of 30 m × 0.25 mm i.d. with 0.25 µm film thickness
Inyector temperature	280 °C
Splitless time	1.2 min
He flow rate	1 mL min^{-1}
Ionizing energy	70 eV
Oven Programme	60ºC 2 min 30 º C/min 240 ºC 10 min 5 º C/min 290 ºC 10 min

Table 10
Instrumental characteristics used for pesticides, PFASs, OPFRs and PPCPs determination.

LC Conditions	
Analytical column	*Pesticides:* Luna C18 (15.0 cm × 0.21 cm) with a 3 µm particle size (Phenomenex, USA) *PFASs* and *OPFRs:* Kinetex XB-C18: 50.0 × 4.6 mm, 1.7 µm (Phenomenex, USA) *PPCPs:* Kinetex 1.7 µm Biphenyl, 1.7 µm. 50 × 2.1 mm, (Phenomenex, USA)
Column temperature	30 °C
Volume injected	5 µL
Mobile phase	*Pesticides:* (A) Water – (B) MeOH both with 0.1 % Formic Acid and 5 mM Ammonium formate *PFASs*: (A) Water – (B) MeOH both with 10 mM Ammonium formate *OPFRs and PPCPs (for positive mode)*: (A) Water – (B) MeOH both with 0.1 % Formic Acid *PPCPs* (for negative mode): (A) Water – (B) MeOH both with 2.4 mM Ammonium fluoride
Flow rate	*PPCPs:* 0.2 mL min^{-1} *PFASs* and pesticides: 0.3 mL min^{-1} *OPFRs:* 0.2 mL min^{-1}
Linear gradient	*Pesticides*: 0 min (50 % B), 10 min (83 % B), 12 min (83 % B), 12.5 min (98 % B), 15.5 min (98 % B), 16 min (50 % B), and return to the initial conditions (equilibration time 10 min). *PFASs*: 0 min (30 % B), 0.5 min (30 % B), 12 min (95 % B), 21 min (95 % B), and return to the initial conditions (equilibration time 12 min). *OPFRs*: 0 min (30 % B), 0.5 min (30 % B), 12 min (95 % B), 18 min (98 % B), 25 min (98 % B) and 26 min (30 % B), and return to the initial conditions (equilibration time 14 min). *PPCPs*: 0 min (30 % B), 12 min (95 % B), 20 min (95 % B), and return to the initial conditions (equilibration time 12 min).

4.5.2. Enrichment factor (ER)

The enrichment factor divides the concentration of metal and metalloids in the sample and the background, by a normalizer element [2] using Eq. (3). In this study, the normalizer used was Fe.

$$EF = \frac{\frac{C_{metal\ \ sample}}{C_{normalizer\ \ sample}}}{\frac{C_{metal\ \ background}}{C_{normalizer\ \ background}}} \tag{3}$$

4.5.3. Pollution load index (PLI)

PLI provides an overall assessment on the level of HMs contamination [9]. PLI was determined using the following equation:

$$PLI = (CF_1 \times CF_2 \times \ldots \times CF_n)^{1/n} \tag{4}$$

where *CF* is the contamination factor and *n* is the number of HMs considered. According to [10] a PLI value greater than 1 indicates that the site is polluted, whereas a PLI less or equal to 1 indicates no pollution.

Potential ecological risks assessment of OCs in surficial sediment were assessed followed the previous study [11]. The equations are as follows:

$$PNEC_{sediment} = \frac{PNEC_{water} \cdot K_p}{\text{Bulk Density}_{Sediment}} \tag{5}$$

$$K_p = OM \cdot 0.411 \cdot K_{ow} \tag{6}$$

$$RQ_{sediment} = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_{sediment\ \ i}} \tag{7}$$

Where Lowest Predicted No Effect Concentrations ($PNEC_{water}$) ($\mu g\ L^{-1}$) values were extracted from the NORMAN Ecotoxicology Database (https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php) and $PNEC_{sediment}$ ($\mu g\ kg^{-1}$) was calculated with Eq. (5). Therefore,

Table 11
Description of the risk factors Er and RI (based on [9]).

Er value	Potential risk factor status	RI value	Potential ecological risk status
<40	Low	<150	Low
40–80	Moderate	150–300	Moderate
80–160	Considerable	300–600	Considerable
160–320	High	>600	Very high
>320	Very high		

Kp (sediment-water partitioning coefficient) was calculated with Eq. (6) (no unit). OM (organic matter carbon content) was measured as total organic carbon (TOC) in surficial sediment (%); K_{ow} is an octonol-water partition coefficient of a compound, 0.411 is an empirical constant; and bulk density of surface sediment was 1.25 (kg m^3) [12]. MEC is measured environmental concentration (mg kg^{-1}), $RQ_{Sediment}$ (no unit) was calculated with Eq. (7) and it is risk quotient of sediment summing ratios of MEC to $PNEC_{Sediment}$ of each compound.

4.5.4. Ecological risk assessment of HMs

A potential ecological risk index (RI) was used to assess the degree of heavy metal and metalloids contamination in sediments, according to the toxicity of HMs.

$$Er = Tr_{metal} \times CF \tag{8}$$

$$RI = \sum_{i=1}^{7} Er \tag{9}$$

where *Er* is the potential risk factor of a given metal and metalloids, Tr_{metal} is the toxic response factor of metals and metalloids (As = 10; Cd=30; Cu=Pb=5; Zn=1; Cr=Ni=2) and CF is the contamination factor. The various classes of the risk factors *Er* and RI are given in Table 11.

Limitations

This type of essays has several limitations. One is that the length of each core section must be selected a priori, and sometimes, sedimentation ratio data is incorrect. Another limitation is the amount of sample that may be present in each core section, which sometimes is not sufficient to conduct all analyses. Furthermore, as in this case, it can occur that the age of sediments in different sections is not correlational, which complicates the analysis. Another aspect is that not all contaminants being studied are present, and sometimes explaining the profile is complicated.

Ethics Statement

The authors have read and follow the ethical requirements for publication in Data in Brief and confirming that the current work does not involve human subjects, animal experiments, or any data collected from social media platforms.

CRediT Author Statement

Yolanda Soriano: Conceptualization, Methodology, Data curation, Writing – original draft preparation, Writing – review & editing, Visualization. **Eugenia Gimeno-García**: Conceptualization, Methodology, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Julian Campo**: Investigation, Writing – review & editing, Visualization. **Carmen Hernandez-Crespo**: Resources, Writing – review & editing. **Vicente Andreu**: Methodology, Resources, Writing – review & editing. **Yolanda Picó**: Supervision, Project administration, Funding acquisition, Conceptualization, Methodology, Investigation, Writing.

Data Availability

Dataset on trace elements and legacy and emerging organic contaminants concentrations in sediments cores in L'Albufera Natural Park (Valencia, East of Spain): Association with "in-deep" sediment chara (Original data) (Mendeley Data).

Acknowledgments

This work has been supported by the Grant CIPROM/2021/032 funded by the Generalitat Valenciana. Y. Soriano acknowledges her pre-doctoral contract by the grant PRE2019-089042 funded by MCIN/AEI/ 10.13039/501100011033 and by "ESF Investing in your future". The instrumental used in this study has been supported by the project IDFEDER-2021-083 "X-ray of pollution and the effects of the anthropocene/climate change binomial (X pollutants)" action co-financed by the EU through the operational program of the European Regional Development Fund (ERDF) of the Valencian Community 2014–2020.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SECCIÓN 5

Presencia de contaminantes orgánicos en aguas superficiales de las cuencas de los rios Acongagua y Maipo en Chile Central

ARTICLE 06

Co-ocurrence and spatial distribution of organic micropollutans in surface waters of the River Aconcagua and Maipo basins in Central Chile

Science of the Total Environment 954 (2024) 176314

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Co-occurrence and spatial distribution of organic micropollutants in surface waters of the River Aconcagua and Maipo basins in Central Chile

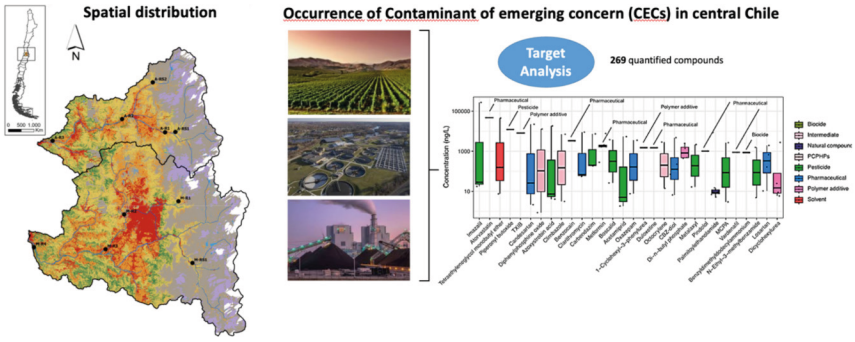
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HIGHLIGHTS

- Organic Micropollutants (OMPs) were assessed in Chilean surface water.
- Imazalil and atorvastatin were detected at the highest levels in central Chile.
- Chemicals with neuroactive properties frequently detected in central Chile.
- Understanding land use will enhance OMPs monitoring and mitigation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Shuzhen Zhang

Keywords:
Micropollutants
Large-volume solid phase extraction
Surface waters
Land uses

ABSTRACT

Organic Micropollutants (OMPs) might pose significant risks to aquatic life and have potential toxic effects on humans. These chemicals typically occur as complex mixtures rather than individually. Information on their co-occurrence and their association with land use is largely lacking, even in industrialized countries. Furthermore, data on the presence of OMPs in freshwater ecosystems in South America is insufficient. Consequently, we assessed the co-occurrence and distribution of OMPs, including pharmaceuticals, pesticides, personal care products, surfactants, and other industrial OMPs, in surface waters of two river basins in central Chile. We focused on identifying and ranking quantified chemicals, classifying their mode of actions, as well as correlating their occurrence with distinct land uses. We identified and quantified 311 compounds that occurred at least once in the River Aconcagua and River Maipo basins, encompassing compounds from urban, agricultural, industrial, and pharmaceutical sectors. Pharmaceuticals were the most frequently occurring chemicals, followed by pesticides, personal care and household products. OMPs with neuroactive properties dominated surface waters in

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https://doi.org/10.1016/j.scitotenv.2024.176314
Received 30 July 2024; Received in revised form 13 September 2024; Accepted 14 September 2024
Available online 19 September 2024
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Central Chile, along with OMPs known to alter the cardiovascular and endocrine systems of humans and aquatic animals. Finally, we observed positive correlations between agricultural and urban land uses and OMPs. Our findings represent a step forward in extending current knowledge on the co-occurrence patterns of OMPs in aquatic environments, particularly in developing countries of the southern hemisphere.

1. Introduction

The rapid pace of industrialization and urbanization has led to the widespread release of synthetic organic chemicals into surface waters worldwide. Organic micropollutants (OMPs), including pesticides, pharmaceuticals, and personal care products (PPCPs), perfluoroalkyl substances (PFASs), organophosphate flame retardants (OPFRs), surfactants, industrial chemicals, and transformation products, have gained significant attention in recent years due to their novelty, widespread detection, uncertain risks, lack of regulatory oversight, and potential ecological harm (Ankley et al., 2008; Lapworth et al., 2012). A large number of OMPs are considered pseudo-persistent due to their continuous release from wastewater treatment plants (WWTPs) (Boxall et al., 2004; Kolpin et al., 2002), agricultural runoff (Reiber et al., 2021), untreated discharge from rural and urban areas as well as industrial sites (Khan et al., 2022; Peng et al., 2017). This continuous release is facilitated by their hydrophilic features, which favor water transport (Fairbairn et al., 2016; Massey et al., 2010; Sengupta et al., 2014).

OMPs are detected at concentrations ranging from pg/L to ng/L in the aquatic environment (Li et al., 2021; Vörösmarty et al., 2010; Zhao et al., 2022). Nevertheless, they pose potential risks to ecosystems and human health since they bioaccumulate in aquatic organisms, for example in invertebrates (Inostroza et al., 2016; Miller et al., 2015), and fish (Carrizo et al., 2022; Fu et al., 2022; Guo et al., 2008; Moreno-González et al., 2016). Several OMPs disrupt the endocrine systems of exposed animals (Salgueiro-González et al., 2015; Tang et al., 2023), they might alter aquatic biodiversity (Sigmund et al., 2023), and might promote antibiotic-resistant bacteria (Kraemer et al., 2019; Zainab et al., 2020). Therefore, understanding the co-occurrence and distribution of OMPs in the freshwater environment, particularly at the river basin level, is essential for coordinating risk mitigation actions.

Nowadays, OMPs are routinely monitored in developed countries in different environmental compartments such as freshwater systems (Cipriani-Avila et al., 2023; Inostroza et al., 2017; Sim et al., 2022; Soriano et al., 2023), sediments (Chiaia-Hernández et al., 2020; Nikolopoulou et al., 2022; Thiebault et al., 2021), and the marine environment (Arpin-Pont et al., 2016; Brumovský et al., 2017; Čelić et al., 2021; Inostroza et al., 2023a; Postigo et al., 2023). Although increasing research is being conducted on OMPs in the aquatic environments of developing countries, the number of studies remains limited (Agunbiade and Moodley, 2014; Gwenzi and Chaukura, 2018; Kandie et al., 2020a, 2020b; Rimayi et al., 2018), particularly South America (Cipriani-Avila et al., 2023; Fabregat-Safont et al., 2023; Inostroza et al., 2024b, 2023b; Tovar-Salvador et al., 2023).

Available information on the co-occurrence and distribution of OMPs is scattered, revealing knowledge gaps in particular with respect to remote areas. Indeed, the identification and quantification of emerging chemicals, such as pharmaceuticals and pesticides, have been identified as key research priorities in Latin America by members of the Society of Environmental Toxicology and Chemistry (SETAC) Latin America (Furley et al., 2018).

In recent decades, Chile has witnessed a significant increase in agricultural production in the central valleys of the country, leading to a rise in pesticide use (Coria and Elgueta, 2022). The country possesses a well-established wastewater treatment system that serves over 96 % of the urban population. However, it is important to note that only two-thirds of urban areas are connected to systems that also offer secondary or tertiary treatment. This indicates that while a significant portion of the population has access to wastewater treatment, not all areas benefit from the more advanced stages beyond primary treatment. Additionally, it is important to emphasize that CECs are not entirely removed from wastewater treatment plants, even with advanced treatment processes. (OECD/ECLAC, 2016). Therefore, Chile may serve as a good case study for assessing the co-occurrence and distribution of OMPs in stream and rivers in developing countries, particularly in South America. Pharmaceuticals have been studied in rivers running through the central part of the country (Wilkinson et al., 2022), and the first study assessing several groups of OMPs, such as pharmaceuticals, pesticides, and industrial chemicals, was recently conducted in the River Aconcagua basin (Inostroza et al., 2023b). Additional efforts to monitor legacy and emerging chemicals have been carried out in the marine environment, particularly marine sediments in the northern part of the country where mining activities take place (Tovar-Salvador et al., 2023) and in surface water, sediment and interstitial waters in northern Patagonia (Inostroza et al., 2024b).

Most studies focus on the occurrence and distribution of OMPs in surface water near known point sources, but only a few have attempted to examine the relationship between OMPs and land use (Bókony et al., 2018; Fairbairn et al., 2016; Hong et al., 2018; Huang et al., 2013; Sardiña et al., 2019; Shekofteh et al., 2017; Smalling et al., 2021). Understanding the relationship and co-occurrence of OMPs with various land uses offers several benefits, including the ability to identify potential sources of contamination. This is crucial for understanding how pollutants enter the environment. Identifying specific land use types, such as agriculture or urban development, that are associated with elevated OMPs levels allows for the development of targeted mitigation strategies and the design of more effective regulatory measures and land management practices to reduce the release of contaminants into water bodies. OMPs originate from a variety of sources, including point sources such as urban and industrial WWTPs, as well as diffuse sources like surface runoff, leaching, and atmospheric deposition. The latter are examples of transport mechanisms that can vary depending on landuse and environmental conditions. This study investigates the co-occurrence and spatial distribution of OMPs (pesticides, pharmaceuticals, drugs, flame retardants, fragrances, industrial chemicals, PAHs, surfactants, plastic additives, personal care products, and some of their main transformation products) in two river basins running through the central valleys of Chile, serving as a case study for South American freshwater systems. The central valleys of Chile host approximately 50 % of the country's population. The study links the co-occurrence of OMPs to land use for a better understanding of possible pollution sources. Furthermore, OMPs were prioritized based on their mode of action, and pollution fingerprints were correlated with different land uses in the river basins.

2. Material and methods

2.1. Sampling design and water collection

Ten surface water samples were collected from the River Maipo and Aconcagua basins in central Chile in October 2021 (Fig. 1). Sampling sites were selected based on land use types across the two river basins (Table S1). For the River Aconcagua basin, two reference sites were included in the sampling campaign, located in the pre-Andes region of the basin (A-RS1 and A-RS2). Additionally, three sites were situated along the main course of the River Aconcagua: A-R1, downstream of rural areas and mining operations; A-R2, downstream of middle-size urban areas and impacted by receiving water from upstream

wastewater treatment plant discharges; and A-R3, located close to the river mouth.

Regarding the River Maipo basin, one reference site was located in the pre-Andes region (M-RS1), and four sites were at location with distinct land uses. M-R1 was located downstream of mining operations in the pre-Andes area, M-R2 was situated in urban regions upstream of Santiago's main WWTPs, while M-R3 was set in an urban/agricultural area downstream of Santiago's main WWTPs. Lastly, M-R4 was placed close to the River Maipo's mouth. Detailed information including geographical coordinates and physical-chemical parameters of the different sampling sites is provided in Tables S2-S3, respectively.

For the collection of surface water samples, an on-site Large-Volume Solid Phase Extraction (LVSPE) device from MAXX Mess-und Probenahmetechnik GmbH, Rangendingen, Germany, was employed, collecting up to 50 L of water per sampling site. This sampling device has been successfully used to collect surface waters in freshwater (Inostroza et al., 2023b; Schulze et al., 2017; Välitalo et al., 2017) and marine environments (Inostroza et al., 2023a).

The samples were pre-filtered using a Sartopure GF + MidiCap filter with a 0.65 μm separation size from Sartorius, and then extracted using cartridges filled with 10 g of polystyrene divinylbenzene copolymer (Chromabond HR-X, 85 μm) as the solid phase from Macherey-Nagel. A detailed description of the LVSPE sampler, method development, cartridge preparation, conditioning, and extraction procedures can be found in Schulze et al. (2017). In addition to the environmental samples, one sample blank was prepared by filtering LC-MS grade water in the LVSPE to assess any carryover due to transportation and/or preparation of the cartridges (Sampling blank). The blank sample was processed together with the field sampling cartridges.

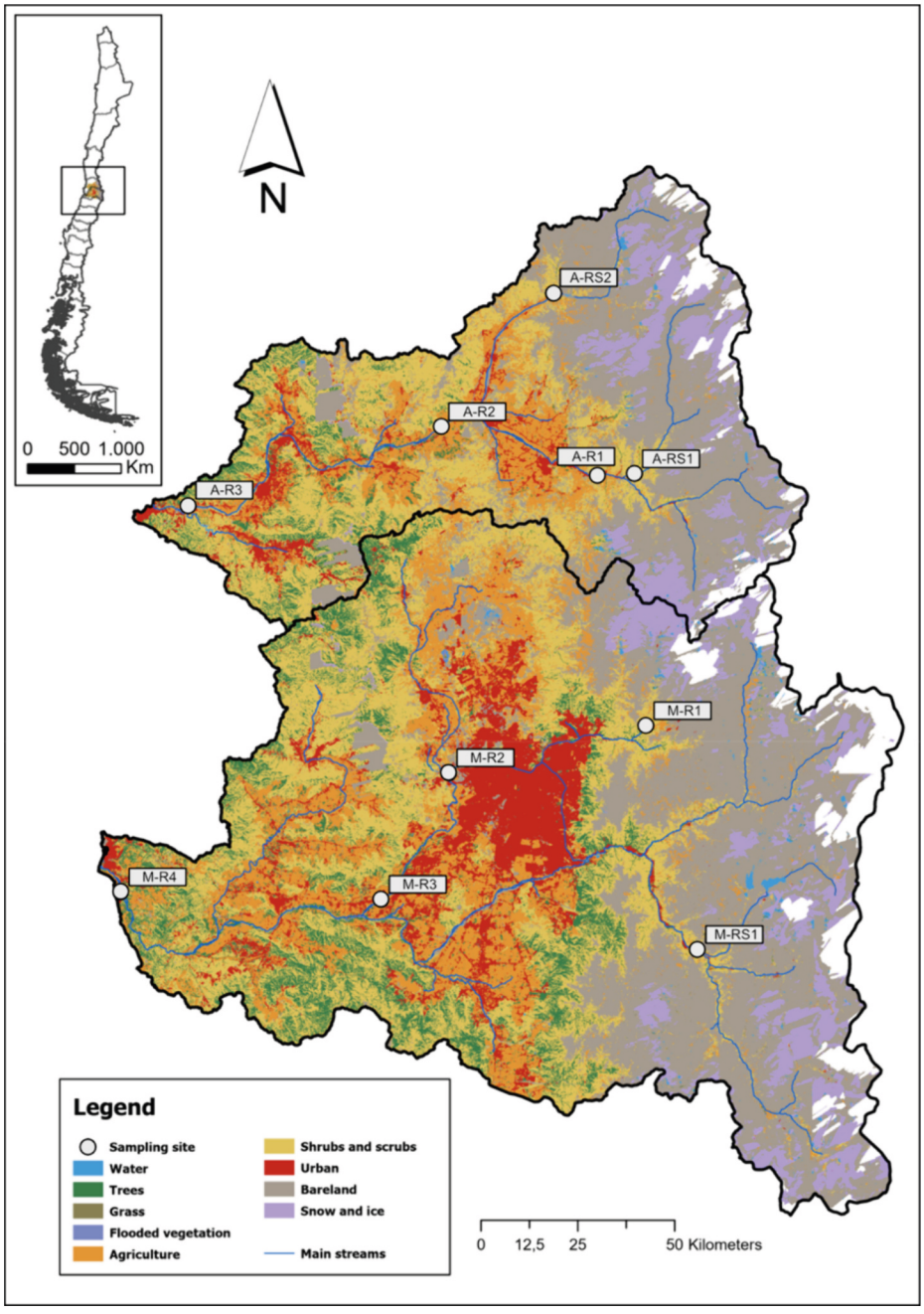


Fig. 1. Map showing location of sampling sites in River Aconcagua basin and River Maipo basin in central Chile. Land uses are coloured code and explained in legend.

2.2. Characterization of land uses in the River Aconcagua and Maipo basins

The basin, sub-basin, and water stream information was obtained from Geoportal Chile (2017, 2022). Meanwhile, the land use/land cover data was created using the Google Earth Engine with the Dynamic World V1 dataset (Brown et al., 2022). This dataset utilises high-resolution (10 m) Sentinel-2 imagery and employs an automated, deep learning-based classification system for near real-time analysis. The time frame for creating our layer spanned from January 1, 2021, to December 31, 2021, to align with the sampling period in October 2021. The Dynamic World dataset classifies land cover into categories such as water, trees, grass, flooded vegetation, crops (renamed as "Agriculture"), shrubs and scrubs, built (renamed as "Urban"), bareland, and snow and ice. Areas with no available data appear as empty (white) areas on the map, likely due to their geographical position in the high and irregular areas of the Andes Mountains' belt.

For the land use/land cover analysis, the data included in the raster files were used to calculate the area of each class. This calculation was performed for the entire study area (1), the Aconcagua basin (2), and the Maipo basin (3). To determine the area, the pixel count was multiplied by the resolution of each pixel (10 m × 10 m = 100 m^2), and then converted to square. The total area was summed up and used to calculate the relative area of each class. This provides an understanding of the contribution of each class to the overall landscape in the analyzed area.

2.3. Reagents and chemicals used for the target analysis of OMPs

Methanol (LC grade, Honeywell, USA), ethyl acetate (LC-MS grade, Honeywell), formic acid (98–100 %, Merck), 7 N Ammonia in Methanol (Honeywell), LC-MS grade water (Fisher Optima LC/MS, Fisher Chemical), dichloromethane (LC grade, Merck), and acetone (LC grade, Honeywell) were used. GC-grade ethyl acetate was purchased from Merck (Darmstadt, Germany).

All solvents used for extraction and instrumental analysis were of LC-MS grade. Analytical standards with at least 90 % purity for structural confirmation and quantification were obtained from various suppliers. The isotope-labeled internal standards for LC and GC are described in Table S4 and Table S5, respectively.

