



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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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 ¹⁴C-data of the organic matter present

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in the different layers of the sediment cores, and the ¹⁴C-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: <i>University of Valencia, Research Center on Desertification (CIDE)</i> City/Town/Region: <i>Moncada, Community of Valencia</i> Country: <i>Spain</i> 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 L'Albufera 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 ($39^{\circ}20'39.10''\text{N}$ $0^{\circ}21'29.60''\text{W}$) and South ($39^{\circ}19'16.50''\text{N}$ $0^{\circ}21'46.00''\text{W}$) 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:

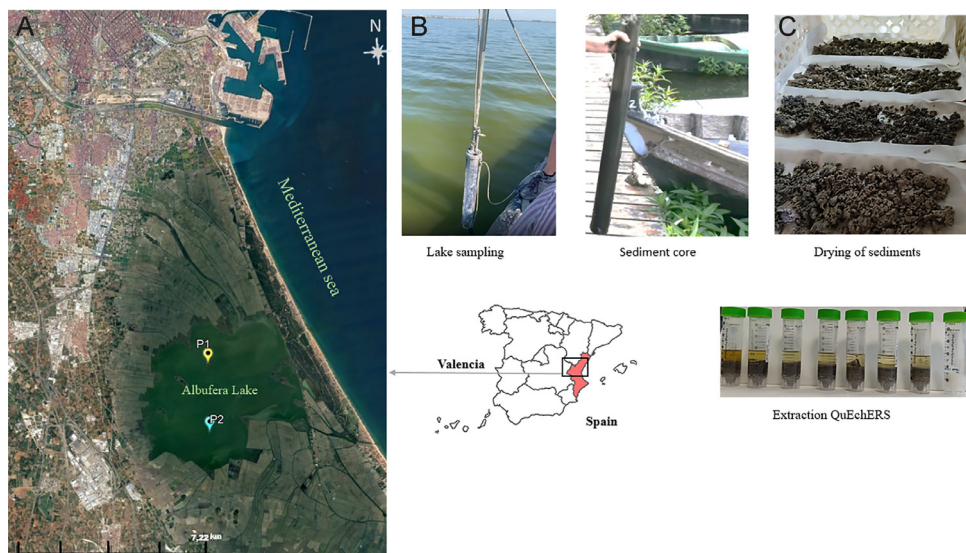


Fig. 1. Overview of the sampling procedure. a) Study area and sampling locations b) Sampling c) Extraction protocol.

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 re-sults 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 im-portant information are provided:

- [Fig. 2](#) is an overview of the ^{14}C dating 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 $\text{mean}+2\sigma$ and expressed in mg kg^{-1} dry weight.
- [Fig. 4](#) illustrates the enrichment factors (ER) of the heavy metal (HMs) and metalloids.

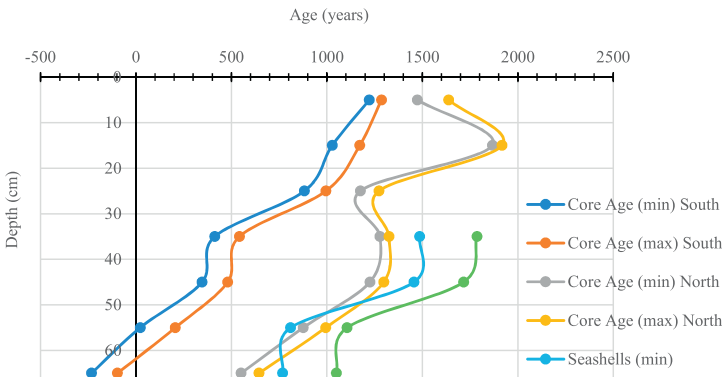


Fig. 2. Relationship between the depths and calibrated ages in the North and South sediment cores and in Seashells in the North.

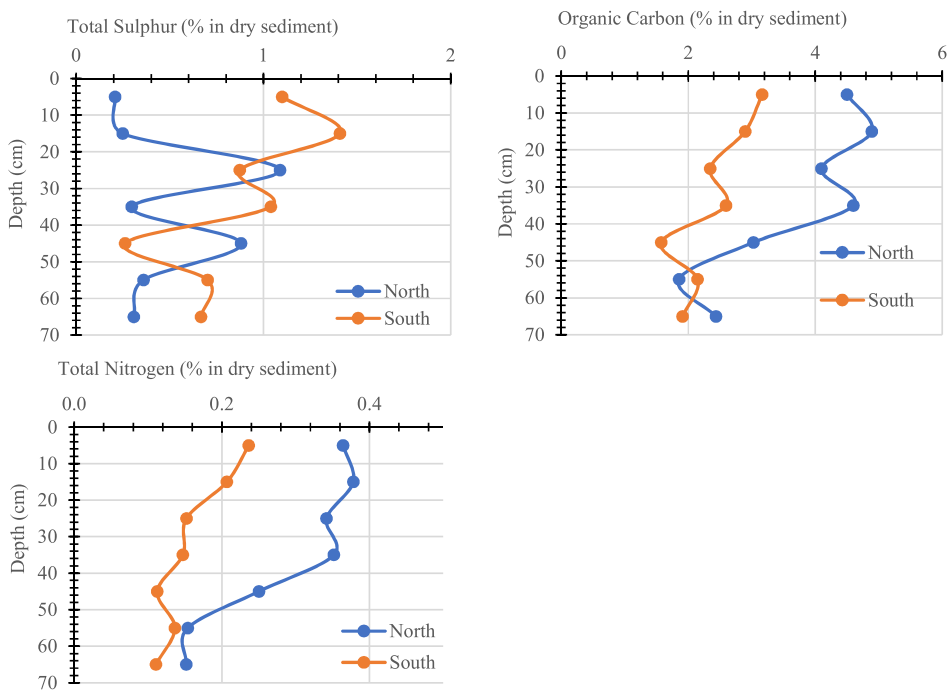


Fig. 3. Organic Carbon, Total Nitrogen and Total Sulphur, expressed in% in dry sediment, at different sampling sites.

- 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).