2.4. Cartridge conditioning and extraction

LVSPE cartridges were conditioned using an HPLC pump at a flow rate of 10 mL/min with 200 mL of ethyl acetate, followed by 200 mL of methanol, and finally, 100 mL of water (LC-MS grade). The conditioned cartridges were stored in a refrigerator at 4 °C before sampling. After sampling, all cartridges were dried with nitrogen for 60 min and freeze-dried to remove the remaining water. The analytes were eluted from each cartridge with 100 mL of ethyl acetate, 100 mL of methanol, 100 mL of methanol with 1.0 vol% formic acid, and 100 mL of methanol with 2 vol% of 7 N ammonia in methanol. The eluate volume was reduced using rotary evaporation (40 °C water bath) and a gentle stream of nitrogen. Subsequently, all extracts were finally re-dissolved in LC-methanol at a relative enrichment factor (REF) of 1000 and stored at −20 °C until further analysis to ensure sample integrity. Blanks (device and sampling) were treated in the same manner as environmental samples. For detailed information on established procedures, including conditioning, extractions, and elution of the LVSPE cartridges, refer to Inostroza et al. (2023b); Machate et al. (2022); Nanusha et al. (2021).

2.5. Data processing and evaluation

LC–HRMS raw data analysis was converted into .mzML format (centroid mode) using ProteoWizard v3.0.18265 (Chambers et al., 2012). Subsequently, peak detection, sample alignment, and target-compound annotation were processed using the software MZmine v2.38 (Pluskal et al., 2010). For blank correction, calibration, and quantification, we used the R workflow MZquant (v0.7.8) (Schulze et al., 2021). GC-HRMS quantitative analysis was performed using the vendor software TraceFinder 4.1 (from Thermo Scientific).

2.6. Target analysis methods

The extracts were screened for 699 target compounds using LC- and GC-HRMS. Monitoring information on OMPs is limited in South America and, particularly, in Chile with only few studies analysing multi-classes of OMPs in freshwater and marine environments (Inostroza et al., 2024b, 2023b). Additionally, a retrospective analysis was conducted (Muschket et al., 2021). In this analysis, the sample chromatograms (.mzML files) were re-processed using the secondary calibration sequence of additional compounds ("calibration 2"). Retention time shifts were corrected using a model implemented in the R package MZquant (version 2.38).

The chemical target list is primarily based on chemicals commonly detected in European streams and rivers. Also the classification of chemical classes is predominantly Europe-based (Finckh et al., 2024), aiming to represent various sources of WWTP contaminants, such as medical sector (pharmaceuticals), industrial compounds, the agricultural sector (current-use agricultural pesticides) and biocides. Furthermore, the targets include persistent chemicals that are known to undergo long-range transport, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pyrethroid insecticides, and legacy pesticides, such as dichlorodiphenyltrichloroethane (DDT) and hexachlorobenzene (HCB), remain a significant concern. Although the use of HCB as a pesticide was phased out during the 1980s and 1990s, its primary source of contamination today arises from incineration processes.

Analytes, primarily including herbicides, fungicides, insecticides, and personal care products, were analyzed using an UltiMate 3000 LC system (Thermo Scientific, Germany) coupled to a QExactive Plus MS (Thermo Scientific, Germany), featuring a heated electrospray ionization (ESI) source. A set of method-matched calibration and internal standards, consisting of 7 (GC) and 38 (LC) isotope-labeled compounds (Table S4 and S5), were used for quantification. Semi-volatile hydrophobic analytes were measured using a QExactive GC system (Thermo) equipped with a Thermal Desorption Unit (TDU-2; Gerstel, Mulheim/Ruhr, Germany) and a cooled injection system (CIS; Gerstel). The calibration standards were treated the same way as the river water samples. Further details about the target chemical analysis in the LC- and GC-HRMS platforms can be found in Text S1.

Target compounds were identified by matching *m/z* and retention time between water samples and calibration standards, with a mass and retention time tolerance of 5 ppm and +/− 0.1 min, respectively. Before clearing false positives from the annotated list, the cutoff intensity was set to 10^4 to exclude signals due to noise and background. Seven blanks were analyzed with the samples to remove noise and background contaminants (blank correction).

Finally, all detected compounds were annotated by their broad and specific modes of action (MoAs), as well as by their molecular target based on Kramer et al. (2024).

2.7. Statistical analysis

We assessed relationships between OMPs and land use, and not detected compounds were excluded from any analyses. The Shapiro-Wilk test was used to analyze the normality of the distribution, and Kendall's tau tests were applied to examine the correlation and significance between the different numbers of chemicals quantified and the land use. Significance at the 0.05 and 0.01 probability levels was considered for the models. All statistical analyses were performed using SPSS 15.0 for Windows.

3. Results and discussion

3.1. Co-occurrence of OMPs in surface water in Central Chile

Out of the 699 compounds included in the target analysis, we detected and identified 311 OMPs, of which 269 were quantified at least once in either river basin. Detailed tables containing information on the detected and quantified OMPs, their concentrations, and their respective chemical identifiers are available via the open-access repository Zenodo (Inostroza et al., 2024c).

Our results reveal a widespread co-occurrence of OMPs, including pharmaceuticals, pesticides, polymer additives, personal care and household products, and intermediate compounds in the central valleys of Chile (Fig. 2). We did not observe major differences between the main chemical classes in the River Aconcagua basin (Fig. 2B) and the River Maipo basin (Fig. 2C). Pharmaceuticals represented 31.3 % of the quantified chemicals in both river basins, followed by pesticides (19.2 %), and personal care and household products (10.5 %). Although our focus was on OMPs, we observed that legacy chemicals, including persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs), accounted for up to 7.2 % of the quantified chemicals in central Chile (Fig. 2A).

The number of detected and quantified chemicals varied across sampling sites, showing a clear increase in chemicals from reference sites to the river mouth in both river basins (Table 1). A total of 141 OMPs were quantified at least once in the Aconcagua River, while 243 OMPs were detected in the Maipo River. Our study suggests that the elevated abundance of OMPs in tributary streams can be attributed to intensive agricultural practices, as evidenced by the high levels of detected pesticides and WWTP discharges near the sampling locations. Additionally, populations discharging wastewater without treatment could also contribute to the elevated levels of OMPs. Conversely, the limited presence of OMPs at M-RS1, A-RS1, and A-RS2 validates their designation as 'reference sites', reflecting comparatively lower levels of urbanization.

From a basin-specific perspective, A-R2 and M-R4 exhibited the highest number of quantified chemicals (107 and 186, respectively; Table 1). The high number of OMPs at A-R2, part of the Aconcagua's River main course, likely results from the influence of seven upstream WWTP discharges. The increase at M-R4 is likely attributable to its proximity to the river mouth. In contrast, the low number of OMPs found at M-RS1 (20), A-RS1 (18), and A-RS2 (22) can be attributed to lower levels of urbanization in those regions.

The higher number of OMPs in the Maipo River basin compared to the Aconcagua River basin aligns with Maipo's higher degree of urbanization and industrialization. It hosts the city of Santiago (approximately 7.5 million inhabitants) and the country's largest WWTP (Farfana), which treats domestic and industrial effluents. Our findings support existing studies identifying WWTPs as primary sources of OMPs in streams and river systems globally (Anliker et al., 2020; Brezina et al., 2017; Veach and Bernot, 2011; Vidal-Dorsch et al., 2012). These studies show that OMPs from, for example, industrial wastewater can not only leave a clear mark on the effluents of the respective WWTP, but also influenced the quality of the water.

3.2. Concentrations of OMPs in river basins of Central Chile

We classified chemicals by class and ranked them based on their environmental concentrations within and across river basins to offer an overview of Central Chile. Fig. 3 summarizes the top 30 highest chemical concentrations in both river basins. The results were initially compared with other studies conducted in Chile, followed by comparisons with studies from South America, Europe, and other developing countries in elsewhere.

3.2.1. Industrial compounds

Industrial chemicals, including solvents and intermediates, exhibited notably high mean concentrations in the Aconcagua River basin. Tetraethyleneglycol monobutyl ether and diphenylphosphine oxide reached the highest concentrations in surface water, at 45 and 12 µg/L respectively (Table 2). The elevated level of tetraethyleneglycol monobutyl ether, a common brake fluid component (Khamidullin et al., 2006), could be attributed to heavy traffic on the main road connecting Chile and Argentina. Furthermore, several mining operations in the Andes region employ heavy-duty dump trucks, which may serve as another source of tetraethyleneglycol monobutyl ether. To the best of our knowledge, no studies documenting tetraethyleneglycol monobutyl ether and diphenylphosphine oxide in South American surface waters have been published. Polyfluoroalkyl substances (PFAS) ranked third in the River Maipo basin, with 6:2 fluorotelomer sulfonic acid (6:2 FTS) reaching up to 1.5 µg/L (Table 2). The concentration of 6:2 FTS in surface water samples was higher compared to previous studies conducted in the United States (DeNicola et al., 2023; Houtz et al., 2016), South America (Madeira et al., 2023) and in Europe (Zarębska et al., 2024). This compound is commonly found in formulations of aqueous film-forming foam (AFFF) (Madeira et al., 2023). Zarębska et al. (2024) detected 6:2 FTS in the Oder River (Poland), with concentrations up to 2.9 ng/L, which were notably lower than those identified in our research (1.5 µg/L). 6:2 FTS was also detected by DeNicola et al. (2023) and Madeira et al. (2023) in lakes and waterways of the northwestern Great Basin and Sierra Nevada, and in surface water in São Paulo, Brazil, respectively, with maximum concentrations of 80 ng/L and 50 ng/L, both lower than those observed in our study.

3.2.2. Pesticides

Pesticides exhibited the second highest concentrations in the River

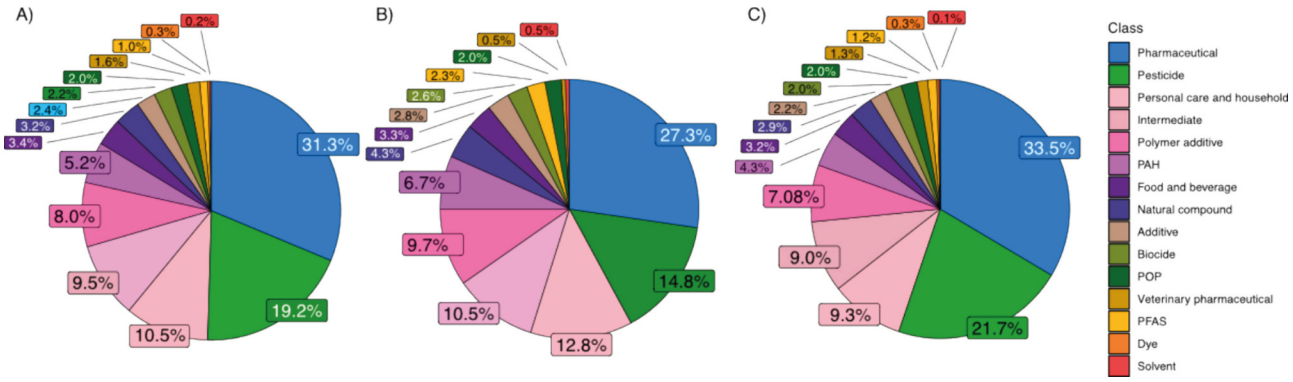


Fig. 2. Percentage of OMPs classes including some legacy chemicals in: A) both river basins, B) Aconcagua, and C) Maipo. Chemical classes are colour coded. PAH = polycyclic aromatic hydrocarbon, POP = persistent organic pollutant, PFAS = polyfluoroalkyl substances.

Table 1
Overview of chemicals detected and quantified per sampling sites and river basin. Organic Micropollutants (OMPs), Polycyclic-aromatic hydrocarbons (PAH), *Per*- and polyfluoroalkyl substances (PFAS), Persistent Organic Pollutants (POP).

	River Aconcagua basin					River Maipo basin				
	A-RS1	A-RS2	A-R1	A-R2	A-R3	M-RS1	M-R1	M-R2	M-R3	M-R4
Total number OMPs detected	46	57	67	152	70	54	68	129	218	223
Total number OMPs quantified	18	22	37	107	32	20	39	88	184	186
Additive	2	2	2	4	1	2	2	2	4	5
Food and beverage	–	1	3	4	5	1	4	5	6	6
Intermediate	7	7	9	14	4	9	7	13	17	16
Natural Compound	4	4	4	4	1	3	4	4	5	4
PAH	4	7	8	7	–	5	5	7	6	7
Personal care and household	9	9	11	13	8	8	14	16	13	13
Pesticide	2	5	5	30	16	2	4	15	58	71
PFAS	2	1	1	3	2	1	–	3	1	3
Pharmaceutical	12	13	13	56	13	17	17	44	80	74
Polymer additive	2	4	8	12	12	2	5	10	18	14
POP	2	2	2	2	–	3	3	3	2	3
Solvent	–	–	1	1	–	–	–	1	–	–
Veterinary pharmaceutical	–	–	–	2	–	1	–	–	4	4
Biocide	–	2	–	–	8	–	3	6	3	2
Dye	–	–	–	–	–	–	–	–	1	1
Maximum concentration (μg/L)	0.085	0.42	8.6	270	0.72	1.0	2.9	3.3	47	22
Average concentrations (μg/L)	0.0040	0.019	0.33	2.4	0.027	0.036	0.096	0.14	0.49	0.33
Lowest concentrations (ng/L)	0.025	0.0070	0.0080	0.0070	0.0050	0.047	0.000040	0.000030	0.0090	0.061

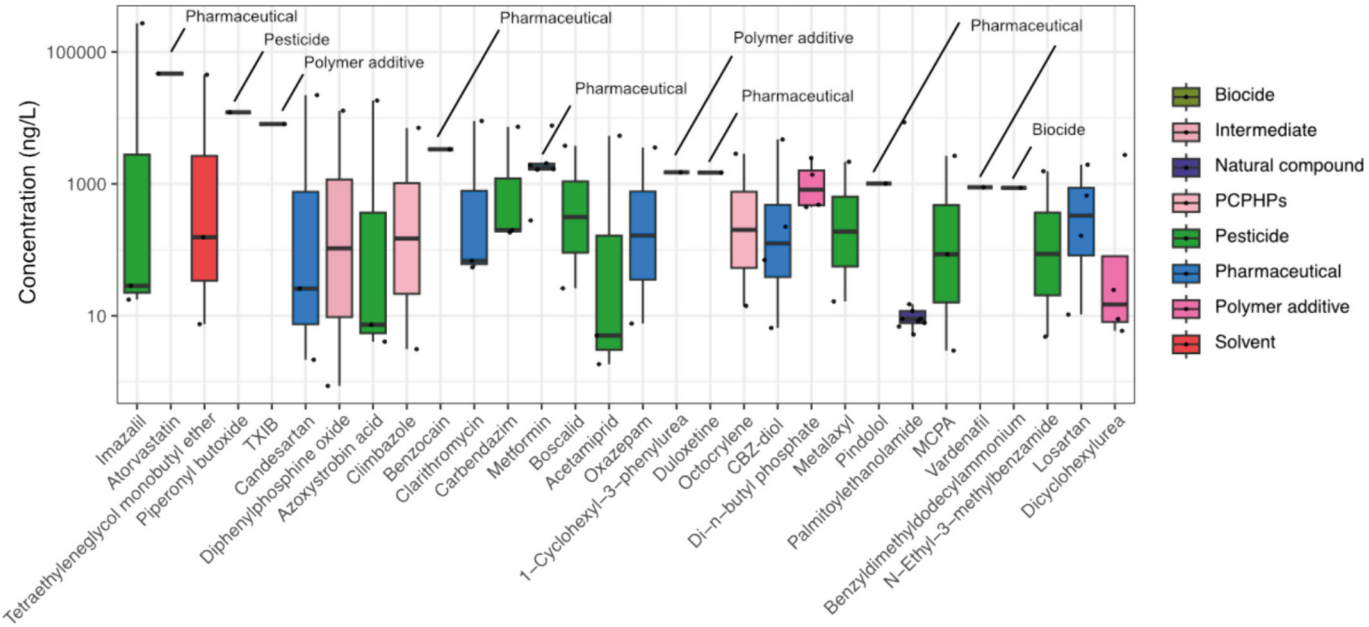


Fig. 3. Selected highest concentrations of OMPs co-occurring in River Aconcagua and Maipo basins. Chemical classes are colour coded. Abbreviation as follows: TXIB = 2,2,4 – Trimethyl–1,3 – pentanediol diisobutyrate, MCPA = 2-methyl-4-chlorophenoxyacetic acid, CBZ-diol = 10,11 – Dihydro–10,11 – dihydroxycarbamazepine.

Aconcagua basin, with the fungicides imazalil, carbendazim, and boscalid reaching 270, 7.3, and 3.7 μg/L, respectively (Fig. S1). These fungicides are seasonally applied to vineyards, fruit orchards, and vegetables in the river basin. The elevated concentrations of imazalil, in comparison to other pesticides, are of significant concern, as highlighted in the JRC Technical Report "Selection of Substances for the 3rd Watch List under the Water Framework Directive" (European Commission et al., 2020). Besides, imazalil is classified as a Group 2B carcinogen by the International Agency for Research on Cancer (IARC), indicating it is possibly carcinogenic to humans. Studies reporting imazalil and boscalid in surface waters are limited in South America (Sandoval et al., 2024). Nevertheless, Lima-Junior et al. (2024) recently reported average concentrations of imazalil (6.0 ng/L) at a river basin level in Brazil, which are lower compared to our study. Nevertheless, imazalil has been previously identified in surface waters in Europe. Ccanccapa et al. (2016) reported maximum concentrations of imazalil reaching 750 ng/L in the Turia and Júcar Rivers (Valencian Community, Eastern Spain). In contrast, Soriano et al. (2023) observed only low levels of imazalil (17.7 ng/L) in surface water within the L'Albufera Natural Park. Carbendazin has been quantified most frequently in South America and particularly in Brazil and south of Chile, with average concentrations between 6.0 and 96 ng/L in Brazilian surface waters (Caldas et al., 2019; Lima-Junior et al., 2024; Sposito et al., 2018) and 1.8 μg/L in surface waters in an agricultural–forestry basin in Southern Chile (Palma et al., 2004). Additionally, Kandie et al. (2020a) reported concentrations of carbendazim >1.0 μg/L in freshwater systems within the southern basin of Lake Victoria, Kenya. These concentrations are lower than those reported in our study. To the best of our knowledge, we have not

Table 2
Ranking of quantified chemicals by mean concentrations in Central Chile by river basin. Concentrations in ng/L. Chemical classes with only one entry value were omitted. PCPHPs = Personal care and household products.

Basin	Class	Minimum	Maximum	Mean	Median	Chemical	CAS RN
Aconcagua	Solvent	7.5	45,000	23,000	23,000	Tetraethyleneglycol monobutyl ether	23,783–42-8
	Pesticide	0.56	270,000	9500	3.0	Imazalil	35,554–44-0
	Intermediate	0.75	12,000	620	8.5	Diphenylphosphine oxide	4559-70-0
	Natural compound	0.84	8600	570	5.0	Palmitoylethanolamide	544–31-0
	Polymer additive	1.9	8100	550	8.4	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	6846-50-0
	Pharmaceutical	0.57	5700	270	6.0	Methenamine	100–97-0
	PCPHPs	0.62	380	21	3.4	*N*, *N*-Dimethyltetradecylamine-N-oxide	3332-27-2
	PFAS	2.3	130	79	85	6:2 fluorotelomer sulfonic acid	27,619–97-2
	Food and beverage	0.63	530	68	20	Acesulfame	33,665–90-6
	PAHs	33	33	33	33	Phenanthrene	85–01-8
	Additive	6.9	16	14	14	Ethylene glycol diphenylether	104–66-5
	Biocide	1.9	4.0	3.0	2.9	Cyromazine	66,215–27-8
	Veterinary pharmaceutical	1.5	1.5	1.5	1.5	Emamectin B1a	121,124–29-6
Maipo	Solvent	160	160	160	160	Tetraethyleneglycol monobutyl ether	1559-34-8
	Pharmaceutical	0.61	47,000	680	13	Atorvastatin	134,523–00-5
	Pesticide	0.67	18,000	700	8.3	Azoxystrobin acid	1,185,255–09-7
	PFAS	1.2	1600	320	57	6:2 fluorotelomer sulfonic acid	27,619–97-2
	PCPHPs	0.74	7100	310	14	Climbazole	38,083–17-9
	Polymer additive	0.84	2700	280	8.4	Dicyclohexylurea	2387-23-7
	PAHs	27	200	130	170	Phenanthrene	85–01-8
	Biocide	0.86	870	100	3.5	Benzyldimethyldodecylammonium	10,328–35-5
	Intermediate	0.76	990	100	17	3,4,5-Trichlorophenol	609–19-8
	Veterinary pharmaceutical	1.3	100	18	6.6	Enrofloxacin	93,106–60-6
	Additive	3.2	39	15	13	N-Ethyl-o-toluenesulfonamide	1077-56-1
	Food and beverage	0.57	95	14	5.7	Saccharin	81–07-2
	Natural compound	0.97	77	14	8.6	Chenodeoxycholic acid	474–25-9
	Dye	0.62	0.62	0.62	0.62	7-(Ethylamino)-4-methylcoumarin	28,821–18-3

encountered studies documenting boscalid in surface waters within South America. However, boscalid has been reported in other European country. In our study, the concentration of boscalid exceeded the levels previously reported by Tsaboula et al. (2016) in the Pinios River Basin of Central Greece (0.24 μg/L). In contrast, pesticides with the highest concentrations in the River Maipo basin were piperonyl butoxide, azoxystrobin acid (an azoxystrobin metabolite), and acetamiprid, reaching 18, 12, and 5.0 μg/L, respectively. Few studies have documented the presence of piperonyl butoxide in surface waters across South America or Europe. However, Chebii et al. (2024) reported lower concentrations (62 ng/L) in the River Athi basin, Kenya, compared to our findings. Zhao et al. (2024) documented the presence of azoxystrobin acid at maximum concentrations of 9.1 ng/L in surface water collected from the Dongjiang River basin in southern China, with frequent detections across the sampled water bodies. These findings revealed concentrations lower than those observed in our investigation. Acetamiprid, a neonicotinoid widely employed in global agriculture, has been frequently quantified at lower concentrations within the River Tagus basin (Portugal) and River Yangtze in China (Casillas et al., 2022; Wang et al., 2023). Acetamiprid was included in the EU watch list in 2018 due to concerns about its potential as a water pollutant, necessitating monitoring (Cossi et al., 2020). Acetamiprid is highly toxic to various organisms, particularly pollinators like bees, and it poses risks to aquatic invertebrates, fish, and other wildlife.

3.2.3. Pharmaceuticals

Pharmaceuticals constituted the third main class in the River Aconcagua basin with methenamine, 10,11-dihydro-10-hydroxycarbamazepine (a carbamazepine metabolite), and metformin, reaching 5.6, 4.7 and 1.6 μg/L, respectively (Fig. S1). Methenamine, a high-production-volume chemical widely used in various industrial processes and everyday products, is not frequently quantified in surface water samples. However, it has been identified as a significant chemical in effluents from WWTPs (Anliker et al., 2020). 10,11-dihydro-10-hydroxycarbamazepine is typically quantified in WWTP's effluents (Brezina et al., 2017; Miao et al., 2005) and has been quantified in surface waters at concentrations up to ten times lower in Germany (Brezina et al., 2017) and in freshwater systems within the Lake Victoria South Basin, Kenya (Kandie et al., 2020a), and up to a hundred times lower in the Danube River (Ginebreda et al., 2018). Metformin, a medication used to treat diabetes, was quantified at higher concentrations (4.4 μg/L) in surface waters in the Paraibuna River (Brazil) (Quadra et al., 2021). Additionally, metformin was among the suggested candidates for inclusion in the 3rd Watch List (European Commission et al., 2020) due to its adverse effects on aquatic organisms. Besides, metformin has the potential to act as an endocrine disruptor (Niemuth and Klaper, 2015).

In contrast, the River Maipo basin exhibited pharmaceuticals with the highest mean concentrations, particularly atorvastatin, candesartan, and clarithromycin reaching up to 46, 22, and 8.0 μg/L respectively in surface water (Fig. S1). Atorvastatin, a lipid-lowering pharmaceutical used to prevent cardiovascular diseases, has been found below the limit of quantification (<0.030 ng/L) in Brazilian surface waters (Roveri et al., 2021). The atorvastatin concentrations observed in this study were higher compared to measurements in southern Poland and the Amazon River in Brazil (Fabregat-Safont et al., 2021; Styszko et al., 2021). However, da Silva et al. (2011) reported significantly lower concentrations of atorvastatin in surface water in the Ebro River basin, Spain, compared to those documented in our study. da Silva et al. (2011) reported maximum concentrations of 50 ng/L in river water. This finding indicates that the highest concentrations of atorvastatin were detected in samples collected downstream of WWTPs, underscoring the substantial contribution of WWTP effluents to pharmaceutical contamination in the river. Regarding candesartan, Ng et al. (2023) reported lower concentrations (31 ng/L) compared to our study in the surface water of the Danube River basin. However, the concentrations of candesartan observed in this study were lower than those measured in European streams. Finckh et al. (2024) reported candesartan concentrations of 34 μg/L in these streams. To the best of our knowledge, no studies have documented candesartan in surface waters in South America. Clarithromycin, an antibiotic, has previously been quantified in Chilean surface waters at concentrations of up to 10 ng/L (Inostroza et al., 2023b) and it has been identified as a mixture risk driver contributing considerably to environmental risks (Inostroza et al., 2024a). Overall, we observed elevated Claithromycin concentrations

compared to these and other published studies from Chile and other South American river systems in Brazil and Argentina (Bertrand et al., 2019; Reis et al., 2021; Valdés et al., 2021). Clarithromycin and other antibiotics may contribute to antimicrobial resistance due to overuse or misuse. According to the World Health Organization, antibiotic resistance is a major threat to global health, food security, and developmental progress (OECD, 2021, 2019). Particular emphasis should be placed on the potential role of WWTPs as significant sources of antibiotic emissions, contributing to the proliferation of resistance genes within surface water ecosystems (Kairigo et al., 2020).

The observed results likely reflect the dominant land uses within each basin. The Aconcagua basin is characterised by extensive copper mining, a major transport route between Chile and Argentina, and intensive agriculture. Conversely, the Maipo basin houses the country's largest wastewater treatment plant (WWTP), a highly populated area, intensive agriculture, and a major industrial zone. The presence of most quantified chemicals can be attributed to their ubiquitous, worldwide utilization in everyday life, industrial processes, and agricultural practices. This finding is further supported by the use of a target list derived from commonly assessed OMPs in European aquatic environments.

3.3. Characterization of OMPs based on their mode of action (MoA)

We could assign 169 of the 269 quantified chemicals to at least one broad MoA and they were grouped in 24 categories (Fig. 4) according to Kramer et al. (2024) (Refer to Table S6 for the minimum, maximum, mean, and median values of the quantified compounds). For 100 chemicals a mode of action could not be assigned, and their MoA was therefore classified as "unknown". A prevailing pattern was observed regarding the top three modes of action across both river basins: neuroactive chemicals exhibited the highest prevalence in surface waters in Central Chile (34.5 %), followed by chemicals affecting the cardiovascular and endocrine systems, at 13.1 % and 6.9 %, respectively (Fig. 4). The lipid metabolism category was the fourth most significant in the Maipo River basin (4.9 %) compared to the Aconcagua River basin (3.3 %). Conversely, the sterol biosynthesis inhibition category was more important in the Aconcagua River basin (4 %) than in the Maipo River basin (<3 %).

Neuroactive chemicals were predominantly pesticides and pharmaceuticals. Notably, neuroactive pharmaceuticals such as 10,11-dihydro-10-hydroxycarbamazepine, oxazepam, benzocaine, and duloxetine reached the highest concentrations (1.4–4.7 μg/L), followed by acetamiprid, a neonicotinoid insecticide, which reached concentrations up to 5.4 μg/L. The cardiovascular mode of action was primarily dominated by antihypertensive pharmaceuticals, including candesartan, losartan, and pindolol. The endocrine mode of action included several chemical groups from pharmaceuticals, personal care and household products, pesticides, and others, with anastrozole, benzophenone-4, and metolachlor showing the highest concentrations. While pharmaceuticals and pesticides are designed to have specific effects on humans and insects, only a few lack information regarding their MoAs (Atzei et al., 2021). However, compounds such as plastic and rubber additives, corrosion inhibitors, surfactants, and primarily industrial chemicals, often belong to use groups with unknown modes of action.

There is a paucity of studies characterizing OMPs in surface waters across South America or Europe based on their modes of action. A previous study conducted on wastewater treatment plant effluents (Finckh et al., 2022), provided information on the MoA of the detected compounds. Finckh et al. (2022) clustered emerging chemicals into three main groups: pharmaceuticals, pesticides, and biocides, with neuroactive chemicals, photosynthesis inhibitors, and lipid metabolism disruptors being the most prominent MoAs, respectively. Our findings are similar to those of Finckh et al. (2022), though there are some differences in the order of the modes of action. Finckh et al. (2022) demonstrated a distinct predominant pattern among the three principal modes of action, with neuroactive chemicals exhibiting the highest prevalence at 24.5 %, followed by lipid metabolism modes of action at 11.5 % and photosystem inhibitors at 10.1 %.

3.4. OMPs and land use in central Chile

Regarding land use percentages (%) within the Aconcagua and Maipo River basins, bareland exhibited the highest proportion of land use, accounting for 36.6 % and 30.4 % in the River Aconcagua and Maipo basins. In the Aconcagua River basin, agriculture and urban land proportions, were 15.4 % and 5.08 %, respectively. In the Maipo River basin, these proportions were 17 % for agriculture and 10.1 % for urban areas (Table S1). From a site-specific perspective, A-R2 (29.02 %) and M-R3 (41.36 %) exhibited the highest agricultural land use in the River Aconcagua and Maipo basins, respectively. These sampling sites are located in the central area within both river basins (Fig. 1). Also, in Fig. S2, it is observed that the pesticides in A-R2 exhibit higher total concentrations. Meanwhile, A-R3 (9.02 %) and M-R2 (47.13 %) showed the highest urban land uses in River Aconcagua and Maipo. M-R2 subbasin hosts Santiago and the largest WWTP in the country. We detected the highest concentrations of contaminants in this basin, primarily pharmaceutical, personal care, and household products (Table 1 and Fig. S3).

Correlation analyses were conducted to describe the extent to which land use is associated with the quantified number of chemicals (Tables 3 and S6–7). It is noteworthy that chemicals and landuse percentages were analyzed separately for each basin and collectively. Observations in the River Maipo basin revealed a stronger association between land use and the number of chemicals compared with Aconcagua. We focused on two relevant land uses in the context of organic micropollutants: agriculture and urban land use. We observed a positive correlation between urban land uses and polymer additives in the River Aconcagua basin (Table S7). Furthermore, several positive correlations were determined in the River Maipo between agriculture land use and food and beverage chemicals, pharmaceuticals, and polymer additives (Table S8). To complement our findings, we observed strong negative correlations between bareland land use, pharmaceuticals and industrial chemicals,

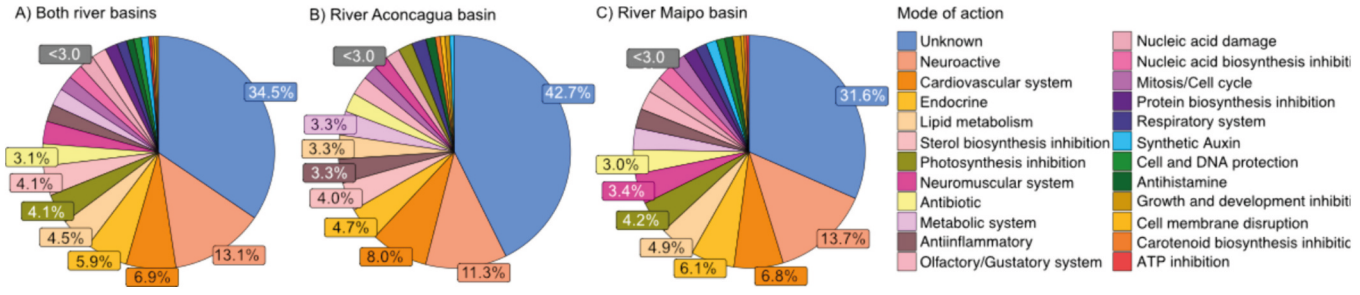


Fig. 4. Distribution of the distinct mode of action in A) both river basins, B) only Aconcagua, and C) only Maipo. Frequency of mode of action was transformed to percentage.

Table 3
Correlations between land use and number of chemicals quantified in both basins. AGR, agriculture land use; BAR, bareland land use; VEG, flooded vegetation land use; GRASS, grass land use; SHR, shrubs and scrubs land use; SNOW, snow and ice land use; TREES, trees land use; URB, urban land use; WAT, water land use. Bold values represent significant correlation.

	AGR	BAR	VEG	GRASS	SHR	SNOW	TREES	URB	WAT
Additive	0.36	−0.31	0.24	0.31	0.31	−0.36	0.25	0.19	−0.14
Food and beverage	**0.59**	**−0.77**	**0.76**	**0.71**	**0.68**	**−0.58**	**0.85**	**0.77**	−0.35
Intermediate	0.40	−0.30	0.33	0.49	0.21	**−0.54**	0.28	0.40	−0.16
Natural compounds	0.24	−0.24	0.033	0	0.060	−0.18	0.092	0.12	−0.060
PAH	−0.15	0.096	−0.078	0.17	0	0.048	0.12	0.048	−0.096
Personal care and household	0.24	−0.28	0.21	0.12	0.24	−0.094	0.41	0.42	0.047
Pesticide	**0.61**	**−0.66**	0.47	**0.60**	**0.70**	**−0.66**	**0.71**	0.48	−0.48
PFAS	0.38	−0.28	0.19	0.31	0.33	**−0.53**	0.36	0.28	−0.28
Pharmaceutical	**0.63**	**−0.58**	**0.56**	**0.57**	0.44	−0.44	0.47	**0.54**	−0.12
Polymer additive	**0.66**	**−0.75**	0.49	**0.60**	**0.70**	**−0.70**	**0.76**	**0.61**	−0.39
POP	−0.027	0.027	0.33	0.17	−0.19	0.25	0	0.083	0.33
Solvent	−0.032	0.16	−0.25	0.032	0.032	−0.032	0.098	0.23	0.097
Veterinary pharmaceutical	0.53	−0.42	0.39	0.48	0.25	−0.53	0.28	0.30	−0.14
Biocide	0.32	**−0.56**	0.45	0.25	**0.51**	−0.17	**0.57**	**0.51**	−0.32
Dye	0.52	**−0.60**	**0.65**	**0.60**	0.37	**−0.60**	0.45	0.37	−0.30

specifically polymer additives.

We merged both river basins to provide a more comprehensive assessment of Central Chile and the results aligned to the river-specific assessment. That is, i) a significant positive correlation between agriculture land use with food and beverage chemicals, pesticides, pharmaceuticals, and polymer additives; ii) urban land use with food and beverage chemicals, pharmaceuticals, polymer additives, and biocides in Central Chile (Table 3). In particular, our correlations between agriculture land use and synthetic organic chemicals are in line with previous studies (Becker et al., 2021) as well as other studies finding correlations between urban land use and pharmaceuticals, industrial compounds, and personal care products (Allan, 2004; Kang et al., 2010). Conversely, strong negative correlations exist between the amount of bareland and OMP concentrations, in particular food and beverage chemicals, pesticides, pharmaceuticals, polymer additives, biocides, and dyes.

4. Conclusions

This study analyzes the co-occurrence of organic micropollutants in Chile and contributes to expanding our understanding of the occurrence patterns of pesticides, pharmaceuticals, and industrial chemicals in the aquatic environment of South America. While previous studies have primarily focused on either pesticides or pharmaceuticals, this research examined complex mixtures of organic micropollutants from multiple chemical classes, aligning with studies conducted in Europe, North America, and China.

The overall pollution fingerprint exhibited a slightly different pattern compared to those observed in Europe, North America, Kenya, and China. This suggests a globalisation of chemical use, encompassing the agricultural, industrial, and pharmaceutical sectors. This potential global pattern could aid in identifying chemicals of global concern and mitigating their impact on aquatic environments.

The prevalence and frequency of chemicals with neuroactive properties in this study and other freshwater systems are of particular concern. These pesticides and pharmaceuticals, designed to alter the central nervous system of insects and mammals (humans), respectively, may collectively threaten aquatic life. Disruption of neurological functions in these organisms can result in altered behavior, impaired reproduction, reduced growth rates, and even mortality. We advocate for effect-based methods to assess the adverse effects of these chemicals.

While the findings may seem less surprising from a Northern Hemisphere perspective, this study focused on under-researched regions in countries with transitional economies aspiring to economic development. The results can inform the development of environmental monitoring and assessment strategies in Chile, similar to those established in the European Union.

CRediT authorship contribution statement

Eric Carmona: Writing – review & editing, Writing – original draft, Methodology, Data curation. **Javier Renovell:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis. **Yolanda Picó:** Writing – review & editing, Writing – original draft, Supervision. **Werner Brack:** Writing – review & editing, Writing – original draft, Resources. **Martin Krauss:** Writing – review & editing, Writing – original draft, Supervision, Methodology. **Thomas Backhaus:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Pedro A. Inostroza:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All research data is available in open repositories (see Material and methods section)

Acknowledgments

We thank Margit Petre and Jörg Ahleim (UFZ) for LVSPE training as well as cartridge extractions. This work was supported by the FRAM Centre for Future Chemical Risk Assessment and Management at the University of Gothenburg. The QExactive Plus LC-HRMS used at UFZ is part of the major infrastructure initiative CITEPro (Chemicals in the Terrestrial Environment Profiler) funded by the Helmholtz Association.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.176314.

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ARTICLE 06

SUPPLEMENTARY MATERIAL:

Co-ocurrence and spatial distribution of organic micropollutans in surface waters of the River Aconcagua and Maipo basins in Central Chile

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Keywords: micropollutants, large-volume solid phase extraction, surface waters, land uses

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Text S1. Target chemical analysis

LC-HRMS analysis:

For water analysis, 100 µL of LVSPE samples (REF 1000) were transferred into a 2 mL autosampler vials (Phenomenex Verex LC-MS purity) with a 200 µL conical glass insert and 10 µL of an internal standard mixture containing isotope-labelled compounds (1 µg/mL), 30 µL of methanol (LC-MS grade) and 60 µL of water (LC-MS grade) were added. For sediment analysis, 50 µL of samples were transferred into a 2 mL autosampler vial with a 200 µL conical glass insert and 5 µL of the internal standard mixture were added. Instrumental blanks were prepared with the same composition (methanol: water 70:30) and run for 4–6 replicates in each sequence.

In total, 499 compounds were selected for target analysis of water samples by liquid chromatography-tandem mass spectrometry (LC-MS/MS). Sample aliquots, calibration aliquots and instrumental blanks were analysed in a wide-scope target screening by LC-HRMS. Chemical screening was performed on an UltiMate 3000 LC system (Thermo Scientific) coupled to a hybrid quadrupole - Orbitrap MS (Q ExactiveTM Plus, Thermo Scientific) with a heated electrospray ionization (HESI) source. For the measurement, a reversed-phase LC separation on a Thermo Ultimate 3000 LC and an injection volume of 5 µL were used. For chromatographic separation, a Kinetex 2.6 µm EVO C18 (50 × 2.1 mm, 2.6 µm particle size, Phenomenex, pre-column 4 × 2.1 mm and in-line filter 0.2 µm) was used, using a gradient elution with 0.1 % of FA (eluent A) and methanol containing 0.1 % of FA (eluent B) at a flow rate of 300 µL/min. After 1 min of 5 % B, the fraction of B was linearly increased to 100 % within 12 min and 100 % B were kept for 11 min. The eluent flow was diverted to waste and the column was rinsed for 2 min using a mixture of isopropanol + acetone 50:50 / eluent B / eluent A (85 % / 10 % / 5 %) to remove hydrophobic matrix constituents from the column. Finally, the column was re-equilibrated to initial conditions for 5.7 min. The injection volume was 5 µL. The column temperature was 40 °C. All MS and MS/MS analyses were performed in ESI positive (ESIpos) and negative (ESIneg) mode.

GC-HRMS analysis

In total, 200 compounds were selected for target analysis of water samples by gas chromatography-mass spectrometry (GC-MS) analysis. In the case of GC-MS analysis, a Trace 1310 GC coupled with a Thermal Desorption Unit (TDU-2), a Cooled Injection System (CIS, both from Gerstel, Mülheim, Germany) and a QExactive HF mass spectrometer was used (Thermo Fisher, Scientific, Germany).

For water analysis, 100 µL of LVSPE samples (REF 1000) were transferred into a 2 mL autosampler vials (Phenomenex Verex LC-MS purity) with a 200 µL conical glass insert and 10 µL of an internal standard mixture containing isotope-labelled compounds (1 µg/mL) were added. For sediments analysis, 100 µL of extract were transferred into a 2 mL autosampler vial with a 200 µL conical glass insert and 10 µL of the internal standard mixture were added. Instrumental blanks were prepared from methanol and run for 4–6 replicates in each sequence.

For GC-HRMS measurement, injection of 2 µL of extract aliquots was done splitless into the thermodesorption tubes equipped with glass inserts, which acted as single use liners. GC separation

was done on a DB-5MS capillary column (30 m × 250 µm 0,25 µm; DuraGuard, 10 m, Agilent) using He as carrier gas with a constant flow rate of 1.2 mL/min. The temperature of the transfer line was 250°C. During the HRMS measurements, the temperature of the ion source was 250°C and, electron ionization was used at an emission current of 50 µA and an electron energy of 70 eV. The measurement was performed in full scan mode in the mass range of m/z 50-650 at a resolving power of 60,000 (referenced to m/z 200).

Table S1. Total land use percentages (%) related to the River Aconcagua and Maipo subbasins in Central Chile. Total basin columns represent the total land use for each river basin and not the summed of the individual sampling sites.

Land uses	River Aconcagua basin						River Maipo basin					
	A-RS1	A-RS2	A-R1	A-R2	A-R3	Total river basin	M-RS1	M-R1	M-R2	M-R3	M-R4	Total river basin
Water	1.1	0.20	0.90	0.51	0.22	0.51	1.5	2.0	0.31	0.24	0.23	0.59
Trees	0.17	0.20	0.27	1.3	14	5.5	0.17	0.90	6.0	5.1	18	9.0
Grass	0.010	0.030	0.070	0.060	0.24	0.12	0.19	0.030	0.33	0.98	1.3	0.43
Flooded vegetation	0.00	0.00	0.00	0.00	0.020	0.010	0.010	0.010	0.03	0.11	0.14	0.070
Agriculture	4.4	1.6	1.2	29	20	15	1.8	4.4	8.0	41	26	17
Shrubs and scrubs	5.5	6.3	5.5	32	48	28	3.5	16	20	20	43	26
Urban	0.11	0.040	0.35	5.9	9.0	5.1	0.15	0.88	47	30	7.4	10
Bareland	70	68	71	28	9.4	37	70	47	14	1.7	3.3	30
Snow and ice	19	24	21	4.1	0.33	9.0	22	29	5.0	0.010	0.16	6.1

Table S2. Description of the sampling points. Geographic coordinates in decimal degree (WGS84).

Sampling Point	Type	River basin	Site type	Name Surface water	Latitude (N)	Longitude (E)
A-RS1	"Reference"	Aconcagua	Stream	Maiten	-32.854359	-70.39004
A-RS2	"Reference"	Aconcagua	River	Putaendo	-32.501779	-70.58127
A-R1	Main river	Aconcagua	River	Aconcagua	-32.857138	-70.47742
A-R2	Main river	Aconcagua	River	Aconcagua	-32.763050	-70.83962
A-R3	Main river	Aconcagua	River	Aconcagua	-32.916946	-71.42532
M-RS1	"Reference"	Maipo	Stream	San Gabriel	-33.779162	-70.24630
M-R4	Main river	Maipo	River	Maipo	-33.668390	-71.58292
M-R3	Tributary	Maipo	River	Mapocho	-33.682562	-70.97880
M-R2	Tributary	Maipo	River	Mapocho	-33.437701	-70.82175
M-R1	Tributary	Maipo	Stream	Yerbas Buenas	-33.344554	-70.36401

Table S3. Physical-chemical parameters per sampling site. T: temperature; Cond: conductivity; DOC: Dissolved Organic Carbon.

Sites	pH	Cond	T (ºC)	Oxygen	NO_2 mg/L	NO_3 mg/L	PO_4 mg/L	DOC mg/L
A-RS1	8.2	150	11	12	< 0.0070	1.1	0.016	0.61
A-RS2	8.7	350	11	13	< 0.0070	1.2	< 0.012	1.3
A-R1	8.4	450	12	13	0.020	3.3	< 0.012	1.3
A-R2	8.2	500	14	12	1.0	15	0.22	1.6
A-R3	8.7	800	17	26	1.2	18	0.70	2.5
M-RS1	8.3	130	4.9	12	< 0.0070	2.9	0.017	2.2
M-R4	8.5	1700	18	16	0.35	20	1.3	5.6
M-R3	8.4	1500	17	17	3.4	16	2.5	4.7
M-R2	8.1	760	13	12	0.11	3.6	0.016	3.1
M-R1	6.6	480	4.2	12	< 0.0070	3.4	< 0.012	0.57

Table S4. Internal standards - isotope-labelled compounds for quantitative LC-HRMS screening analysis. Electrospray Ionization Negative Mode (ESI_neg) and Electrospray Ionization Positive Mode (ESI_pos)

Name	Ion	LC-HRMS mode	m/z	RT [min]	Formula
Mono-isobutylphthalate D_4	$M-H^-$	ESI_neg	225.1070	10.6	$C_{12}H_{10}[2]H_4O_4$
4-Nitrophenol D_4	$M-H^-$	ESI_neg	142.0448	5.7	$C_6H_1[2]H_4N_1O_3$
Triclosan D_3	$M-H^-$	ESI_neg	289.9627	13.4	$C_{12}H_4[2]H_3Cl_3O_2$
Mecoprop D_3	$M-H^-$	ESI_neg	216.0512	11.5	$C_{10}H_8[2]H_3Cl_1O_3$
Laurylsulfate D_{25}	$M-H^-$	ESI_neg	290.3048	24.4	$C_{12}H_1[2]H_{25}O_4S$
Bezafibrate D_4	$M-H^-$	ESI_neg	364.1259	11.6	$C_{19}H_{16}[2]H_4Cl_1N_1O_4$
Acesulfame D_4	$M-H^-$	ESI_neg	166.0118	1.5	$C_4H_1[2]H_4N_1O_{14}S$
Hydrochlorothiazide $^{13}C_6$	$M-H^-$	ESI_neg	301.9773	1.7	$C_1[13]C_6H_8Cl_1N_3O_4S_2$
Bentazone D_6	$M-H^-$	ESI_neg	245.0872	9.7	$C_{10}H_6[2]H_6N_2O_3S_1$
Cyclamate D_{11}	$M-H^-$	ESI_neg	189.1234	4.1	$C_6H_2[2]H_{11}N_1O_3S_1$
Creatinine D_3	$M+H^+$	ESI_pos	117.0850	0.6	$C_4H_4[2]H_3N_3O_1$
Diazinon D_{10}	$M+H^+$	ESI_pos	315.1711	12.8	$C_{12}H_{11}[2]H_{10}N_2O_3P_1S_1$
Benzophenone-3 D_5	$M+H^+$	ESI_pos	234.1173	12.3	$C_{14}H_7[2]H_5O_3$
p-Toluene-sulfonamide D_4	$M+NH_4^+$	ESI_pos	193.0933	5.0	$C_7H_5[2]H_4NO_2S_1$
Cotinine D_3	$M+H^+$	ESI_pos	180.1211	0.9	$C_{10}H_9[2]H_3N_2O_1$
Diglyme D_6	$M+H^+$	ESI_pos	141.1392	2.4	$C_6H_8[2]H_6O_3$
Chlormequat D_9	M^+	ESI_pos	131.1296	0.7	$C_5H_4[2]H_9Cl_1N_1$
Carbamazepine D_{10}	$M+H^+$	ESI_pos	247.1650	9.8	$C_{15}H_2[2]H_{10}N_2O_1$
Atrazine $^{13}C_3$	$M+H^+$	ESI_pos	219.1111	10.2	$C_5[13]C_3H_{14}Cl_1N_5$
Benzotriazole D_4	$M+H^+$	ESI_pos	124.0807	3.9	$C_6H_1[2]H_4N_3$
Carbendazim D_4	$M+H^+$	ESI_pos	196.1019	2.2	$C_9H_5[2]H_4N_3O_2$

Name	Ion	LC-HRMS mode	m/z	RT [min]	Formula
Tri-n-butylphosphate D_{27}	$M+H^+$	ESI_pos	294.3414	13.3	$C_{12}[2]H_{27}O_4P_1$
DEET D_7	$M+H^+$	ESI_pos	199.1822	10.4	$C_{12}H_{10}[2]H_7N_1O_1$
Metolachlor D_6	$M+H^+$	ESI_pos	290.1788	12.2	$C_{15}H_{16}[2]H_6Cl_1N_1O_2$
Isoproturon D_3	$M+H^+$	ESI_pos	210.1680	10.4	$C_{12}H_{15}[2]H_3N_2O_1$
Diclofenac D_4	$M+H^+$	ESI_pos	300.0491	12.5	$C_{14}H_7[2]H_4Cl_2N_1O_2$
Caffeine D_3	$M+H^+$	ESI_pos	198.1065	5.6	$C_8H_7[2]H_3N_4O_2$
Clarithromycin D_3	$M+H^+$	ESI_pos	751.5030	10.3	$C_{38}H_{66}[2]H_3N_1O_{13}$
Desisopropylatrazine D_5	$M+H^+$	ESI_pos	179.0855	4.6	$C_5H_3[2]H_5Cl_1N_5$
Decyltrimethylammonium D_{30}	M^+	ESI_pos	230.4256	9.4	$C_{13}[2]H_{30}N_1$
Atenolol D_7	$M+H^+$	ESI_pos	274.2143	1.1	$C_{14}H_{15}[2]H_7N_2O_3$
Progesterone D_9	$M+H^+$	ESI_pos	324.2883	12.6	$C_{21}H_{21}[2]H_9O_2$
Verapamil D_6	$M+H^+$	ESI_pos	461.3281	9.0	$C_{27}H_{32}[2]H_6N_2O_4$
Bezafibrate D_4	$M+H^+$	ESI_pos	366.1405	11.6	$C_{19}H_{16}[2]H_4Cl_1N_1O_4$
Sulfamethoxazole D_4	$M+H^+$	ESI_pos	258.0845	6.4	$C_{10}H_7[2]H_4N_3O_3S_1$
Tebuconazole D_9	$M+H^+$	ESI_pos	317.2089	12.6	$C_{16}H_{13}[2]H_9Cl_1N_3O_1$
Imidacloprid D_4	$M+H^+$	ESI_pos	260.0847	6.6	$C_9H_6[2]H_4Cl_1N_5O_2$

Table S5. Internal standards - isotope-labelled compounds for quantitative GC-HRMS screening analysis

Name	Ion	m/z	Formula
PCB 180-$^{13}C_{12}$	M^+	407.24	$C_{12}H_3Cl_7$
Hexachlorobenzene-$^{13}C_6$	M^+	290.74	$^{13}C_6Cl_6$
Acenaphthene -D_{10}	M^+	164.27	$C_{12}D_{10}$
Phenanthrene-D_{10}	M^+	188.29	$C_{14}D_{10}$
Perylene-D_{12}	M^+	264.38	$C_{20}D_{12}$
Chrysene-D_{12}	M^+	240.36	$C_{18}D_{12}$
Naphthalene-D_8	M^+	136.22	$C_{10}D_8$

Table S6. Maximum, minimum, mean, and median concentrations (ng/L) of the various quantified compounds in both river basins

Compounds	Min	Max	Mean	Median
Cyclamate	40.0	40.0	40.0	40.0
Methenamine	0.61	5700	650	5.3
Desloratadine	0.61	110	90	90
Desisopropylatrazine	4.9	17	11	11
Fenuron	4.9	14	11	11
Tripropylamine	0.96	38	17	13
2-(2-Pyridyl)ethanol	0.96	16	6.0	5.0
Ethylene glycol diphenylether	1.8	23	14	15
Methyl diethanolamine	6.9	680	680	680
Carbendazim	180	7300	2600	200
Di-n-butyl phosphate	180	2500	1200	930
Tebuconazole	1.6	43	16	4.4
N-Ethyl-o-toluenesulfonamide	1.6	40	24	26
Thiacloprid	1.9	1.9	1.9	1.9
Nicosulfuron	1.9	2.3	2.3	2.3
N,N-Dimethyldodecylamine	2.3	5.4	5.4	5.4
4-(Dimethylamino)pyridine	5.4	6.0	6.0	6.0
Clopidogrel	2.4	410	210	210
Erythromycin	2.4	100	100	100
Losartan	10	2000	700	410
Triphenylphosphate	1.9	1.9	1.9	1.9
Tris(2-chloroethyl)phosphate	1.9	920	280	160
Imidacloprid-guanidine	3.45	6.6	6.6	6.6
Duloxetine	6.6	1500	1500	1500
Azoxystrobin acid	4.1	18000	6100	7.3
o-Dianisidine	4.1	690	430	430
Icaridin	1.6	1.6	1.6	1.6
Chlorophene	1.6	3.7	3.7	3.7
Lauryl diethanolamide	3.7	230	120	120
Benzyl benzoate	1.8	5.3	3.9	4.6
2-Methylbenzothiazole	1.8	6.7	4.6	4.6
2,4-Dichlorophenol	2.6	800	520	720
Fipronil	0.85	4.7	2.8	2.8
Anastrozole	0.85	1100	530	530
Isophthalic acid	1.0	30	7.5	3.6
Emamectin B1a	1.0	1.5	1.5	1.5
Cyprodinil	0.79	2.2	1.5	1.5
Sulfadimethoxine	0.79	1.3	1.3	1.3
Galaxolide	1.3	360	100	63
Azelaic acid	5.0	82	82	82

Compounds	Min	Max	Mean	Median
Metazachlor BH 479-11	0.90	1.7	1.2	1.1
Primidone	0.90	40	27	27
Tri-isobutylphosphate	6.7	94	64	100
Celestolide	6.7	19	19	19
Azoxystrobin	16	18	17	17
Spinosyn A	1.2	1.2	1.2	1.2
Epoxiconazole	1.1	7.5	4.8	5.9
DEET	1.1	90	30	1.9
Atorvastatin	1.4	47000	47000	47000
Pindolol	1000	1000	1000	1000
Acetamiprid	1.9	5400	1800	5.0
Tris(1-chloro-2-propyl)phosphate	1.9	230	92	44
TDCPP	25	120	120	120
Lidocaine	24	230	120	120
Dicyclohexyl sulfosuccinate	24	250	250	250
Valsartan	1.0	480	150	72
Imidacloprid	1.0	30	13	10
Candesartan	2.0	22000	7400	26
Prochloraz BTS44596	2.2	43	43	43
Sidenafil	9.2	23	16	16
Tylosin	7.0	14	11	11
Metolachlor-NOA 413173	7.8	610	310	310
Lauric isopropanolamide	1.7	680	170	2.0
N-Lauroylethanolamine	0.62	2800	590	0.94
Decylsulfate	0.62	33	8.2	2.3
Tritosulfuron	1.0	4.7	3.3	3.3
Sulfapyridine	2.01	150	72	48
N,N-Dimethyldecan-1-amide	15	350	350	350
Telmisartan	3.0	210	67	25
Metolachlor OA	3.0	98	52	52
Diclofenac	6.2	250	89	47
Capecitabine	1.5	3.4	2.4	2.4
Efavirenz	1.5	8.8	8.8	8.8
Chlorotoluron	8.8	230	230	230
Carbetamide	1.1	3.4	2.3	2.3
N,N-Dimethyldodecylamine N-oxide	1.1	4.5	4.5	4.5
Celecoxib	2.9	62	26	13
Metolachlor ESA	2.9	210	160	160
Metazachlor ESA	2.5	2.5	2.5	2.5
Boscalid	2.5	3800	1900	1900
Atrazine	15	180	99	99
Oxadiazone	8.4	8.4	8.4	8.4
Memantine	2.4	18	10	9.5
Dimethenamid ESA	0.56	98	26	1.9
Clothianidin	0.56	10	6.8	6.8
Tonalide	3.3	96	27	8.8

Compounds	Min	Max	Mean	Median
Acetyl-sulfamethoxazole	2.0	23	11	9.9
2-Hydroxyatrazine	2.0	7.3	7.3	7.3
Lenacil	3.1	3.1	3.1	3.1
Ketoprofen	1.0	47	13	5.0
Vardenafil	1.0	890	890	890
Tetraethyleneglycol monobutyl ether	7.5	45000	15000	160
Dicyclohexylurea	5.9	2700	700	17
Mycophenolic acid	5.9	56	32	32
5-Carboline	7.9	23	16	16
Bentazone	9.3	1100	580	580
Trifloxystrobin CGA 321113	27	78	78	78
Iminostilbene	1.9	1.9	1.9	1.9
Ethofumesate	1.9	36	22	22
2-Octyl-4-isothiazolin-3-one	3.5	53	29	29
N-Ethyl-3-methylbenzamide	3.5	1600	780	780
1-Benzylpiperazine	1.2	1.2	1.2	1.2
6:2 fluorotelomer sulfonic acid	1.3	1600	330	110
2-Isopropyl-6-methyl-pyrimidin-4-ol	1.8	1.8	1.8	1.8
Chlorothalonil-4-hydroxy	1.0	8.3	4.3	3.6
Isophorone diamine	81	380	230	230
7-(Ethylamino)-4-methylcoumarin	0.62	0.62	0.62	0.62
Atenolol	0.62	320	100	38
Pirimiphos-methyl	1.3	1.6	1.6	1.6
10,11-Dihydro-10-hydroxycarbamazepine	1.6	4700	1300	150
Bis(2-ethylhexyl)phosphate	3.5	3.5	3.5	3.5
Carbamazepine	2.7	250	99	69
Ephedrine	2.7	66	15	4.3
Desethylterbutylazine	2.9	21	21	21
Metobromuron	6.3	8.5	7.4	7.4
Hexa(methoxymethyl)melamine	3.7	72	31	25
Mebendazole	2.1	3.3	2.7	2.7
4-Nitroguaiacol	1.3	8.0	3.5	3.5
Diuron	1.3	64	30	27
Linuron	1.4	68	68	68
Diazinon	1.6	20	11	11
N,N-Dimethyltetradecylamine-N-oxide	0.88	970	270	18
Perfluorooctanoic acid	0.88	2.3	1.6	1.5
Acesulfame	1.2	530	530	530
Cashmeran	1.7	130	24	5.9
Isoproturon	1.7	5.7	4.7	4.7
10,11-Dihydro-10,11-dihydroxycarbamazepine	3.8	10000	490	430
Imazalil	17	270000	91000	28
Labetalol	0.87	0.90	0.89	0.89
Velvione	0.87	6.8	6.8	6.8
Climbazole	3.1	7100	3500	3500
Sotalol	3.1	7.8	7.8	7.8

Compounds	Min	Max	Mean	Median
Nitrendipin	1.2	1.3	1.2	1.2
Benzophenone-4	1.2	420	170	130
Metamitron	1.5	1.7	1.6	1.6
Bezafibrate	1.2	15	6.9	4.6
2(4-morpholinyl)benzothiazole	0.85	0.85	0.85	0.85
2-(Diethylamino)-6-methylpyrimidin-4-one	0.85	7.4	4.65	4.65
Diazepam	0.78	1.0	0.91	0.91
Harmine	0.57	0.72	0.64	0.63
Genistein	0.57	8.7	4.13	3.13
Diphenylphosphine oxide	0.87	13000	6400	64001
Chenodeoxycholic acid	0.84	77	25	6.1
Propyphenazone	0.84	5.1	4.7	4.7
Crotamiton	1.5	1.5	1.5	1.5
Daidzein	1.5	33	17	17
Cyclophosphamide	1.5	2.9	2.2	2.2
Amitriptyline	1.5	6.8	4.5	4.5
Dimethachlor	2.1	210	210	210
Metolachlor	2.4	180	91	91
Metoprolol	2.4	8.0	5.5	5.5
Benzoylecgonin	3.1	36	19	18
Verapamil	2.4	2.4	2.4	2.4
Pyrimethanil	2.4	7.2	6.2	6.2
Furosemide	1.6	200	58	15
Palmitoylethanolamide	1.6	8600	960	9.0
Fluvoxamine	5.2	90	29	9.4
Torasemide	2.4	2.4	2.4	2.4
Metoprolol acid	2.4	29	28	28
Acridone	1.5	62	22	2.1
Domperidone	1.5	9.0	9.0	9.0
Metalaxyl	9.0	2200	1100	1100
Clozapine	3.4	13	8.0	8.0
Dimethylaminophenazone	1.8	1.8	1.8	1.8
Diphenhydramine	1.8	3.6	3.6	3.6
Hydrochlorothiazide	1.2	870	270	160
2-Hydroxyquinoline	0.75	22	9.0	7.6
2-Oxindole	0.75	2.9	2.9	2.9
Terbuthylazine	1.4	250	44	3.0
Citalopram	1.3	170	50	15
Dimethoate	1.3	6.6	4.9	4.9
Phloretin	0.98	13	4.9	3.5
Propiconazole	0.98	8.4	5.5	5.5
Oxazepam	2.5	3600	1800	1800
3,4,5-Trichlorophenol	5.0	990	500	500
Mefenamic acid	1.2	67	25	16
Benzyl-2-naphthylether	1.2	14	14	14
2-(Methylthio)benzothiazole	14	570	380	380

Compounds	Min	Max	Mean	Median
Octocrylene	14	2900	1400	1400
4-tert-Butylbenzenesulfonamide	4.6	4.6	4.6	4.6
Gabapentin-Lactam	4.6	19	12	112
Pentoxifylline	2.1	2.1	2.1	2.1
Metformin	280	7600	2500	1800
Pencycuron	1.5	9.7	4.5	2.3
Cyromazine	1.5	4.4	4.4	4.4
Bisoprolol	1.9	8.2	4.0	2.0
Metazachlor	0.89	0.89	0.89	0.89
Fenpropimorph	0.89	1.4	1.4	1.4
Thiacloprid amide	1.4	2.8	2.8	2.8
Prochloraz	2.8	170	170	170
2-Hydroxycarbamazepine	14	46	27	21
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	14	8100	8100	8100
Cyclohexylphenylketone	15	390	83	32
Sulfathiazole	6.3	6.9	6.6	6.6
Sulfamethoxazole	6.3	1400	520	340
Enalapril	11	11	11	11
Secobarbital	11	15	15	15
Amantadine	15	16	16	16
Triethylcitrate	8.4	8.4	8.4	8.4
Triethylphosphate	2.1	52	26	24
Tri(butoxyethyl)phosphate	1.9	1.9	1.9	1.9
Isophorone	1.9	36	24	27
Sertraline	4.6	11	11	11
Bisphenol S	2.6	51	17	9.0
Saccharin	2.6	95	41	36
Cholic acid	1.3	420	55	5.3
Clarithromycin	54	9000	3000	68
4-Aminoantipyrine	54	140	100	92
Diflufenican	15	31	22	20
Diphenylphosphate	3.7	19	12	12
Cetirizine	3.7	2500	670	93
Raloxifene	4.1	13	7.5	5.5
Lorazepam	2.6	4.4	3.5	3.5
Fluconazole	2.6	175	76	63
Diacetylethylenediamine	3.0	56	30	21
Dimethenamid	11	97	97	97
Clofibric acid	2.7	10	6.5	6.5
1-Cyclohexyl-3-phenylurea	2.7	1500	15000	1500
Myclobutanil	1.1	3.0	2.4	2.9
Bicalutamide	1.1	4.4	3.2	3.2
2-Acetonaphthone	1.0	9.0	3.5	2.7
Enrofloxacin	1.0	100	100	104
2-Aminobenzimidazole	3.4	18	12	15
Glimepiride	2.5	770	260	3.4

Compounds	Min	Max	Mean	Median
Benzocain	2.5	3300	3300	3400
Tetracain	2.3	3.0	2.7	2.7
Piperine	0.72	12	3.5	1.4
MCPA	0.72	2700	920	86
2,4-Dichlorophenoxyacetic acid	1.4	640	240	73
2-Benzothiazolesulfonic acid	1.4	56	25	9.8
Dodecane-12-lactam	7.2	350	350	350
Ondansetron	16	25	20	20
Monensin	2.0	4.3	3.2	3.2
Piperonyl butoxide	2.0	12000	12000	12000
N-isopropyl-N-phenyl-p-phenylenediamine	160	450	280	240
Cyproconazole	39	39	39	39
Fluoranthene	27	27	27	27
Phenanthrene	33	200	120	110
4-Methylbenzylidene camphor	5.2	5.2	5.2	5.2
Benzyldimethyldodecylammonium	5.2	870	870	870
Hexadecyltrimethylammonium	1.9	3.6	2.8	2.8
p-Toluenesulfonamide	21	150	86	91
Cocaine	10	10	10	10
Tricresylphosphate	10	370	370	370
N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylenediamine	9.4	9.4	9.4	9.4
Fluorene	170	170	170	170
3-Hydroxy-2-naphthoic acid	2.3	4.3	3.3	3.3
Mepiquat	2.3	93	55	55
Tetraglyme	12	14	13	13
Denatonium	6.4	13	9.8	10
Dimethachlor ESA	7.2	34	19	18
Acridine	1.1	1.1	1.1	1.1
Diphenylsulfone	6.6	11	9.5	11
Diphenylether	6.6	110	48	34
Diethofencarb	3.2	3.2	3.2	3.2
Tepraloxydim	0.68	3.3	1.7	1.1
Quizalofop	0.68	2.2	2.2	2.2
Metolachlor CGA 368208	2.2	6.0	6.0	6.0
Prochloraz BTS40348	0.75	1200	600	600
Benzyldimethyltetradecylammonium	0.75	1.9	1.3	1.2
Enoxolone	0.86	1700	250	3.3
Losartan Carboxylic acid	1.9	830	340	290
Tetraacetylethylenediamine	2.3	220	65	19
Tetrabutylammonium	2.7	5.0	4.1	4.1
Equilin	3.2	11	9.3	9.3
Triacetin	2.8	7.6	5.2	5.2
Indole-3-acrylic acid	0.76	40	11	1.1
Methocarbamol	0.58	3.2	2.0	2.0
N,N-Dimethyldecylamine	0.58	2.1	2.1	2.1

Table S7. Correlations between land use and number of chemicals quantified in Aconcagua basin

	AGR	BAR	VEG	GRASS	SHR	SNOW	TREES	URB	WAT
Additive	0.20	0.12	-0.76	-0.36	-0.12	0.12	-0.12	-0.12	0.12
Food and beverage	0.45	-0.22	0.18	0.45	0.45	-0.45	0.67	0.67	0
Intermediate	-0.20	0.20	-0.63	0	0	0.20	0.2	0	0
Natural compounds	-0.36	0.60	-0.76	-0.36	-0.60	0.12	-0.36	-0.36	0.60
PAH	0.63	-0.32	-0.25	0	0.32	-0.32	0.32	0.32	0
Personal care and household	0.53	-0.53	0.33	0.53	0.74	-0.32	0.74	0.53	-0.32
Pesticide	0.45	-0.22	0.18	0.45	0.45	-0.45	0.67	0.67	0
PFAS	0.12	0.12	-0.76	-0.36	-0.12	0.12	-0.12	-0.12	0.12
Pharmaceutical	0.11	-0.11	-0.17	0.32	0.32	-0.11	0.53	0.53	-0.11
Polymer additive	0.32	-0.53	0.67	0.74	0.74	-0.74	**0.95**[a]	**0.95**[a]	-0.32
POP	0	0.26	-0.41	0.26	0	0	0.26	0.26	0.26
Solvent	0.63	-0.32	-0.25	0	0.32	-0.32	0.32	0.32	0
Veterinary pharmaceutical	0.12	-0.60	0.76	0.36	0.60	-0.12	0.36	0.12	-0.60
Biocide	0.12	0.12	-0.76	-0.36	-0.12	0.12	-0.12	-0.12	0.12
Dye	0.45	-0.22	0.18	0.45	0.45	-0.45	0.67	0.67	0

AGR, agriculture land use; BAR, bareland land use; VEG, flooded vegetation land use; GRASS, grass land use; SHR, shrubs and scrubs land use; SNOW, snow and ice land use; TREES, trees land use; URB, urban land use; WAT, water land use.
Bold values represent correlation with significance ([a]Significance at the 0,05; probability level; [b]Significance at the 0,01 probability level).

Table S8. Correlations between land use and number of chemicals quantified in Maipo basin

	AGR	BAR	VEG	GRASS	SHR	SNOW	TREES	URB	WAT
Additive	0.60	-0.60	**0.88**[a]	0.84	0.84	-0.60	0.60	0.12	-0.84
Food and beverage	**0.95**[a]	**-0.95a**	**0.88**[a]	0.74	**0.95**[a]	-0.74	0.74	0.53	-0.74
Intermediate	0.74	-0.74	1a	**0.95**[a]	**0.95**[a]	-0.74	0.74	0.32	**-0.95**[a]
Natural compounds	0.84	-0.84	0.50	0.36	0.60	-0.60	0.36	0.60	-0.36
PAH	0	0	0	0	0	0	0.32	0.63	0
Personal care and household	0.11	-0.11	0	-0.11	0.11	0.11	0.32	0.53	0.11
Pesticide	0.80	-0.80	**0.95**[a]	0.80	**1**[a]	-0.60	0.8	0.40	-0.80
PFAS	0.22	-0.22	0.59	0.67	0.45	-0.45	0.67	0.45	-0.67
Pharmaceutical	**1**[a]	**-1**[a]	0.74	0.60	0.80	-0.80	0.60	0.60	-0.60
Polymer additive	**1**[a]	**-1**[a]	0.74	0.60	0.80	-0.80	0.60	0.60	-0.60
POP	0	0	0	0	0	0	0.32	0.63	0
Solvent	0.32	-0.32	0.67	0.74	0.53	-0.53	0.32	-0.11	-0.74

	AGR	BAR	VEG	GRASS	SHR	SNOW	TREES	URB	WAT
Veterinary pharmaceutical	0.11	-0.11	0	-0.11	0.11	0.11	0.32	0.53	0.11
Biocide	0.63	-0.63	0.33	0.32	0.32	-0.63	0	0.32	-0.32
Dye	0.60	-0.60	**0.88**[a]	0.84	0.84	-0.60	0.60	0.12	-0.84

AGR, agriculture land use; BAR, bareland land use; VEG, flooded vegetation land use; GRASS, grass land use; SHR, shrubs and scrubs land use; SNOW, snow and ice land use; TREES, trees land use; URB, urban land use; WAT, water land use.
Bold values represent correlation with significance ([a]Significance at the 0,05; probability level; [b]Significance at the 0,01 probability level).

Figure S1. Selected highest concentrations of quantified OMPs in the River Aconcagua (Left) and Maipo (Right) Basin. Chemical classes are colour coded. Abbreviation as follows: TXIB= 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, MCPA= 2-methyl-4-chloro-phenoxyacetic acid, CBZ-diol= 10,11-Dihydro-10,11-dihydroxycarbamazepine.

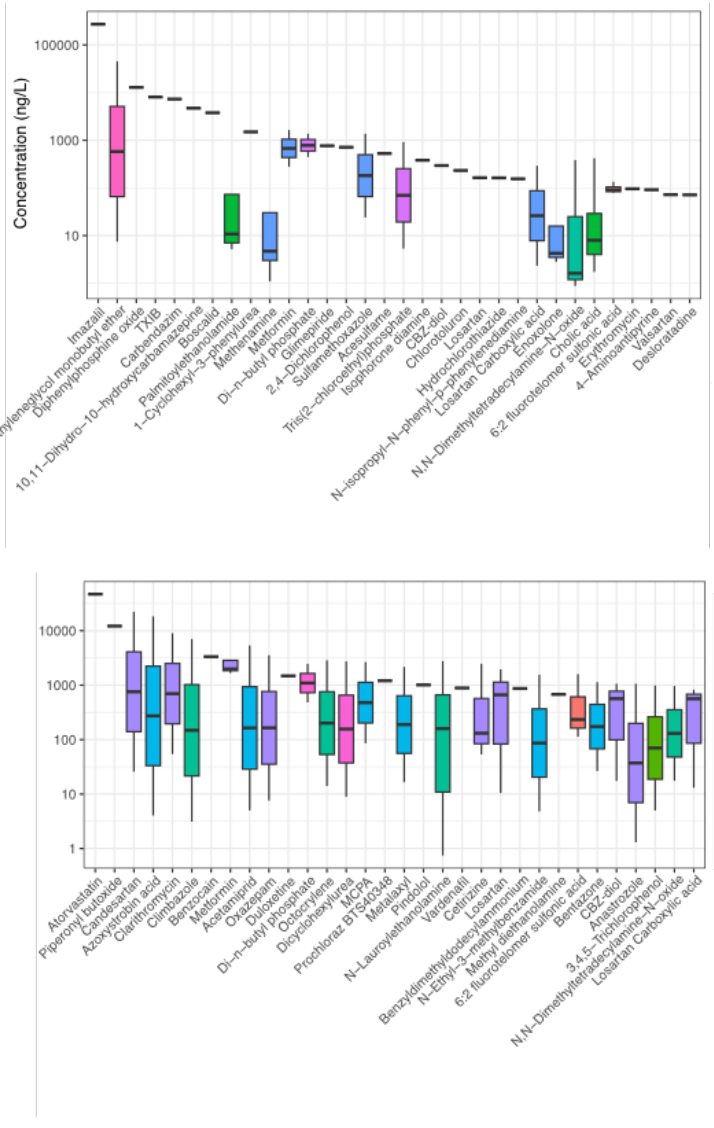
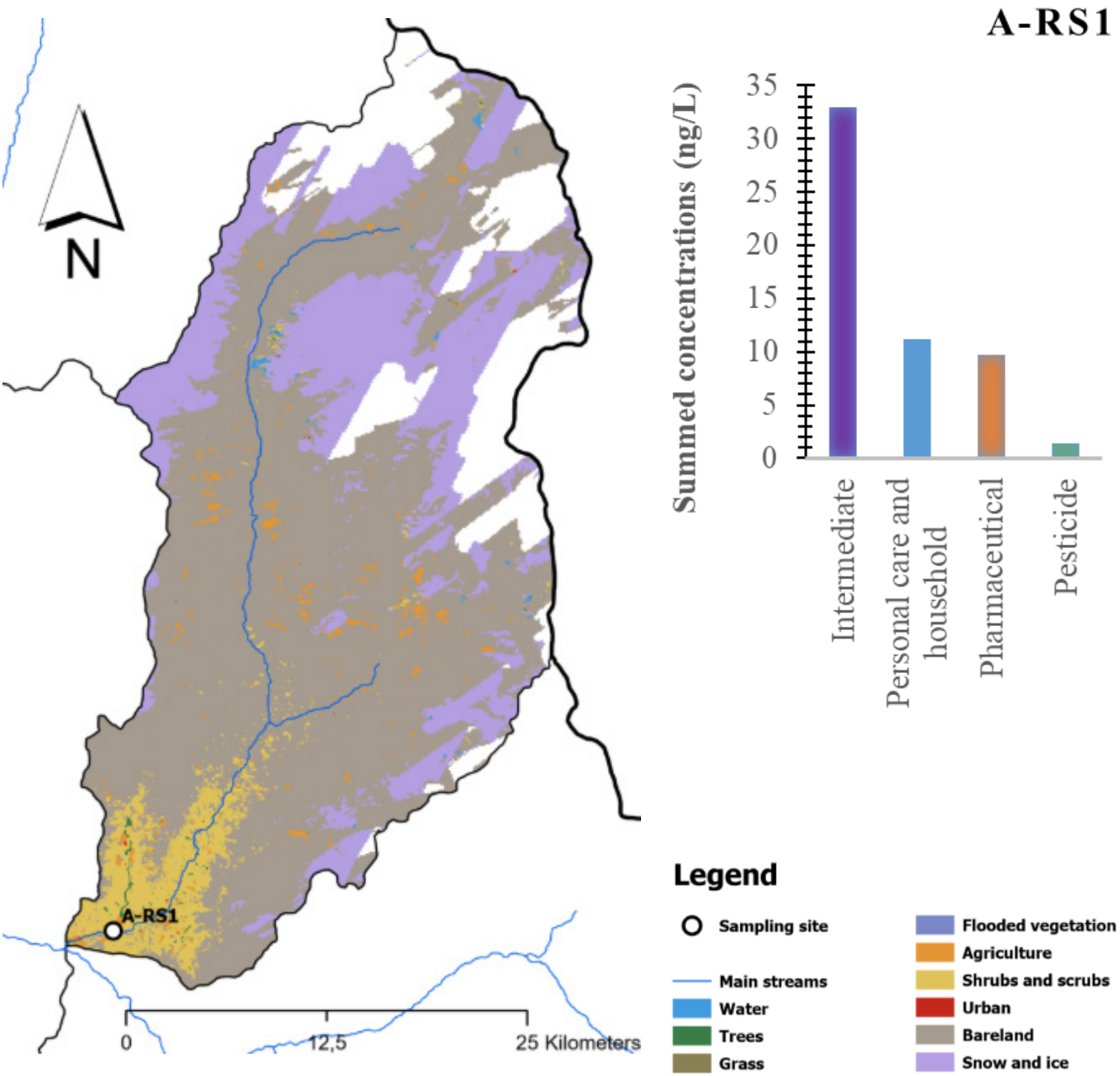
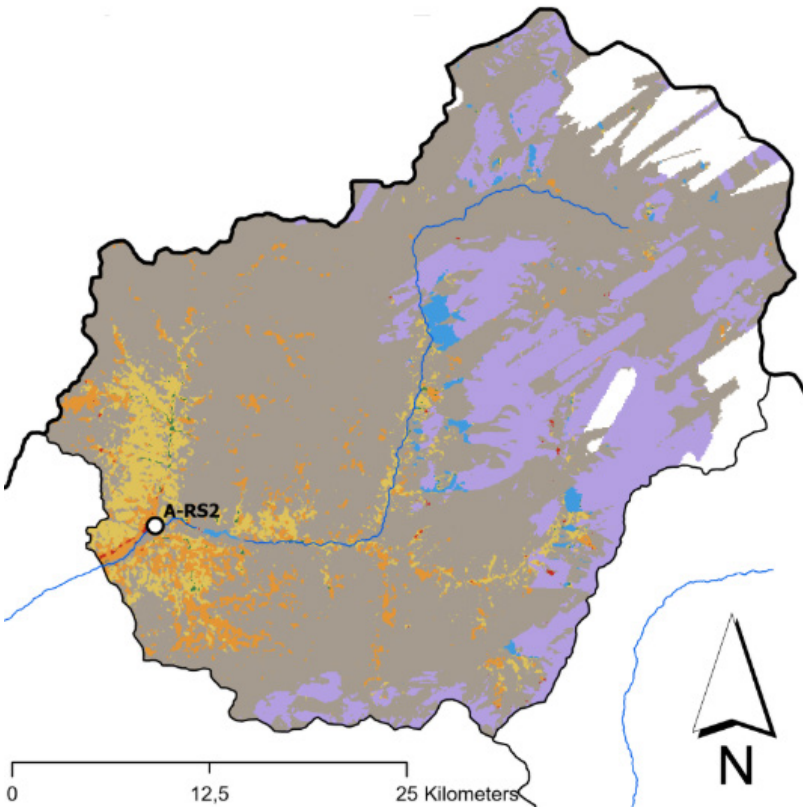
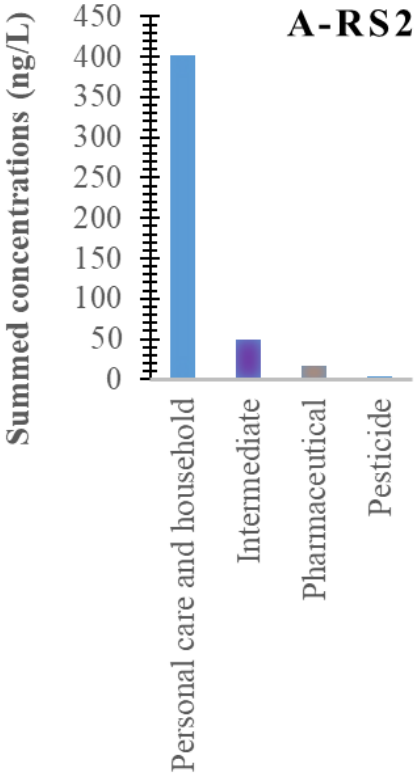
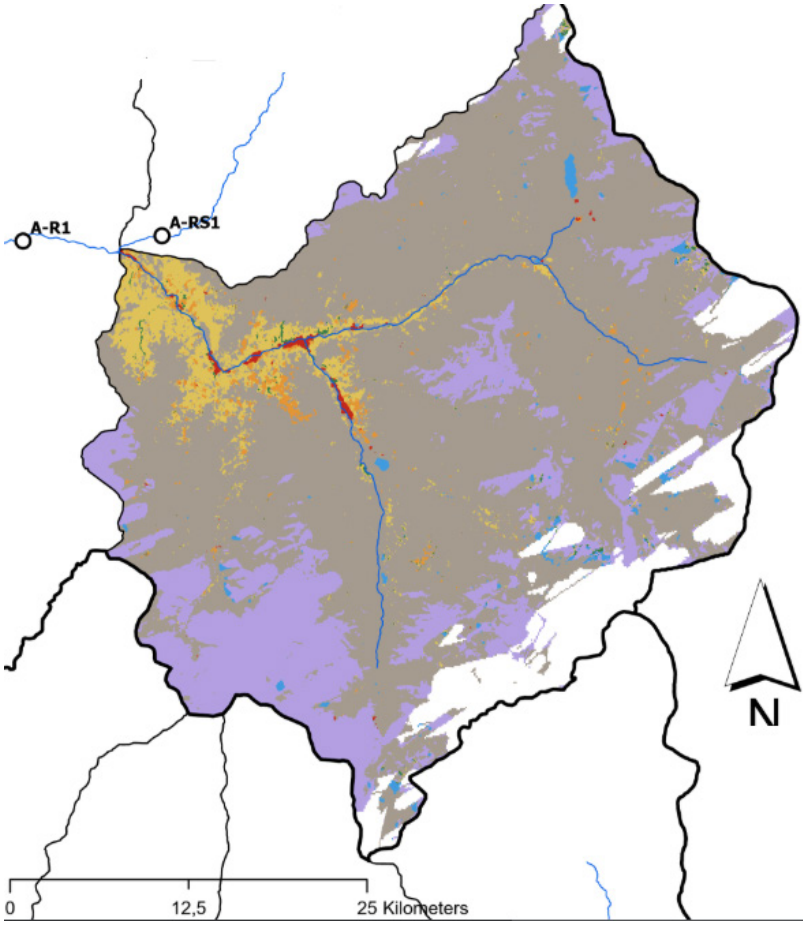


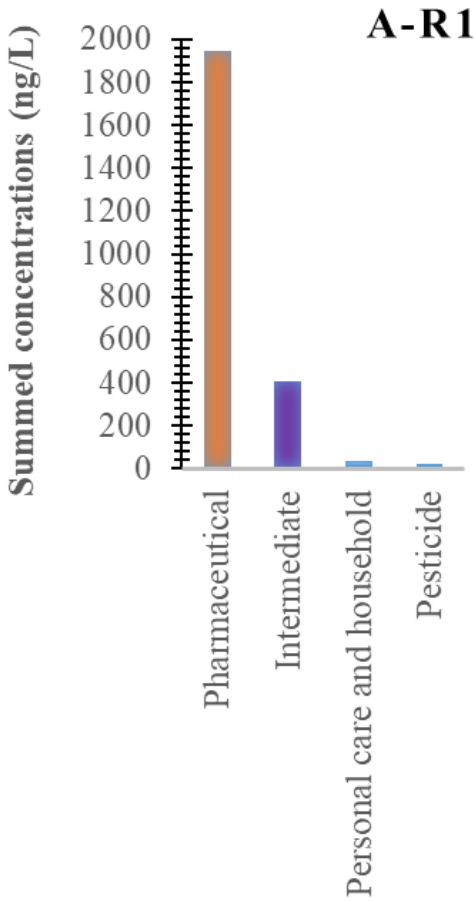
Figure S2. Land use by sampling point and the total concentration of the three primary chemical classes in River Aconcagua basin.

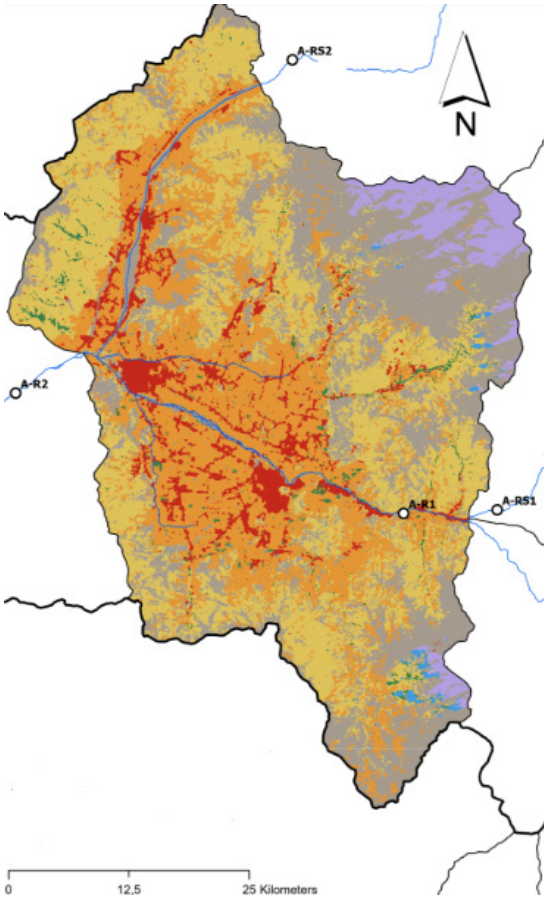


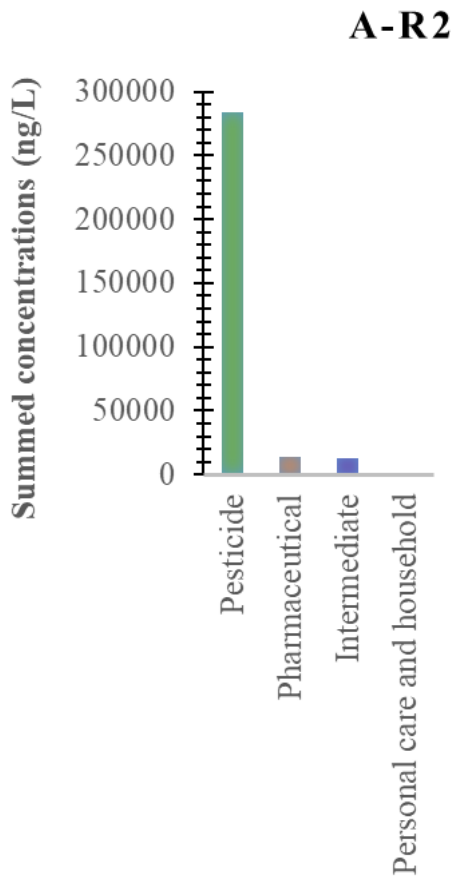

A-RS2
0
12,5
25 Kilometers
N

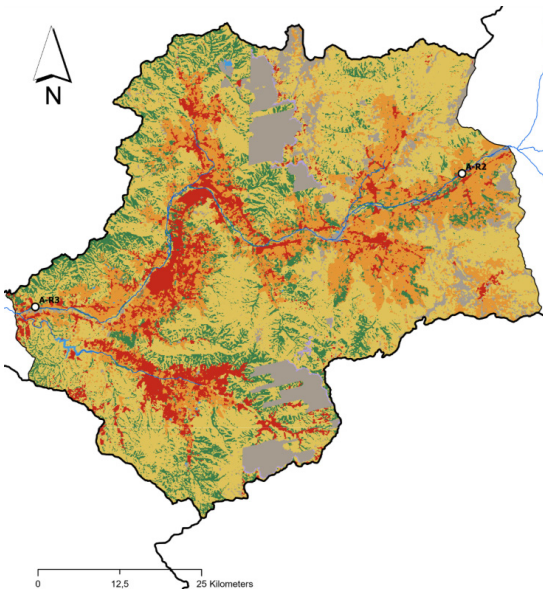

A-RS2
Summed concentrations (ng/L)
450
400
350
300
250
200
150
100
50
0
Personal care and household
Intermediate
Pharmaceutical
Pesticide


A-R1
A-RS1
0
12,5
25 Kilometers
N


A-R1
Summed concentrations (ng/L)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Pharmaceutical
Intermediate
Personal care and household
Pesticide


A-RS2
A-R2
A-R1
A-RS1
N
0
12,5
25 Kilometers


A-R2
Summed concentrations (ng/L)
300000
250000
200000
150000
100000
50000
0
Pesticide
Pharmaceutical
Intermediate
Personal care and household


A-R3
A-R2
N
0
12,5
25 Kilometers

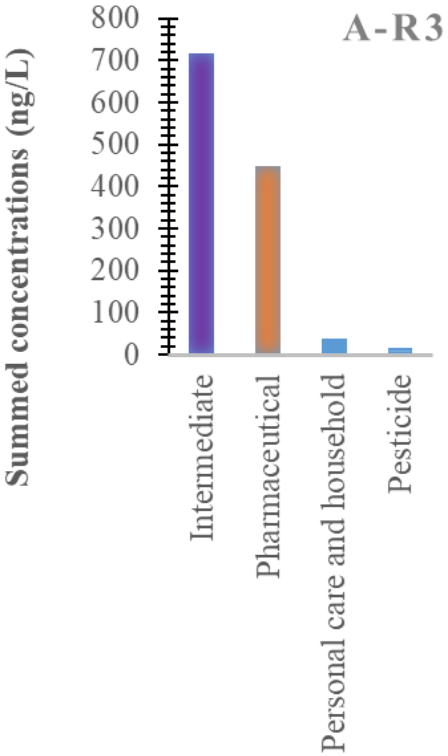
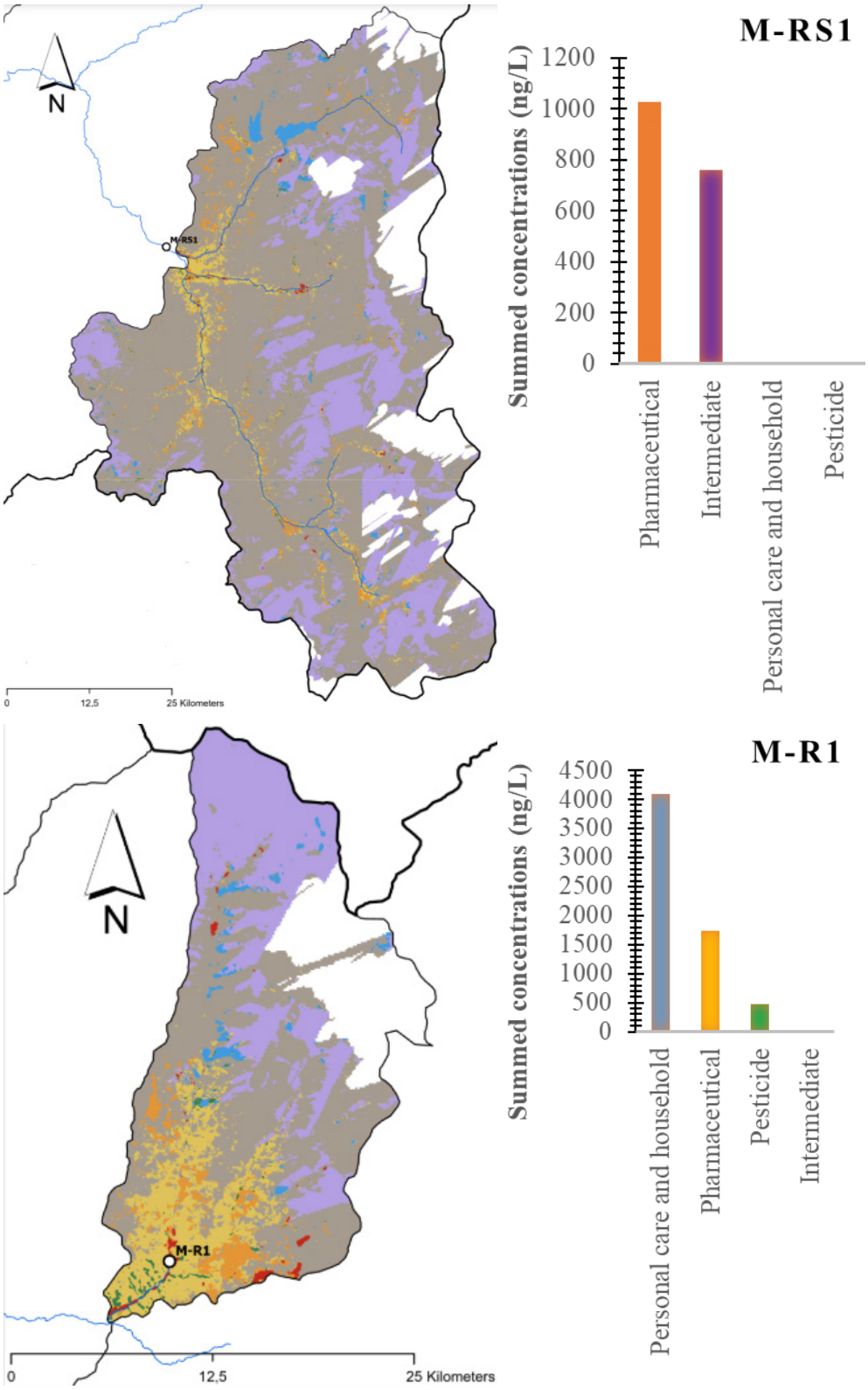
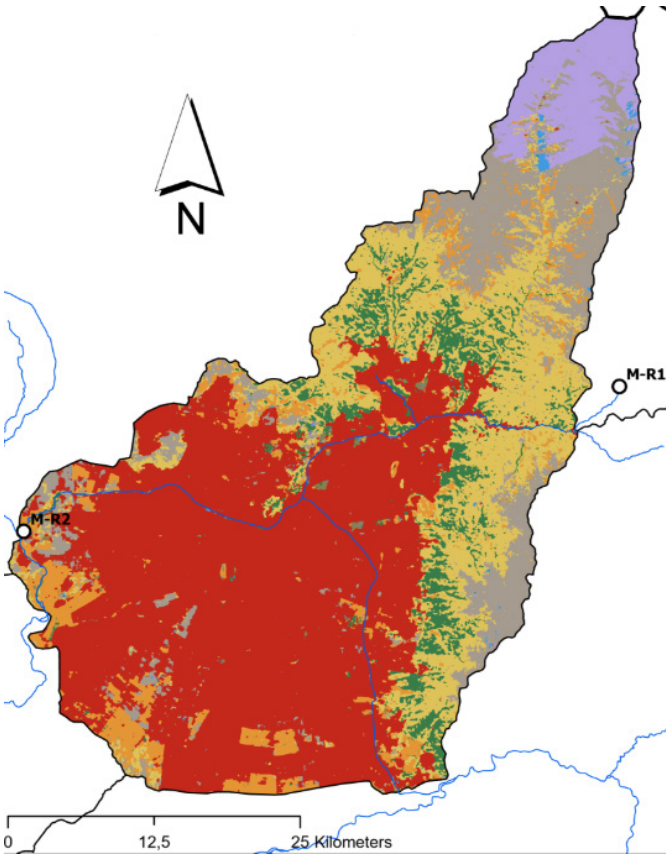
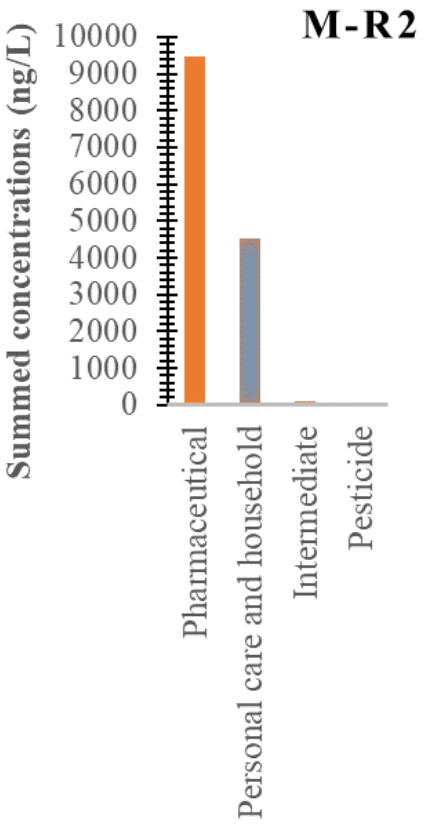
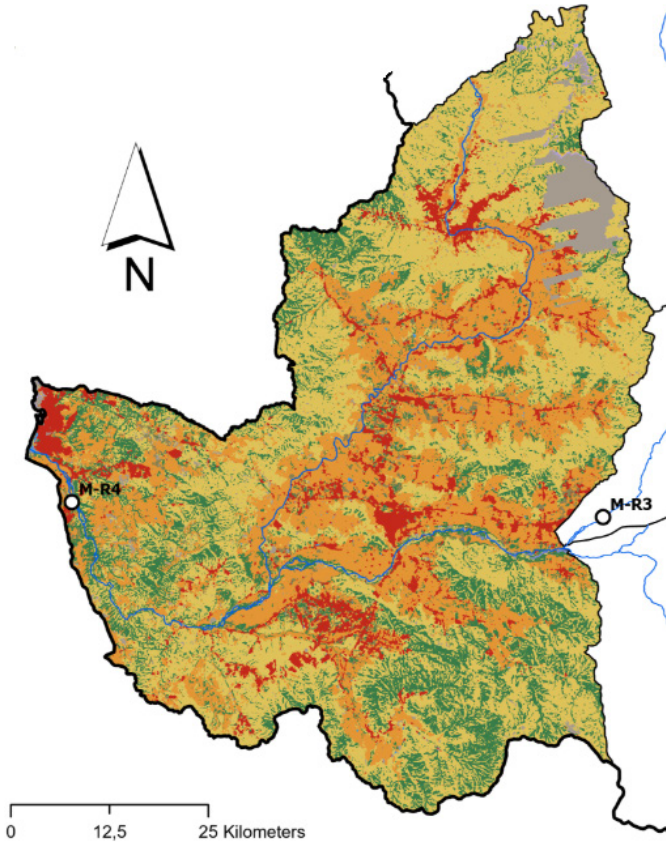

A-R3
Summed concentrations (ng/L)
800
700
600
500
400
300
200
100
0
Intermediate
Pharmaceutical
Personal care and household
Pesticide

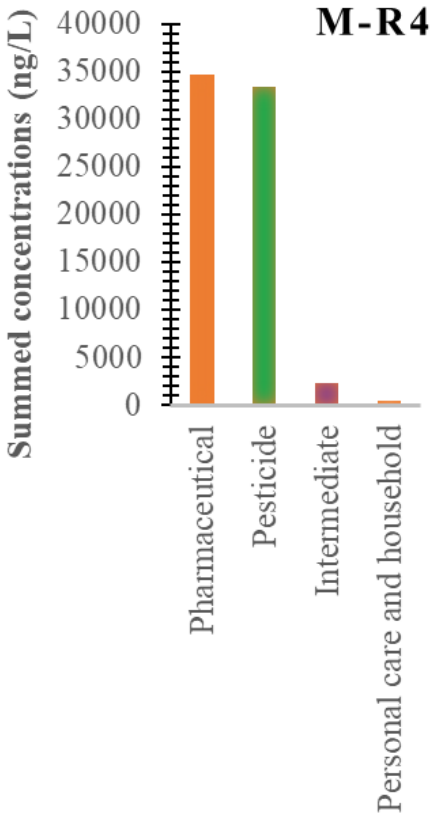
Figure S3. Land use by sampling point and the total concentration of the three primary chemical classes in River Maipo basin.

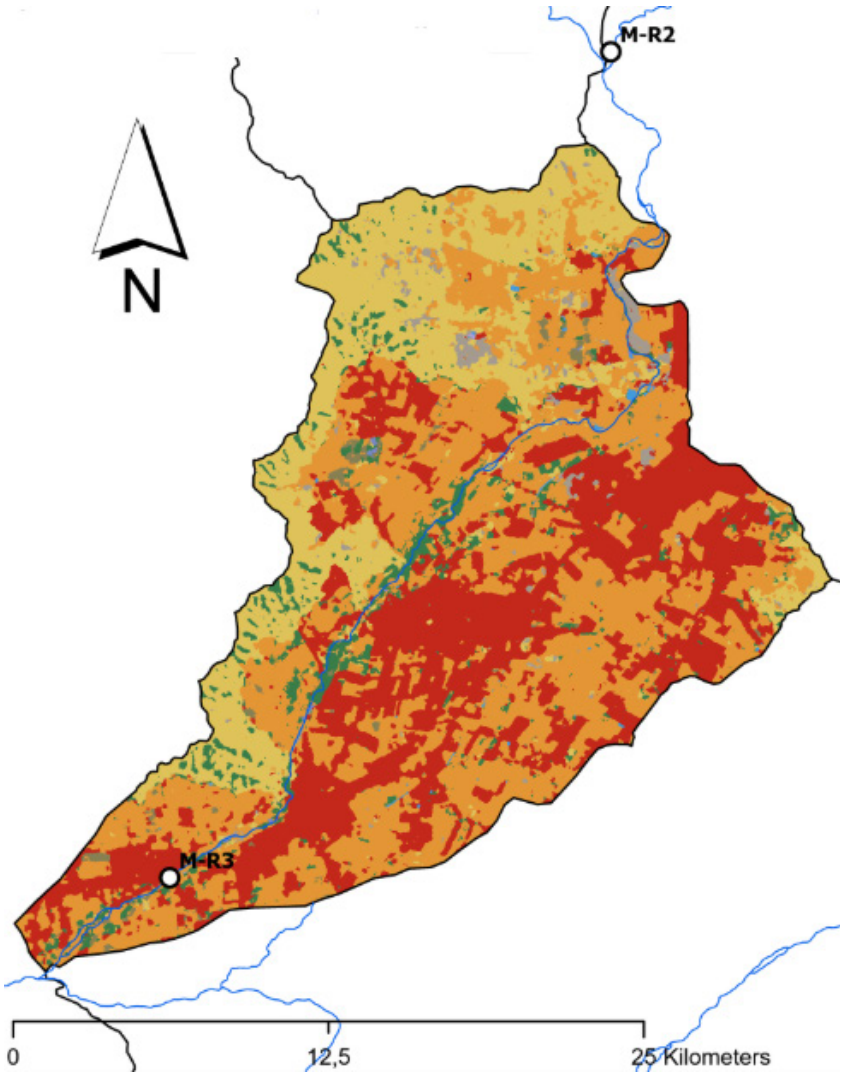


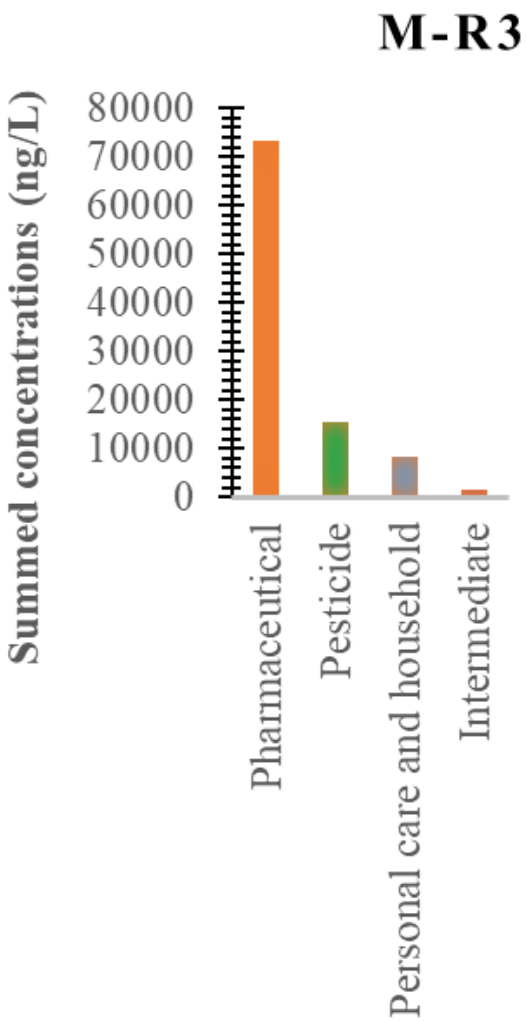

N
M-R1
M-R2
0
12,5
25 Kilometers


M-R2
Summed concentrations (ng/L)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Pharmaceutical
Personal care and household
Intermediate
Pesticide


N
M-R4
M-R3
0
12,5
25 Kilometers


M-R4
Summed concentrations (ng/L)
40000
35000
30000
25000
20000
15000
10000
5000
0
Pharmaceutical
Pesticide
Intermediate
Personal care and household


M-R2
N
M-R3
0
12,5
25 Kilometers


M-R3
Summed concentrations (ng/L)
80000
70000
60000
50000
40000
30000
20000
10000
0
Pharmaceutical
Pesticide
Personal care and household
Intermediate

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SECCIÓN 6

Resumen

RESUMEN

A continuación, se presenta un resumen general de los materiales y métodos, así como de las metodologías desarrolladas y los resultados obtenidos en cada uno de los seis artículos que conforman esta tesis doctoral. En este apartado se presentan cinco estudios realizados en el área de estudio seleccionada, el Parque Natural de la Albufera de Valencia, y un sexto estudio sobre la co-ocurrencia y distribución espacial de contaminantes orgánicos en aguas superficiales de las cuencas de los ríos Aconcagua y Maipo en Chile Central. Estos cinco primeros estudios se enfocan en evaluar el impacto negativo de la actividad agrícola, desarrollada tanto dentro del parque como en sus alrededores, así como de las aguas residuales que ingresan al parque, sobre los ecosistemas acuáticos circundantes. Este Parque Natural, con una extensión de 21.120 hectáreas, se encuentra a unos 10 km de la ciudad de Valencia, España, y se caracteriza por la presencia de cultivos de arroz, cítricos y huertas. Diversos ecosistemas acuáticos se interconectan e influyen de manera dinámica en este parque, incluyendo el propio lago de la Albufera, los arrozales (durante los periodos de inundación y drenaje), las acequias de riego, los manantiales o Ullals, las pequeñas lagunas de la restinga, las golas y los fondos marinos. El lago también se comunica con el Mar Mediterráneo a través de tres canales o golas, cuyo flujo de agua es regulado por una serie de compuertas que mantienen el nivel del lago en los valores deseados. El estudio se centró principalmente en muestras de agua y sedimento del Parque Natural de L'Albufera. Las muestras de agua y sedimento se recolectaron entre mayo y octubre de 2019 en 51 puntos de muestreo del parque.

Entre septiembre y octubre de 2020 se desplegaron los muestreadores pasivos en 12 puntos del parque y se recogieron muestras puntuales de agua superficial. Mientras que en abril de 2021 se tomaron núcleos de sedimento en las partes norte y sur del lago.

6.1. Resumen sección 2: "Perfil general de contaminación en el Parque Natural de L'Albufera: Análisis de agua y sedimento"

A continuación, se presenta un resumen general de las principales metodologías utilizadas, así como los principales resultados obtenidos dentro del Parque Natural de la Albufera obtenidos en la primera y segunda publicación científica. En estos dos estudios se identifican las vías de entrada de contaminantes orgánicos al humedal natural mediante el uso de métodos de análisis dirigidos (Target Analysis, TA) y análisis no dirigidos (Non- Target Analysis, NTA) y se destacan los puntos críticos de contaminación específicos utilizando sistemas de información geográfica (SIG).

El área de estudio incluyó la totalidad del Parque Natural de la Albufera, así como regiones adyacentes a los ríos Turia, Magro y Júcar. En total, se seleccionaron 51 puntos de muestreo, que abarcaban cuatro en los principales ríos, 41 canales de riego, cinco dentro del propio lago de la Albufera, y uno en cada una de las tres golas.

En 2019 se realizaron dos campañas de muestreo de agua en canales de riego: una al inicio del cultivo de arroz (mayo-junio) y otra al inicio de la cosecha (septiembre-octubre), recolectando un total de 100 muestras de agua. Durante la segunda campaña, dos de los canales estaban secos debido al drenaje, limitando la toma de muestras. El número de muestras de sedimentos fue menor debido al revestimiento de hormigón y limpieza periódica de los canales, lo que impide la acumulación de sedimentos.

El método de extracción de contaminantes orgánicos en agua se realizó mediante la extracción en fase sólida (SPE), utilizando cartuchos Strata®-X con sorbente de naturaleza polimérica que actúa en fase reversa para lograr una retención sólida de las diversas clases de compuestos. A continuación, se aplicaron 250 mL de muestra al colector de vacío de 12 puertos a una velocidad constante, mediante la aplicación de vacío. Los cartuchos fueron limpiados con 6 mL de agua destilada y se dejaron secar durante 15 minutos. Los analitos fueron eluidos a gravedad con 6 mL de metanol seguido de 3 mL de una mezcla de metanol y diclorometano (MeOH/DCM, 1:1). Los extractos fueron evaporados, reconstituidos en metanol o una solución de agua/metanol, y transferidos a viales ámbar para el análisis de pesticidas y NTA. Los extractos se almacenaron a -20 ºC hasta su análisis.

El método de extracción para compuestos moderadamente polares en sedimentos, tales como los pesticidas, se llevó a cabo utilizando 1 g de sedimento liofilizado mediante el método Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS). Se procesó 1 g de sedimento liofilizado, humedecido con 7,5 mL de agua, y se añadieron 10 mL de acetonitrilo (ACN). La mezcla fue agitada manualmente durante 1 minuto, seguida de la adición de una combinación de sales ($MgSO_4$, NaCl, citrato de sodio dihidrato y ácido cítrico monohidratado). Posteriormente, se agitó vigorosamente durante 3 minutos, seguido de centrifugación a 2465 rcf por 5 minutos. Una alícuota de 1 mL del sobrenadante fue transferida a un tubo con PSA, $MgSO_4$ y sílice C18, y nuevamente agitada y centrifugada. El extracto limpio se filtró con un filtro de PTFE (0,45/0,22 µm) y se almacenó a -20 ºC hasta su análisis.

El método de extracción para compuestos polares como fármacos y productos del cuidado personal (PPCPs), sustancias perfluoroalquiladas (PFASs) y retardantes de llama organofosforados (OPFRs) se llevó a cabo mediante extracción sólido-líquido (SLE) siguiendo el procedimiento de Carmona et al. (2017). Se procesó 1 g de sedimento liofilizado utilizando una mezcla de disolventes (MeOH, agua Milli- Q y buffer McIlvaine-EDTA, pH=4,5). Se añadieron 50 µL de una mezcla de estándares internos (1 µg mL^{-1}), se homogeneizó con agitación y sonicación, y se centrifugó. El sobrenadante se diluyó a 200 mL con agua Milli-Q antes de su extracción por SPE. La SPE utilizó cartuchos con sorbente HLB (Strata-X), activados con MeOH y agua Milli-Q. Tras secar los cartuchos, los analitos se eluyeron con MeOH y una mezcla MeOH/DCM (1:1). Los extractos se evaporaron bajo flujo de nitrógeno a 40ºC, se redisolvieron en agua-MeOH (70:30), y se filtraron con filtros de nailon (0,22 µm). Finalmente, los extractos fueron almacenados a -20 ºC hasta su análisis por NTA.

La técnica de análisis empleada fue la cromatografía líquida acoplada a espectrometría de masas (LC-MS), con métodos de análisis dirigidos para la detección de pesticidas. Estos se analizaron mediante cromatografía líquida de fase reversa, utilizando un sistema LC Vanquish

Horizon (Thermo Scientific) acoplado al espectrómetro de masas Orbitrap Exploris 120 con ionización por electropulverización calentada (HESI). La LC en fase reversa es ampliamente empleada en la separación de CECs, siendo comúnmente utilizada la fase estacionaria apolar, gel de sílice (C18).

Para identificar compuestos fuera del alcance del análisis dirigido, se implementó un método de analisis no dirigido utilizando el software Compound Discoverer 3.2 (CD) con análisis dependiente de datos (DDA), centrado en la intensidad máxima como parámetro clave. Este método seleccionó y fragmentó los cuatro iones más intensos por ciclo instrumental, empleando mzCloud como biblioteca principal y ChemSpider® como base de datos complementaria. El análisis Fragment Ion Search (FISh) ayudó a reconocer patrones moleculares basándose en fragmentos generados durante la etapa MS2, verificando los resultados de ChemSpider® con datos de espectrometría en tándem. Los candidatos no dirigidos se aislaron aplicando un filtro de masa exacta con una ventana de ± 5 ppm.

Los archivos sin procesar se analizaron junto con una muestra en blanco, empleada para filtrar señales de interferencia asociadas a contaminación cruzada. Este flujo de trabajo predijo composiciones elementales para todos los compuestos y eliminó el fondo químico utilizando las muestras en blanco. La identificación de compuestos se llevó a cabo mediante búsquedas en mzCloud® (ddMS2 y/o DIA), ChemSpider® (masa exacta o fórmula) y bases de datos locales con listas de masas (masa exacta con o sin tiempo de retención). El software Compound Discoverer® generó una gran cantidad de resultados a partir de los datos sin procesar, lo que requirió un proceso de filtrado. Las muestras en blanco fueron clave para evaluar posibles contaminaciones o interferencias derivadas de la matriz o el instrumento. La principal ventaja del NTA radica en su capacidad para identificar compuestos, como metabolitos, incluso cuando los estándares de referencia son escasos o inexistentes.

La columna utilizada para la determinación de pesticidas fue Luna C18 (15.0 cm × 0.21 cm) con un tamaño de partícula de 3 µm. Para la detección del NTA se utilizó una columna Kinetex 1.7 µm Biphenyl de 50 × 2.1 mm. La fase móvil empleada en el modo de ionización positiva para la determinación de pesticidas consistió en (A) H2O con un 0.1 % de ácido fórmico y 5 mM de formiato de amonio, y (B) MeOH con un 0.1 % de ácido fórmico y 5 mM de formiato de amonio. En cuanto al modo de ionización negativa del NTA, la fase móvil consistió en (A) H2O con 2.5 mM de fluoruro de amonio y (B) MeOH con 2.5 mM de fluoruro de amonio.

Por último, la fase móvil empleada para la detección de NTA en el modo de ionización positiva consistió en (A) H2O con un 0.1 % de ácido fórmico y (B) MeOH con un 0.1 % de ácido fórmico. El volumen de inyección fue 5 µl y la temperatura de la columna se mantuvo a 30 °C. El gradiente utilizado para el análisis de pesticidas fue el siguiente: 0 minutos (50% B), 10 minutos (83% B), 12 minutos (83% B), 12.5 minutos (98% B), 15.5 minutos (98% B), 16 minutos (50% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 10 minutos). Finalmente, el gradiente para el análisis de compuestos polares mediante NTA fue: 0 minutos (30% B), 12 minutos (95% B), 20 minutos (95% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 12 minutos). Todos estos métodos demostraron ser eficaces en la separación y detección precisa de los compuestos objetivo.

Además, se llevó a cabo una evaluación del riesgo ambiental. Así, el posible impacto de estos compuestos sobre el ecosistema fue evaluado utilizando el índice de riesgo ecológico o cociente de riesgo (RQ) tanto en muestras de agua como en muestras de sedimento. Los valores de RQ se definen como la relación entre la concentración ambiental medida o predicha (MEC) y su toxicidad crónica, generalmente expresada como la NOEC (Concentración Sin Efecto Observado) o la PNEC (Concentración Prevista Sin Efecto), tal como se muestra en la ecuación 1.

$$RQ_i = \frac{MEC_i}{PNEC_i} \quad (1)$$

Donde MEC representa la concentración ambiental media o máxima cuantificada en las muestras de agua o sedimento para cada compuesto (ng L^{-1} o ng g^{-1}), utilizada tanto para estimar el riesgo general como para considerar el escenario más desfavorable. Por otro lado, PNEC representa la concentración prevista sin efecto más baja (ng L^{-1} o ng g^{-1}). Los valores de PNEC se obtuvieron de la base de datos de ecotoxicología NORMAN, seleccionando el valor más bajo predicho por los modelos QSAR (Relación Cuantitativa Estructura-Actividad), los cuales se emplean para estimar la toxicidad acuática de los contaminantes en ausencia de datos experimentales. En los casos donde existían datos experimentales disponibles, estos fueron utilizados para determinar los valores de PNEC.

Como resultado general del estudio, se destaca que más de la mitad de los pesticidas objetivo (43 de 71) fueron detectados en las aguas superficiales del Parque Natural de L'Albufera, lo que refleja de manera clara los usos del suelo, predominantemente dominados por arrozales y, en menor medida, por los huertos de cítricos circundantes. El tebuconazol fue el pesticida que presentó la mayor concentración en agua superficial durante la primavera con una concentración media de 175.92 ng L^{-1}.

En la misma estación, también presentaron concentraciones medias elevadas la azoxystrobina y el tiabendazol con concentraciones medias de 131.49 ng L^{-1} y 61.52 ng L^{-1} respectivamente. En contraste, durante el otoño, el tebuconazol, la azoxistrobina y el imidacloprid registraron las concentraciones más elevadas, con valores medios de 1104 ng L^{-1}, 669 ng L^{-1} y 388 ng L^{-1}, respectivamente.

El tebuconazol y la azoxistrobina muestran concentraciones más elevadas durante el muestreo de otoño en comparación con el de primavera, manteniéndose en niveles altos a lo largo de ambas estaciones. Ambos fungicidas se emplean principalmente en el cultivo de arroz. La azoxistrobina tiene una autorización excepcional en la región para su aplicación aérea, destinada al control de Pyricularia y Helminthosporium en cultivos de arroz, lo que ha generado una contaminación difusa en toda el área. Por su parte, el tebuconazol se utiliza habitualmente como fungicida postemergente, siendo aplicado comúnmente desde mediados de julio hasta la cosecha del arroz, que usualmente inicia en octubre, según la severidad de la infección por Pyricularia en cada ciclo agrícola. Además, el tebuconazol se emplea tras la

cosecha en cultivos de cítricos.

En otoño, los fungicidas predominaron en áreas arroceras, mientras que, en las zonas de cítricos, los insecticidas fueron más relevantes. En primavera, las concentraciones de insecticidas, herbicidas y fungicidas estuvieron equilibradas.

El estudio identificó pesticidas prohibidos por la Unión Europea en las muestras de agua, incluidos los neonicotinoides, clotianidina, tiametoxam e imidacloprid, cuya autorización expiró en fechas cercanas al periodo de muestreo (2019-2020). Esto sugiere un uso intensivo previo a su prohibición o incluso inmediatamente después. También se detectó propanil en otoño, un herbicida prohibido en la UE desde 2008, pero autorizado de forma excepcional en España para el control de malas hierbas en arrozales entre mayo y julio. Estas prácticas reflejan el uso continuado de compuestos restringidos en los cultivos de la región.

Con respecto a los sedimentos, más de la mitad de los pesticidas analizados se detectaron, al menos, en un punto de muestreo en los sedimentos superficiales del Parque Natural de L'Albufera (59 de los 71 pesticidas analizados), aunque en bajas concentraciones, medidas en ng g^{-1} de peso seco. El tebuconazol fue el pesticida detectado en mayor concentración en el sedimento, con una concentración media de 182,26 ng g^{-1}, seguido por el procloraz, que presentó una concentración de 106,51 ng g^{-1}. Los compuestos detectados exclusivamente en los sedimentos, tales como diclofentión, etión, etofenprox, fenitrotión, metiocar y propazina, no fueron hallados en las muestras de agua. Estas sustancias se caracterizan por ser no polares, insolubles o con baja solubilidad en agua, así como por su escasa movilidad y un alto log Kow.

Una excepción notable son los metabolitos y productos de degradación de pesticidas como amitraz, carbofurano y fentión, que poseen alta solubilidad en agua, como 2,4-dimetilanilina (DMA), N, N- dimetilformamida (DMF), carbofurano-2-OH y sulfona de fentión. Su mayor solubilidad se relaciona con una degradación más lenta y una actividad microbiana intensificada en los sedimentos, favoreciendo su transformación. Estos compuestos, detectados principalmente en sedimentos y con alta persistencia, podrían evidenciar un uso histórico de dichos pesticidas.

El estudio mediante NTA, utilizando una biblioteca de más de 600 compuestos, identificó 72 contaminantes en aguas superficiales, incluyendo pesticidas (18, como tebuconazol, imazalil y azoxistrobina), PPCPs (41), compuestos industriales (8) y otros (5). Los productos farmacéuticos destacaron por su alta solubilidad y polaridad. En los sedimentos se detectaron 41 compuestos, principalmente pesticidas (12, como imazalil y bentazona), productos químicos industriales (17) y PPCPs (5). A diferencia del agua, en los sedimentos predominan los compuestos industriales y pesticidas, debido a su naturaleza lipofílica que facilita su adsorción y acumulación.

Además de los pesticidas identificados mediante target analysis, se detectaron en el agua nueve pesticidas adicionales, principalmente fenilureas como monourona, pencicurona y tebutiurona, junto con sus productos de degradación, como monodesmetil isoproturona. También se encontraron fungicidas como metalaxil, piraclostrobina y carboxina. Las fenilureas son mayormente herbicidas, mientras que el pencicurona es un fungicida utilizado para controlar

Pyricularia. La detección en primavera fue ligeramente superior a la de otoño. Además, se identificó paclobutrazol, un regulador de crecimiento vegetal. Este análisis complementa el perfil de pesticidas en el agua, mostrando que algunos compuestos solo son detectables mediante enfoques NTA. Por lo tanto, la huella de contaminación en los sedimentos difiere significativamente de la observada en las aguas. El único compuesto presente tanto en el agua como en los sedimentos fue PPG n5. Además, se identificaron otros polietilenglicoles (PEG) y polipropilenglicoles (PPG) en los sedimentos.

El PPG y el PEG, al igual que otros surfactantes, son solubles en agua y están asociados con ecosistemas impactados por aguas residuales, como es el caso de L'Albufera. Estos compuestos son contaminantes importantes en los sedimentos debido a su naturaleza lipofílica, que les permite adsorberse fácilmente a las partículas y acumularse en los sedimentos acuáticos.

Además, se realizó una evaluación del riesgo ecológico que reveló que, en primavera, 13 de los 43 pesticidas detectados en el Parque Natural de L'Albufera presentaban un riesgo ecológico elevado, considerando la concentración máxima. Sin embargo, al evaluar la concentración media, solo tres pesticidas (clorpirifos, fluvalinato y ometoato) mostraron un alto riesgo ecológico (RQ > 1).

En otoño, 17 pesticidas presentaron un alto riesgo ecológico basado en la concentración máxima. Al considerar la concentración media, se identificaron ocho pesticidas (acetamiprid, azoxistrobina, clorfenvinfos, clorpirifos, fluvalinato, imidacloprid, ometoato, tebuconazol y terbutilazina) con un alto riesgo ecológico, lo que aumentó el número de compuestos con RQ > 1, pasando de tres en primavera a nueve en otoño. El imidacloprid presentó el valor de RQ más elevado durante el otoño en los escenarios de contaminación más desfavorables (es decir, considerando la concentración máxima). Las concentraciones elevadas de imidacloprid detectadas podrían potencialmente causar daño a los ecosistemas acuáticos mediterráneos.

Estos altos niveles de imidacloprid pueden tener implicaciones significativas para las comunidades de invertebrados en dichos ecosistemas. Además, los valores de RQ para los sedimentos fueron considerablemente más altos para todos los compuestos, a menudo superando el 10. Esto resalta la necesidad de realizar un análisis exhaustivo en los estudios de sedimentos.

Además, se evaluó el RQ en cada punto como la suma de todos los contaminantes presentes en cada muestra de agua analizada, agregando los índices de riesgo ecológico de cada compuesto (∑RQ) para obtener una visión integral de la contaminación del agua por pesticidas en la zona y del riesgo ecotoxicológico asociado, aplicando un modelo aditivo.

Los resultados indicaron que, durante el otoño, los puntos de muestreo 19, correspondiente a una acequia de arrozal, y 42, correspondiente a una acequia de cítricos, mostraron el índice de riesgo acumulado más alto en agua superficial. La suma de la exposición a los pesticidas detectados en cada punto de muestreo puede plantear preocupaciones ambientales específicas para ciertas comunidades biológicas. Por otro lado, los puntos 24, correspondiente a una acequia de arrozal, y 48, correspondiente a una acequia de huerta exhibieron un mayor riesgo asociado a las concentraciones de sedimentos. Estos hallazgos resaltan la importan-

cia de examinar exhaustivamente todas las combinaciones de pesticidas para evaluar el riesgo ambiental de manera integral, así como la importancia de continuar monitoreando estos parámetros para garantizar la viabilidad futura del parque, dado que la calidad del agua se vio comprometida en parte debido a la presencia de estos compuestos.

Por lo tanto, es fundamental comprender la variabilidad espaciotemporal de pesticidas y otros compuestos para caracterizar sus impactos y desarrollar estrategias de monitoreo y mitigación fundamentadas. La aplicación exitosa del análisis combinado de TA y NTA, utilizando espectrometría de masas de alta resolución, en la investigación sobre la ocurrencia y variación temporal en muestras de aguas superficiales y sedimentos, demuestra que la contaminación antropogénica influye significativamente en estos ecosistemas. Además, la evaluación del riesgo ecológico sugiere que algunas áreas con un cociente de riesgo significativamente elevado deben ser priorizadas para su monitoreo y gestión.

Es fundamental llevar a cabo investigaciones adicionales para reducir la entrada de contaminantes antropogénicos en los entornos acuáticos y reevaluar las necesidades regulatorias. Asimismo, es imperativo implementar prácticas agroecológicas que promuevan la calidad del agua y del suelo en este Parque Natural, el cual posee un alto valor ecológico, pero se encuentra en un estado de conservación desfavorable.

6.2. Resumen sección 3: "Evaluación de la contaminación del Parque Natural de L'Albufera mediante el uso de muestreadores pasivos"

Este estudio tuvo como objetivo emplear un método de muestreo complementario al muestreo convencional para mejorar la comprensión de la presencia y las concentraciones de contaminantes en el Parque Natural de L'Albufera. Además, busca generar una estimación precisa del riesgo ambiental asociado a estos contaminantes, con el fin de identificar compuestos de interés, así como sus posibles fuentes y factores de riesgo. Además de determinar la presencia y concentración de una amplia gama de contaminantes en diferentes zonas del Parque Natural de L'Albufera, se cartografió su variabilidad espacial para identificar las áreas críticas del humedal y evaluar el riesgo potencial que representan para el parque.

Este estudio se llevó a cabo durante los meses de septiembre y octubre de 2020. Se instalaron muestreadores pasivos MPT en 12 ubicaciones estratégicamente seleccionadas a lo largo del Parque Natural de L'Albufera. Estos muestreadores fueron desplegados directamente en el agua y permanecieron sumergidos en agua durante 14 y 21 días. De manera simultánea, se recolectaron muestras puntuales de agua durante el despliegue de los muestreadores pasivos (día cero) y en los días 14 y 28, con el fin de compararlas con las concentraciones promedio obtenidas en ellos. Los muestreadores pasivos permiten determinar las concentraciones promedio ponderadas en el tiempo de los contaminantes orgánicos en agua. Para este propósito, fue necesario conocer la tasa de muestreo (Rs) de los contaminantes. Los valores de Rs se recopilaron de la literatura y se presentan en la Tabla S8 del Artículo III para ciertos compuestos.

Las ubicaciones seleccionadas en este estudio abarcaron tres hábitats distintos: el lago, un humedal artificial y los canales. Además, se investigaron sitios con diversas fuentes potenciales de contaminantes: PPCPs provenientes de efluentes de EDARs y pesticidas procedentes de la escorrentía agrícola que llega a los humedales y canales. Se seleccionaron dos puntos de control: (i) la piscifactoría para la conservación y preservación de especies autóctonas gestionada por el gobierno local y (ii) el canal Real del Júcar, que transporta agua dulce desde el río Júcar hacia los huertos y arrozales. También se tomaron dos puntos en el humedal artificial de Milia, uno a la entrada y otro a la salida. Este se alimenta del agua proveniente del tratamiento terciario de la planta de tratamiento urbano de L'Albufera Sur, para su tratamiento final antes de ser descargada en el lago.

En este estudio se emplearon dos configuraciones del muestreador pasivo MPT: una para la recolección de muestras de glifosato y su metabolito ácido aminometilfosfónico (AMPA), la cual estaba rellena de gel de agarosa y polvo de óxido de titanio (IV) (TiO2); y otra configuración diseñada para el muestreo de pesticidas, PPCPs, OPFRs y PFASs, la cual estaba rellena de una fase absorbente lipófila hidrófila: Strata-X, un polímero de estireno y divinilbenceno modificado en superficie en fase inversa funcionalizado con N-vinil-2-pirrolidona.

A continuación, se describirán los métodos de extracción utilizados en este estudio, y las técnicas de análisis utilizadas.

La técnica de análisis empleada fue la cromatografía líquida acoplada a un espectrómetro de masas, utilizando target analysis. Los contaminantes orgánicos seleccionados, que incluyeron pesticidas, PPCPs, PFASs y OPFRs fueron analizados mediante cromatografía líquida (LC) de fase reversa, utilizando un sistema LC Vanquish Horizon de Thermo Scientific, acoplado al Orbitrap Exploris 120, equipada con una fuente de ionización por electropulverización en caliente (HESI). La LC en fase reversa es ampliamente empleada en la separación de CECs, siendo comúnmente utilizada la fase estacionaria apolar, gel de sílice (C18). La columna utilizada para la determinación de pesticidas fue Luna C18 (15.0 cm × 0.21 cm) con un tamaño de partícula de 3 µm. Para la detección de PFASs y OPFRs, se empleó una columna Kinetex 1.7 µm XB-C18 100 Å 50 x 2.1 mm. Por último, para la detección de PPCPs se utilizó una columna Kinetex 1.7 µm Biphenyl de 50 × 2.1 mm.

La fase móvil empleada en el modo de ionización positiva para la determinación de pesticidas consistió en (A) H2O con un 0.1 % de ácido fórmico y 5 mM de formiato de amonio, y (B) MeOH con un 0.1 % de ácido fórmico y 5 mM de formiato de amonio. Para el modo de ionización negativa de los PFASs, se utilizó una fase móvil compuesta por (A) H2O con 10 mM de formiato de amonio y (B) MeOH con 10 mM de formiato de amonio. En cuanto al modo de ionización negativa de los PPCPs, la fase móvil consistió en (A) H2O con 2.4 mM de fluoruro de amonio y (B) MeOH con 2.4 mM de fluoruro de amonio. Por último, la fase móvil empleada para la detección de OPFRs y PPCPs en el modo de ionización positiva consistió en (A) H2O con un 0.1% de ácido fórmico y (B) MeOH con un 0.1% de ácido fórmico. El volumen de inyección fue 5 µl y la temperatura de la columna se mantuvo a 30 ºC. El gradiente utilizado para el análisis de pesticidas fue el siguiente: 0 minutos (50% B), 10 minutos (83% B), 12 minutos (83% B), 12.5 minutos (98% B), 15.5 minutos (98% B), 16 minutos (50% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 10 minutos). Para el análisis de PFASs, el gradiente

empleado fue: 0 minutos (30% B), 0.5 minutos (30% B), 12 minutos (95% B), 21 minutos (95% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 12 minutos).

El gradiente utilizado en el análisis de OPFRs fue: 0 minutos (30% B), 0.5 minutos (30% B), 12 minutos (95% B), 18 minutos (98% B), 25 minutos (98% B), 26 minutos (30% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 14 minutos).

Finalmente, el gradiente para el análisis de PPCPs fue: 0 minutos (30% B), 12 minutos (95% B), 20 minutos (95% B), seguido por el retorno a las condiciones iniciales (tiempo de equilibrio: 12 minutos). Todos estos métodos demostraron ser eficaces en la separación y detección precisa de los compuestos objetivo.

El método de extracción de las muestras de agua fue descrito en el apartado anterior. El método de extracción de los muestreadores pasivos MPT fue descrito por McKay et al. (2020). En primer lugar, los MPT fueron retirados de sus jaulas de implementación y se procedió a lavar con agua destilada y eliminar los residuos restantes. Posteriormente, cada tubo MPT fue colocado en tubos Falcon de polipropileno de 15 mL. En el interior de cada tubo Falcon se añadió una mezcla de estándares internos (50 µL del mix de estándar interno a una concentración de 1 µg mL^{-1}) al sorbente, retirando ambas tapas del MPT. Se agregaron 4 mL de metanol en cada tubo Falcon, los cuales fueron posteriormente centrifugados durante 15 minutos. Acto seguido, el extracto y el sorbente sólido remanente en cada tubo Falcon fue vertido en tubos de cartucho SPE vacíos, de polipropileno de 12 cc, equipados con fritas para tubos SPE de 12 cc, 20 µm, fabricados en polietileno por Phenomenex®. Estos cartuchos fueron eluidos con acetona (4 ml) y metanol acidificado al 2 % (v/v) (2x2 mL de MeOH ácido), respectivamente.

Posteriormente los extractos fueron concentrados hasta 1 mL bajo una corriente suave de nitrógeno. Seguidamente, se transfirieron 500 µL de esta solución a un vial de 1.5 mL, para el análisis de pesticidas. Los 500 µL restantes fueron evaporados (40ºC) a 25 µL y se les añadieron 475 µL de agua-metanol (70:30 v/v). El extracto resultante se transfirió a un vial con inserto de polipropileno de 200 µL, para el análisis de PPCPs, PFAS y OPFRs. Los extractos se almacenaron a -20 ºC hasta la inyección.

Como resultado, en el Parque Natural de L'Albufera se detectaron ciento cuatro contaminantes orgánicos, incluyendo 45 pesticidas, 30 PPCPs, 22 PFAS y 7 OPFR, mediante el uso de muestreadores pasivos y la recolección de muestras puntuales de agua. En los muestreadores MPT se detectaron 87 compuestos, que incluyen 43 pesticidas, 20 PPCPs, 20 PFASs y 4 OPFRs.

En contraste, en las muestras puntuales de agua se detectaron 61 compuestos, que incluyen 24 pesticidas, 14 PFASs, 16 PPCPs y 7 OPFRs. Los pesticidas fueron los contaminantes más destacados en L'Albufera. Esto es coherente con el uso agrícola de las tierras circundantes, dedicadas al cultivo de arroz y cítricos. El fungicida tebuconazol fue detectado en los muestreadores pasivos con la concentración más alta, alcanzando un valor máximo de 153 ng por muestreador. No obstante, el acetamiprid fue el pesticida que presentó la mayor concentración en el agua superficial, con un valor máximo de 71,0 ng L^{-1}. Los compuestos 3,4-dicloroanilina, DEET, propiconazol, difenoconazol, MCPA, clorpirifos, acetamiprid, tebumeton desetilo, terbutilazina-2OH, tebuconazol, diclofentión y procloraz fueron detectados en ≥ 50 % de las

muestras, con valores máximos registrados superiores a 3,0 ng por muestreador. Por otro lado, imidacloprid, acetamiprid, atrazina-desetil, carbendazim, tiabendazol, tebumeton desetilo, terbutilazina-2OH, terbutilazina desetilo, tebuconazol y procloraz mostraron concentraciones superiores a 10 ng L^{-1} y fueron detectados con una frecuencia igual o superior al 50 %.

Las concentraciones de PPCPs en los muestreadores pasivos MPT variaron entre 0,10 ng $muestreador^{-1}$ (sulfadiazina, atenolol, temazepam) y 13,5 ng $muestreador^{-1}$ (ácido salicílico). En contraste, en las muestras puntuales de agua, las concentraciones oscilaron entre 1,34 ng L^{-1} (cafeína) y 1470 ng L^{-1} (ibuprofeno). La cafeína, temazepam, acesulfamo, gabapentina y tramadol fueron detectados en los muestreadores pasivos con una frecuencia ≥ 50 % de las muestras, alcanzando valores máximos de ≥ 3,0 ng por muestreador. Por otro lado, el ácido salicílico, naproxeno, diclofenaco e ibuprofeno se detectaron en el agua superficial con una frecuencia ≥ 50 % de las muestras, registrando valores máximos superiores a 100 ng L^{-1}.

Se calcularon las concentraciones en agua de dieciséis compuestos detectados en los muestreadores pasivos MPT, utilizando las tasas de muestreo disponibles. Algunos contaminantes, como buprofezina, clorpirifos, clotianidina, y otros, fueron identificados exclusivamente en los muestreadores pasivos, mientras que otros, como propanil, spinosad A, y varios fármacos, solo se detectaron en las muestras puntuales de agua. Esto puede explicarse por diferentes interacciones entre los contaminantes y el material del muestreador pasivo, lo que dificulta su acumulación. Además, la diferencia en los factores de concentración entre ambos métodos también podría influir, ya que las muestras puntuales se extraen en volúmenes mayores (250 mL), mientras que los muestreadores pasivos acumulan contaminantes a tasas de mililitros por día. Considerando un rango de Rs reportado de 3 a 30 ml/día, esto produce entre 84 y 840 ml para implementaciones de 28 días. Aunque el valor de 84 ml es solo tres veces menor que el de 250 ml, no se puede descartar que tenga alguna influencia en la ausencia de algunos compuestos en los muestreadores pasivos. Por lo tanto, los muestreadores MPT pueden ser menos sensibles dependiendo de las tasas de acumulación de los compuestos y la duración de la implementación.

La necesidad de aplicar tasas de muestreo específicas para cada compuesto impidió cuantificar algunos contaminantes orgánicos detectados en concentraciones elevadas en los muestreadores pasivos, debido a la falta de calibración de las tasas de muestreo para ciertos compuestos. El análisis espacial reveló mayores concentraciones de pesticidas en la zona norte de L'Albufera, mientras que los puntos de control mostraron menores concentraciones, aunque estas fueron más altas en promedio en comparación con Obera y Els Campets. Esto puede explicarse porque las muestras de agua de arrastre fueron tomadas en septiembre, cuando la cosecha en el norte aún no había terminado, mientras que en el sur, en Obera y Els Campets, ya se había completado la cosecha. Los niveles de pesticidas fueron más bajos en el punto de entrada del humedal artificial Milia y más elevados en su punto de salida. Este humedal, un antiguo arrozal adyacente a L'Albufera, ha sido transformado en un filtro verde o humedal artificial con el fin de depurar el agua que desemboca en la laguna. El humedal artificial (punto 4) se alimenta de agua tratada proveniente de la planta de tratamiento de L'Albufera Sur, situada a 10 km de distancia.
No obstante, es posible que el agua depurada de la EDAR haya sido contaminada con pesticidas debido a la deriva de las pulverizaciones aéreas o a la contaminación aguas arriba, lo

que evidencia una capacidad limitada del humedal artificial para eliminar ciertos pesticidas. No obstante, se observó una reducción en la concentración de PPCPs en la salida del humedal artificial.

Para concluir el estudio, se llevó a cabo un análisis del cociente de riesgo (RQ), previamente explicado, el cual reveló que el ibuprofeno, el diclofenaco y el PFOS representan un motivo de preocupación para la conservación de la biota acuática en la región estudiada. Los efectos toxicológicos comprobados de estos compuestos orgánicos contaminantes (OC) en peces incluyen malformaciones en el desarrollo, estrés oxidativo, daño celular, alteraciones en el comportamiento, así como modificaciones en parámetros bioquímicos, inmunológicos y hematológicos, entre otro. En términos generales, el enfoque de muestreo MPT se perfila como una herramienta prometedora para la evaluación de riesgos, al facilitar una comprensión más precisa del transporte y destino de los contaminantes orgánicos en áreas protegidas

6.3. Resumen sección 4: "Detección simultánea de contaminantes antropogénicos en núcleos de sedimentos utilizando análisis dirigidos y no dirigidos".

A continuación, se presenta un resumen general de la metodología aplicada y los principales resultados obtenidos en la cuarta y quinta publicación científica, enfocada al análisis de la distribución vertical de contaminantes orgánicos en núcleos de sedimentos.
En estos estudios se analizaron núcleos de sedimento datados del lago de L'Albufera (Valencia, España) para evaluar la distribución vertical de contaminantes orgánicos, considerando diversos factores clave que influyen en la dinámica de contaminantes en este ecosistema. El lago de L'Albufera recibe afluentes de diversas fuentes, incluyendo barrancos, canales de drenaje y riego, manantiales locales (ullals) y ríos principales (Turia y Júcar) (3). Esta variedad de fuentes de entrada introduce una gama amplia de contaminantes en el lago.

Por otro lado, el nivel del agua en el lago se controla para mantener la calidad del agua dulce y para facilitar el drenaje y la inundación de los campos de arroz ubicados en la zona pantanosa alrededor del lago. Este manejo del nivel del agua puede influir en la deposición y la movilidad de los contaminantes en los sedimentos del lago. Por lo tanto, evaluar la distribución vertical de los contaminantes en los núcleos de sedimentos permite entender cómo los contaminantes se han depositado y acumulado a lo largo del tiempo, proporcionando información crucial sobre las fuentes de contaminación y los procesos de transporte y deposición en este sistema acuático complejo.

Las campañas de muestreo se realizaron en abril de 2021, utilizando una barca y un muestreador de núcleo de sedimento que preserva la interfaz sedimento-agua con una columna de agua de 80 cm de profundidad.

Los núcleos de sedimento, de 70 cm de longitud, se almacenaron en un recipiente con hielo y luego se congelaron en el laboratorio. Posteriormente, se segmentaron en secciones de 10 cm utilizando un cortador de acero inoxidable, se liofilizaron y se almacenaron a -20 ºC hasta su análisis. El agua suprayacente no se eliminó para evitar la oxidación de los sedimentos.

El protocolo de extracción de pesticidas y compuestos polares, como PPCPs, PFASs y OPFRs en sedimento ya ha sido descrito en el apartado anterior. Sin embargo, el método de extracción utilizado para compuestos no polares, como los hidrocarburos aromáticos policíclicos (PAHs), fue llevada a cabo con una mezcla de hexano - diclorometano (1:1 v/v), seguida de una etapa de limpieza utilizando cartuchos de SPE de alúmina neutra. Inicialmente, se introdujo 1 g de sedimento previamente liofilizado en un tubo Falcon de 15 ml conteniendo 6 ml de hexano-diclorometano (1:1 v/v), al cual se adicionaron 50 µL de una mezcla de estándares internos a una concentración de 1 µg mL^{-1} en cada muestra. Posteriormente, el tubo se colocó en un baño de ultrasonidos durante 10 minutos, seguido de una centrifugación durante 5 minutos a 2500 rpm. Estos dos últimos pasos se repitieron en tres ocasiones. Los extractos obtenidos tras la sonicación fueron evaporados en un evaporador rotatorio hasta casi su completa sequedad (aproximadamente 0,5 ml) para una limpieza adicional.

En ambos casos, los extractos fueron purificados mediante un procedimiento de limpieza utilizando cartuchos de extracción en fase sólida de alúmina neutra. En resumen, se preacondicionaron los cartuchos Alumina-N SPE (Supelclean™ LC-Alumina-N SPE Tube bed, con un peso de 2 g y un volumen de 6 ml) con 2 ml de hexano. Posteriormente, se pasó una muestra de 0,5 ml a través de los cartuchos sin aplicación de vacío, y se eluyó con 100 ml de hexano, seguido de 20 ml de una solución concentrada de hexano-diclorometano (2:1 v/v) a una velocidad de 250 µL/min. Finalmente, se añadieron 250 µL del extracto purificado a un vial LC de 1,5 ml, y los extractos resultantes fueron almacenados a -20°C hasta su inyección.
La metodología analítica utilizada para la determinación de pesticidas, PPCPs, PFASs y OPFRs mediante el método TA fue detallada en el apartado anterior. No obstante, con el fin de ampliar el estudio y mejorar la evaluación de los datos, se llevó a cabo un análisis adicional utilizando cromatografía de gases acoplada a un espectrómetro de masas, así como el método NTA. Esto último también ha sido descrito anteriormente.

Sin embargo, la determinación de PAHs en muestras de sedimento se llevó a cabo mediante cromatografía de gases-espectrometría de masas (GC-MS). Los PAHs se analizaron mediante el sistema JASCO Serie YL6900. La separación de los HAP se llevó a cabo utilizando una columna capilar Zebron ZB-5MS (30 m x 0,25 mm de diámetro interior con un espesor de película de 0,25 µm) con una temperatura del inyector de 180°C.

Como resultado, las muestras obtenidas de los dos núcleos de sedimentos presentaron una cronología progresivamente más antigua conforme aumenta la profundidad de los mismos. En el núcleo del Norte, la edad obtenida mediante C14 para la capa superficial (primeros 10 cm) fue de 1474 - 1638 cal AD (476 - 312 cal BP), lo que indica una antigüedad relativamente mayor que la de la capa inmediatamente inferior, correspondiente a los 10-20 cm de profundidad, cuya edad es de 1867 - 1917 cal AD (83 - 33 cal BP). Un fenómeno similar se observó en el núcleo del Sur. Las fluctuaciones en las edades obtenidas por 14C podrían deberse a varios factores: (1) la entrada de materiales orgánicos terrestres con carbono más antiguo al lago, conocido como el "efecto del carbono antiguo"; (2) el efecto del reservorio de 14C en agua dulce; o (3) la pérdida o redistribución de sedimentos en esas capas. La hipótesis más plausible es la afluencia de materiales orgánicos terrestres arrastrados por eventos de desbordamiento o inundación.

Adicionalmente, la falta de información sobre la cantidad de sedimento extraído del lago para el relleno de arrozales desde 1850 podría contribuir a estas discrepancias. Otro factor a considerar es la acción del viento, especialmente en la zona sur, donde puede generar la resuspensión de sedimentos del lago bajo determinadas condiciones, lo que influiría en los resultados de la datación. Se detectaron 31 contaminantes orgánicos de los 159 investigados. Estos incluyen 10 pesticidas, 7 PPCPs, 6 PFASs, 1 OPFR y 7 PAHs, con concentraciones que varían desde menos de 0,11 ng g^{-1} hasta más de 520 ng g^{-1} (peso seco). La distribución de los contaminantes orgánicos entre los sedimentos y el agua de poro depende de la hidrofobicidad química, su coeficiente de partición octanol-agua (Kow), de la solubilidad en agua, del coeficiente de adsorción de la materia orgánica carbonada (Koc) y el contenido orgánico de las partículas de sedimento (foc), pero es independiente de la concentración química. Por lo tanto, la distribución de los contaminantes analizados en el presente estudio exhibió patrones variados.

La concentración de PAHs en los núcleos de sedimentos osciló entre 5,20 y 521 ng g^{-1} en el norte, y entre 1,40 y 156,8 ng g^{-1} (peso seco) en el sur. Las diferencias espaciales en la presencia de PAHs entre el norte y el sur pueden atribuirse al mayor tráfico turístico en el área, debido a la ubicación de varios puertos pequeños que ofrecen paseos en bote por el lago. Además, en el norte, la distribución vertical de los PAHs mostró una concentración constante a lo largo del núcleo, con la excepción del fenantreno, el cual se encontró en concentraciones más altas que los otros PAHs hasta una profundidad de 40 cm. La relativa proximidad de una autopista de tráfico en el norte del área de estudio puede explicar la presencia de fenantreno.

En el sur, la distribución vertical de los PAHs indicó una concentración constante a lo largo del núcleo de acenafteno y fluoreno. Estos PAHs ya estaban relacionados previamente con la quema de paja de arroz.

La concentración de PFAS en los núcleos de sedimento varió entre 0,11 y 8,79 ng g^{-1} en el norte, y entre 0,13 y 5,59 ng g^{-1} (peso seco) en el sur. Los PFOS tendieron a mostrar concentraciones más elevadas en comparación con otros compuestos PFAS. Gen X, PFDA y PFHxA solo fueron detectados en la capa superficial del núcleo de sedimento en el norte, lo que sugiere que la incorporación de estos PFAS es relativamente reciente. Los PFAS de cadena larga (C8–C12), como PFOS, PFOA y PFDA, representaron aproximadamente el 50 % del total de PFAS detectados. En contraste, los PFAS de cadena corta pudieron difundirse a través del agua intersticial en la columna de sedimento, en lugar de quedar retenidos en las partículas sedimentarias. Esto se debe a que los PFAS de cadena corta son más hidrófilos que los de cadena larga, lo que implica que la solubilidad en agua de los PFAS disminuye a medida que aumenta la longitud de la cadena.

Existe muy poca información sobre la distribución de pesticidas en los núcleos de sedimentos. La presencia de concentraciones más elevadas en las capas superficiales del sedimento en el norte podría estar relacionada con aplicaciones recientes de estos compuestos. Por otro lado, el aumento de las concentraciones en capas más profundas podría deberse a la ausencia de aportes recientes, lo que favorecería la acumulación de residuos de pesticidas de periodos anteriores. Sin embargo, en nuestro estudio, las concentraciones de pesticidas oscilaron entre 0,14 y 28,6 ng g^{-1} en la región norte, y entre 0,18 y 132,8 ng g^{-1} (peso seco) en

la región sur. En el norte, el pesticida con las concentraciones más altas fue el acetamiprid, mientras que en el sur fueron el tebuconazol y el fluvalinato. La distribución vertical de los pesticidas mostró tres tipos de patrones: (i) distribuidos verticalmente a través del núcleo en diferentes concentraciones (molinato, fluvalinato y acetamiprid); (ii) una tendencia a aparecer en las capas de sedimentos profundas y no en las superiores (ometoato); (iii) los pesticidas solo se detectaron en las capas de sedimentos más superficiales (azoxitrobina, imazalil, tebuconazol, tiablendazol y triciclazol).

Azoxistrobina, tebuconazol, tiabendazol, imazalil y triciclazol fueron detectados únicamente en las capas superiores de ambos núcleos de sedimentos. La alta concentración de tebuconazol en la región sur puede estar relacionada con las prácticas agrícolas, ya que este pesticida se utiliza ampliamente en las últimas etapas del cultivo del arroz. El ometoato, por ejemplo, se detecta en capas de sedimento entre los 10 cm y 50 cm de profundidad. El comportamiento de este pesticida es difícil de interpretar debido a la escasez de datos disponibles. Aunque es un insecticida por sí mismo, también puede encontrarse como producto de degradación del dimetoato, un compuesto cuyo uso fue prohibido en 2020. La azoxistrobina, el tebuconazol, el tiabendazol, el imazalil y el triciclazol, detectados únicamente en las capas superficiales de ambos núcleos de sedimento, se clasifican como compuestos con movilidad moderada, ligera o limitada.

Esto sugiere que su presencia en las capas superiores podría estar relacionada con aplicaciones recientes y su limitada capacidad para desplazarse a través de las capas más profundas del sedimento. Por otro lado, la concentración de PPCPs en los núcleos de sedimentos osciló entre 0,2 y 10,5 ng g^{-1} en la región norte y entre 0,24 y 9,10 ng g^{-1} (peso seco) en la región sur. El origen de estos compuestos podría ser el vertido de aguas tratadas de varias EDARs que se descargan en el lago para mantener el caudal ecológico, así como el vertido de aguas no tratadas de pequeños asentamientos y casas aisladas. Los PPCPs detectados mostraron una distribución vertical irregular en ambos núcleos de sedimento. Más del 50% de los PPCP detectados pertenecen a la clase química de los parabenos, lo que indica que estos podrían ser los principales contaminantes en el área estudiada debido a su uso generalizado como conservantes en productos farmacéuticos, de cuidado personal y alimentarios. La codeína, el único fármaco detectado, se encontraba exclusivamente en la capa superior del núcleo de sedimento en el norte, lo que sugiere que su ingreso fue reciente. Las concentraciones de bisfenol A en los núcleos de sedimento oscilaron entre 0,73 y 9,74 ng g^{-1} en el norte, y entre 1,60 y 6,27 ng g^{-1} (peso seco) en el sur.

En 2007, la Agencia de Protección Ambiental de los Estados Unidos (USEPA) clasificó al bisfenol A como un contaminante prioritario, ya que en las últimas décadas varios estudios han confirmado sus efectos potencialmente adversos en humanos y animales, incluyendo propiedades mutagénicas y cancerígenas. Este compuesto no se hidroliza en agua debido a su estructura química, y más del 50 % de él se adsorbe en sedimentos.

El etilparabeno, el metilparabeno y el ácido salicílico mostraron una afinidad de sorción moderada a alta por el sedimento, mientras que el butilparabeno y el propilparabeno mostraron una afinidad de sorción alta y una movilidad limitada. Los parabenos exhibieron una tendencia similar en su distribución vertical en ambos núcleos de sedimento. Las concentraciones

de etilparabeno, propilparabeno y butilparabeno fueron casi constantes en los núcleos de sedimento tanto en el norte como en el sur.

Las altas concentraciones de estos parabenos en sedimentos anóxicos más profundos también pueden atribuirse a la falta de degradación anaeróbica, lo que conduce a su persistencia en condiciones anóxicas. El metilparabeno, el etilparabeno, el propilparabeno y el butilparabeno están actualmente incluidos en la lista de posibles disruptores endocrinos de la Unión Europea. Esta clasificación se debe a sus propiedades químicas y a sus potenciales efectos adversos en la salud humana y el medio ambiente.

La relación entre la distribución de contaminantes en profundidad y la edad del carbono orgánico (Corg) en los sedimentos del lago de L'Albufera fue difícil de establecer. Esto se debe, a las incertidumbres inherentes al proceso de datación de sedimentos, especialmente por el posible origen terrígeno de estos y su arrastre hacia el lago durante lluvias torrenciales.

La falta de conocimiento sobre los procesos de resuspensión de sedimentos en el lago de L'Albufera complica la interpretación de los resultados, haciendo especulativa la conclusión de que los sedimentos reflejan un registro histórico de contaminantes. Para identificar compuestos no detectados por los métodos convencionales, se utilizó un análisis NTA, que reveló la presencia de dimetilo sebacato, galaxolidona, oleamida y polietilenglicoles (PEG n6), este último utilizado en diversas industrias.

El estudio de la contaminación ambiental durante el Antropoceno mediante la sedimentación requiere protocolos mejorados para identificar aquellos casos en los que se pueda establecer una relación directa y fiable. En este análisis, la distribución en profundidad de los contaminantes no reveló una tendencia clara. No obstante, establecer una relación directa entre la edad del sedimento y las concentraciones de contaminantes, y así esclarecer la tendencia histórica de la contaminación a partir de núcleos de sedimentos datados, puede resultar sumamente desafiante. La información disponible sobre la concentración de contaminantes orgánicos, en particular los emergentes, en sedimentos es limitada. Por lo tanto, los datos obtenidos en el presente estudio ofrecen información valiosa sobre la distribución y dinámica de los contaminantes en sedimentos, y contribuyen a corroborar los resultados presentados en investigaciones anteriores.

6.4. Resumen sección 5: "Microcontaminantes orgánicos en aguas superficiales de las cuencas de los ríos Aconcagua y Maipo en Chile Central".

Esta sección ofrece un resumen detallado de las principales metodologías empleadas para el análisis de muestras de agua en el estudio, junto con una síntesis de los resultados más relevantes obtenidos en ambas cuencas fluviales de la zona central de Chile.

La información sobre la presencia de CECs en ecosistemas de agua dulce en América del Sur es limitada, especialmente en países en desarrollo como Chile, caracterizado por un clima mediterráneo, una agricultura intensiva y una alta densidad de población.

En las últimas décadas, Chile ha experimentado un aumento significativo en la producción agrícola en los valles centrales, lo que ha conllevado un incremento en el uso de pesticidas. Además, Chile dispone de sistemas de tratamiento de aguas residuales que cubren a más del 96% de la población urbana; sin embargo, solo dos tercios de las áreas urbanas están conectadas a tratamientos secundarios o terciarios. Por lo tanto, comprender la coexistencia y distribución de los CECs en ambientes de agua dulce, particularmente a nivel de cuenca fluvial, es esencial para implementar acciones coordinadas de mitigación en ecosistemas y de protección de la salud pública. Para ello, se recolectaron diez muestras de agua superficial de las cuencas de los ríos Maipo y Aconcagua en la zona central de Chile. En la cuenca del río Aconcagua, se establecieron dos sitios de referencia en la región preandina.

Además, se seleccionaron tres sitios a lo largo del curso principal del río Aconcagua: uno aguas abajo de áreas rurales y operaciones mineras, otras aguas abajo de áreas urbanas de tamaño medio e impactado por las descargas de plantas de tratamiento de aguas residuales situadas aguas arriba, y un último sitio cercano a la desembocadura del río.

En la cuenca del río Maipo, se estableció un sitio de referencia en la región preandina y cuatro sitios adicionales en áreas con distintos usos del suelo. Uno de estos sitios se ubicó en la región preandina, aguas abajo de las operaciones mineras; otro en áreas urbanas, aguas arriba de las principales EDARs de Santiago; un tercer sitio se situó en una zona urbano-agrícola, aguas abajo de las principales EDARs de Santiago; y, por último, un sitio se estableció cerca de la desembocadura del río Maipo. Para la recolección de muestras de agua superficial, se empleó un dispositivo de extracción en fase sólida de gran volumen (LVSPE) in situ, el cual permitió recoger hasta 50 litros de agua por cada sitio de muestreo. Se identificaron y cuantificaron 311 compuestos al menos una vez en las cuencas del río Aconcagua y del río Maipo, abarcando compuestos provenientes de los sectores urbano, agrícola, industrial y farmacéutico. De estos, 141 compuestos se cuantificaron al menos una vez en la cuenca del río Aconcagua y 243 en la cuenca del río Maipo, existiendo solapamientos de compuestos entre ambas cuencas. El mayor número de CECs en la cuenca del río Maipo en comparación con la cuenca del río Aconcagua, y se correlaciona con el mayor grado de urbanización e industrialización del Maipo. La cuenca del río Maipo alberga la ciudad de Santiago, con una población de aproximadamente 7,5 millones de habitantes, y también la EDAR más grande del país, Farfana, encargada del tratamiento de efluentes domésticos e industriales, así como una zona densamente poblada, con agricultura intensiva y una significativa actividad industrial. Por el contrario, la cuenca del río Aconcagua se caracteriza por una extensa actividad minera de cobre, una importante vía de transporte entre Chile y Argentina, y una agricultura intensiva.

La presencia de la mayoría de las sustancias químicas cuantificadas puede atribuirse a su uso generalizado en todo el mundo en la vida diaria, los procesos industriales y las prácticas agrícolas. Este hallazgo se ve respaldado por el uso de una lista de objetivos derivada de CEC comúnmente evaluados en ambientes acuáticos europeos.

Los pesticidas exhibieron concentraciones altas en la cuenca del río Aconcagua, destacándose los fungicidas imazalil, carbendazim y boscalid, con niveles de 272, 7.3 y 3.7 μg L^{-1}, respectivamente. Por otro lado, en la cuenca del río Maipo, los pesticidas con las mayores concentraciones fueron el butóxido de piperonilo, el ácido azoxistrobina (un metabolito de

la azoxistrobina) y el acetamiprid, registrando niveles de 18, 12 y 5 µg L^{-1}, respectivamente. Además, se detectaron productos farmacéuticos como la metenamina, la 10,11-dihidro-10-hidroxicarbamazepina (un metabolito de la carbamazepina) y la metformina, con concentraciones de 5.6, 4.7 y 1.6 µg L^{-1}, respectivamente, en la cuenca del río Aconcagua.

En cuanto a la cuenca del río Maipo, se observaron concentraciones medias más altas de atorvastatina, candesartán y claritromicina, alcanzando hasta 46, 22 y 8 µg L^{-1} en aguas superficiales. Se destaca que la claritromicina, junto con otros antibióticos, puede contribuir al desarrollo de resistencia a los antimicrobianos debido al uso excesivo o inapropiado. La Organización Mundial de la Salud ha señalado que la resistencia a los antibióticos representa una de las principales amenazas para la salud mundial, la seguridad alimentaria y el progreso del desarrollo. Por lo tanto, es necesario destacar el papel potencialmente significativo de las EDARs como importantes fuentes de emisiones de antibióticos, lo que puede contribuir a la proliferación de genes de resistencia en los ecosistemas de aguas superficiales.

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CONCLUSIONES

CONCLUSIONES

De acuerdo con los objetivos fijados para el desarrollo de esta tesis doctoral, así como la investigación realizada y los resultados obtenidos, se llegan a las siguientes conclusiones finales:

1. La revisión bibliográfica realizada revela que, en la actualidad, el uso de muestreadores pasivos se ha consolidado como un método complementario al muestreo puntual de agua para la detección y cuantificación de contaminantes orgánicos. Asimismo, los métodos de análisis non-target han demostrado ser herramientas valiosas para identificar una amplia gama de contaminantes emergentes, permitiendo una comprensión más profunda de la presencia de compuestos no estudiados previamente.

2. Los muestreadores pasivos de tipo MPT han mostrado ser una herramienta eficaz y complementaria para evaluar a mediano plazo el estado de contaminación en humedales costeros. Estos dispositivos ofrecen información adicional sobre compuestos que podrían no ser detectados de manera efectiva mediante muestreo puntual.

3. Las descargas de contaminantes orgánicos como productos farmacéuticos o PFASs en los efluentes de EDARs y la actividad agrícola, constituyen ejemplos destacados de las principales fuentes de vertido de contaminantes de origen antropogénico en el medio acuático, ya que se vierten al Parque a través de diversos canales. Este hallazgo subraya el papel de las EDARs como fuentes importantes de contaminación, lo que indica la necesidad de optimizar los sistemas de tratamiento y gestionar adecuadamente estos vertidos para reducir su impacto ambiental en el Parque y sus ecosistemas.

4. Las lluvias y las aguas de escorrentía derivadas de campos de cultivo pueden ser la causa de episodios puntuales y agudos de contaminación en ecosistemas acuáticos.

5. El carbono orgánico puede desempeñar un papel importante en la determinación de las concentraciones de contaminantes orgánicos en los sedimentos, lo que resalta su relevancia en los procesos de deposición, transporte y degradación de estos compuestos en el tiempo. No obstante, aunque el análisis de otras propiedades físico-químicas, como el carbono inorgánico, el nitrógeno total y el azufre total, permite un mejor entendimiento de estos procesos en distintas profundidades del sedimento, establecer una relación directa y clara entre la edad del sedimento y las concentraciones de contaminantes resulta complejo. Esto dificulta la posibilidad de trazar una tendencia histórica precisa de la contaminación basándose únicamente en núcleos de sedimentos datados.

6. La escasa información disponible sobre la concentración de contaminantes orgánicos, en particular los emergentes, en sedimentos, resalta la relevancia de los datos obtenidos en este estudio. Estos resultados proporcionan un aporte valioso para entender la distribución y dinámica de los contaminantes en los sedimentos, y además contribuyen a validar y complementar los hallazgos de investigaciones previas en este ámbito.

7. Los analisis no dirigidos (o non-target), representan técnicas de detección prometedoras para la identificación cualitativa de contaminantes emergentes sin necesidad de contar con estándares de referencia. Estos métodos tienen la capacidad de detectar una amplia gama de compuestos, incluyendo metabolitos.

8. El muestreo realizado en el Parque Natural de L´Albufera nos permitió observar que, durante la primavera, los pesticidas más destacados fueron tebuconazol (con una concentración media de 175,92 ng L^{-1}), azoxistrobina (con una concentración media de 131,49 ng L^{-1}) y tiabendazol (61,56 ng L^{-1}). El tebuconazol y la azoxistrobina, asociados principalmente con el cultivo de arroz, y el tiabendazol, utilizado predominantemente en cítricos, reflejan patrones específicos de uso agrícola.

9. Los pesticidas experimentan transformaciones al ser descargados en ambientes acuáticos, lo que puede alterar su comportamiento y efectos en estos ecosistemas. Además, el uso de pesticidas está cambiando en respuesta a las variaciones climáticas, lo que añade una capa de complejidad a la evaluación de su impacto ambiental.

10. La evaluación del riesgo, medida mediante el cociente de peligrosidad, de los compuestos orgánicos en los ecosistemas acuáticos revela que ciertas zonas con un cociente de riesgo elevado requieren ser priorizadas para su monitoreo y gestión. Además, el clorpirifos presenta el mayor riesgo durante la primavera. En contraste, el imidacloprid muestra el mayor riesgo en otoño. Es fundamental llevar a cabo más investigaciones para reducir la entrada de contaminantes antropogénicos en los entornos acuáticos y revisar las necesidades regulatorias. Además, es imperativo implementar prácticas agroecológicas que promuevan la calidad del agua y del suelo, especialmente en un Parque Natural de alto valor ecológico, pero en estado de conservación desfavorable, con el fin de garantizar su protección y sostenibilidad a largo plazo.

11. La alta prevalencia y frecuencia de productos químicos con propiedades neuroactivas en los sistemas de agua dulce son motivo de gran preocupación. Los pesticidas, diseñados para afectar el sistema nervioso central de insectos y mamíferos (incluidos los humanos), representan una amenaza significativa para la vida acuática. La presencia continua de estos compuestos en el agua dulce subraya la urgencia de implementar medidas más estrictas para controlar y reducir su uso, con el fin de proteger la salud de los ecosistemas acuáticos

y, por extensión, de los seres humanos. La alteración de las funciones neurológicas en estos organismos puede provocar alteraciones del comportamiento, problemas de reproducción, reducción de las tasas de crecimiento e incluso mortalidad.

12. La presencia de PPCPs, pesticidas, compuestos industriales, PFASs, así como otros contaminantes orgánicos es ubicua en los ambientes acuáticos, como se ha mostrado al ser detectados en diferentes partes del mundo (Chile), en agua superficiales.

13. La información disponible sobre la presencia compuestos orgánicos en agua superficial en Chile es muy escasa. Se identificaron 311 compuestos diferentes en las cuencas de los ríos Aconcagua y Maipo, abarcando una amplia variedad de contaminantes provenientes de los sectores urbano, agrícola, industrial y farmacéutico. Por lo que es de especial interés seguir investigando para el desarrollo de estrategias de monitoreo y evaluación ambiental en el país, en paralelo con las prácticas establecidas en la Unión Europea.

Finalmente, los resultados de la presente tesis doctoral sirven como herramienta de conocimiento y apoyo para la elaboración de planes de monitoreo para evaluar la presencia y distribución de contaminantes orgánicos persistentes emergentes en diversos ecosistemas acuáticos, especialmente en agua y sedimentos. La persistencia, la posible bioacumulación y la toxicidad de estos compuestos permiten que permanezcan en el medio ambiente durante décadas, alcanzando niveles que pueden representar un riesgo significativo tanto para los ecosistemas acuáticos como para los seres humanos que utilizan estos recursos.

CONCLUSIONS

In accordance with the objectives established for the development of this doctoral thesis, as well as the research carried out and the results obtained, the following final conclusions are reached:

1. The literature review indicates that, currently, the use of passive samplers has become a well-established complementary method to point water sampling for the detection and quantification of organic contaminants. Furthermore, non-target analysis techniques have demonstrated their value as effective tools for identifying a broad spectrum of emerging contaminants, thereby facilitating a more comprehensive understanding of previously unstudied compounds.

2. MPT-type passive samplers have proven to be an effective and complementary tool for the medium-term assessment of contamination levels in coastal wetlands. These devices offer valuable additional information on compounds that may not be adequately detected through point sampling.

3. Discharges of priority pollutants, such as pharmaceuticals and PFASs, from wastewater treatment plants (WWTPs) and agricultural activities represent important sources of anthropogenic pollution entering the aquatic environment, as these pollutants are released into the Park through various channels. This finding highlights the role of WWTPs as key contributors to pollution, emphasizing the need to optimize treatment systems and effectively manage these discharges in order to mitigate their environmental impact on the Park and its ecosystems.

4. Rainfall and runoff from agricultural fields can contribute to localized and acute episodes of contamination in aquatic ecosystems.

5. On one hand, organic carbon plays a key role in determining organic contaminant concentrations in sediments, influencing deposition, transport, and degradation processes. On the other hand, analyzing other physicochemical properties, such as inorganic carbon, total nitrogen, and total sulfur, provides deeper insights into these processes at varying sediment depths, establishing a clear relationship between sediment age and contaminant concentrations is complex. This complexity hinders the development of an accurate historical contamination trend based solely on dated sediment cores.

6. The limited information on the concentration of organic contaminants, particularly emerging ones, in sediments underscores the significance of the data obtained in this study. These results offer a valuable contribution to the understanding of the distribution and the dynamics of contaminants in sediments, while also validating and complementing the findings of previous research in this field.

7. Non-target methodologies represent promising detection techniques for the qualitative identification of emerging contaminants without the need for reference standards. These methods have the ability to detect a wide range of compounds, including metabolites.

8. The sampling conducted in L'Albufera Natural Park revealed that, during spring, the most prevalent pesticides were tebuconazole (mean concentration of 175.92 ng L^{-1}), azoxystrobin (mean concentration of 131.49 ng L^{-1}), and thiabendazole (61.56 ng L^{-1}). Tebuconazole and azoxystrobin, primarily linked to rice cultivation, and thiabendazole, predominantly used in citrus farming, reflect distinct agricultural use patterns.

9. Pesticides undergo transformations when discharged into aquatic environments, which can alter their behavior and effects on these ecosystems. In addition, pesticide use is changing in response to climatic variations, which adds a layer of complexity to the assessment of their environmental impact.

10. The risk assessment, measured by the hazard quotient, of organic compounds in aquatic ecosystems indicates that certain areas with high hazard quotients should be prioritized for monitoring and management. Chlorpyrifos presents the highest risk during spring, while imidacloprid shows the greatest risk in autumn. Further research is necessary to mitigate the input of anthropogenic contaminants into aquatic environments and to reassess regulatory requirements. Additionally, it is crucial to implement agroecological practices that enhance water and soil quality, particularly in a Natural Park of high ecological value but in an unfavorable conservation status, to ensure its long-term protection and sustainability.

11. The high prevalence and frequency of chemicals with neuroactive properties in freshwater systems are of great concern. Pesticides, designed to affect the central nervous system of insects and mammals (including humans), pose a significant threat to aquatic life. The continued presence of these compounds in freshwater underlines the urgency of implementing stricter measures to control and reduce their use in order to protect the health of aquatic ecosystems and, by extension, humans. The alteration of neurological functions in these organisms can lead to behavioral alterations, reproductive problems, reduced growth rates and even mortality.

12. The presence of PPCPs, pesticides, industrial compounds, PFASs, and other organic pollutants is widespread in aquatic environments, as evidenced by their detection in surface water across various regions of the world, including Chile.

13. Information on the presence of organic compounds in surface water in Chile is limited. A total of 311 different compounds were identified in the Aconcagua and Maipo river basins, encompassing a broad range of pollutants from urban, agricultural, industrial, and pharmaceutical sectors. For this reason, there is a particular need to continue research aimed at developing environmental monitoring and evaluation strategies in the country, in alignment with practices established in the European Union.

Finally, the results of this doctoral thesis provide a valuable knowledge base and support for the development of monitoring plans aimed at evaluating the presence and distribution of emerging persistent organic pollutants in various aquatic ecosystems, particularly in water and sediments. The persistence, potential bioaccumulation, and toxicity of these compounds allow them to remain in the environment for decades, reaching levels that may pose significant risks to both aquatic ecosystems and humans who rely on these resources.





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En esta sección se describen las abreviaturas y siglas más comunes utilizadas en la presente tesis doctoral. Además, todas las abreviaturas están definidas en los diversos artículos científicos presentados.

ACN	– Acetonitrilo / *Acetonitrile*
CECs	– Contaminantes de creciente preocupación / *Contaminants of emerging concern*
d.w.	– Peso seco / *Dry weight*
DDA	– Análisis dependiente de los datos / *Data dependent analysis*
DO	– Oxígeno disuelto / *Dissolved oxygen*
EPA	– Agencia de Protección del Medio Ambiente / *Environmental Protection Agency*
EQS	– Norma de calidad ambiental / *Environmental quality standard*
GIS	– Sistemas de Información Geográfica / *Geographic Information Systems*
GC	– Cromatografía de gases / *Gas chromatography*
HESI	– Ionización por electrospray calentado / *Heated electrospray ionization*
HPLC	– Cromatografía líquida de alta eficacia / *High performance liquid chromatography*
HRMS	– Espectrometría de masas de alta resolución / *High resolution mass spectrometry*
HQ	– Cociente de peligrosidad / *Hazard quotient*
HRMS	– Espectrometría de masas de alta resolución / *High resolution mass spectrometry*
IS	– Patrón interno / *Internal standard*
LC	– Cromatografía liquida / *Liquid chromatography*
LOD	– Límite de detección / *Limit of detection*
LOQ	– Límite de cuantificación / *Limit of quantification*
LOR	– Límite de reporte / *Limit of report*
MEC	– Concentración ambiental medida / *Measured environmental concentration*
MeOH	– Metanol / *Methanol*
MPT	– Tubo de polietileno microporoso / *Microporous polyethylene tube*

MS	– Espectrometría de masas / *Mass spectrometry*
MS/MS	– Espectrometría de masas en tándem / *Tandem mass spectrometry*
n.d.	– No detectado / *Not detected*
Ns	–Masa del compuesto en la fase receptora del muestreador o sorbente / *Mass of the compound in the sampler receiving phase or sorbent*
OCs	– Contaminantes orgánicos / *Organic contaminants*
o-DGT	– Gradientes orgánico-difusivos en películas delgadas / *Organic-diffusive gradients in thin films*
OPFRs	– Retardantes de llama organofosforados / *Organophosphorus flame retardants*
PAH	– Hidrocarburo aromático policíclico / *Polycyclic aromatic hydrocarbon*
PFASs	– Sustancias perfluoroalquiladas / *Perfluoroalkyl substance*
PNEC	– Concentración sin efecto previsto / *Predicted no effect concentration*
POCIS	– Muestreador químico orgánico polar integrado / *Polar Organic Chemical Integrative Sampler*
POPs	– Contaminantes orgánicos persistentes / *Persistent organic contaminants*
PPCPs	– Productos farmacéuticos y de cuidado personal / *Pharmaceuticals and personal care products*
QuEChERS	– Rápido, fácil, barato, efectivo, robusto y seguro / *Quick, easy, cheap, effective, rugged and safe*
RQ	– Cociente de riesgo / *Risk quotient*
Rs	– Tasa de muestreo / *Sampling rate*
SLE	– Extracción sólido-líquido / *Solid Liquid Extraction*
SPE	– Extracción en fase sólida / *Soild phase extraction*
UTM	– Sistema de coordenadas universal transversal de Mercator / *Universal Transverse Mercator*
WWTP	– Estación depuradora de aguas residuales / *Wastewater treatment plant*

Diseño editorial realizado por
Vicente Dasí Gómez



CIDE Centro de Investigaciones Sobre Desertificación

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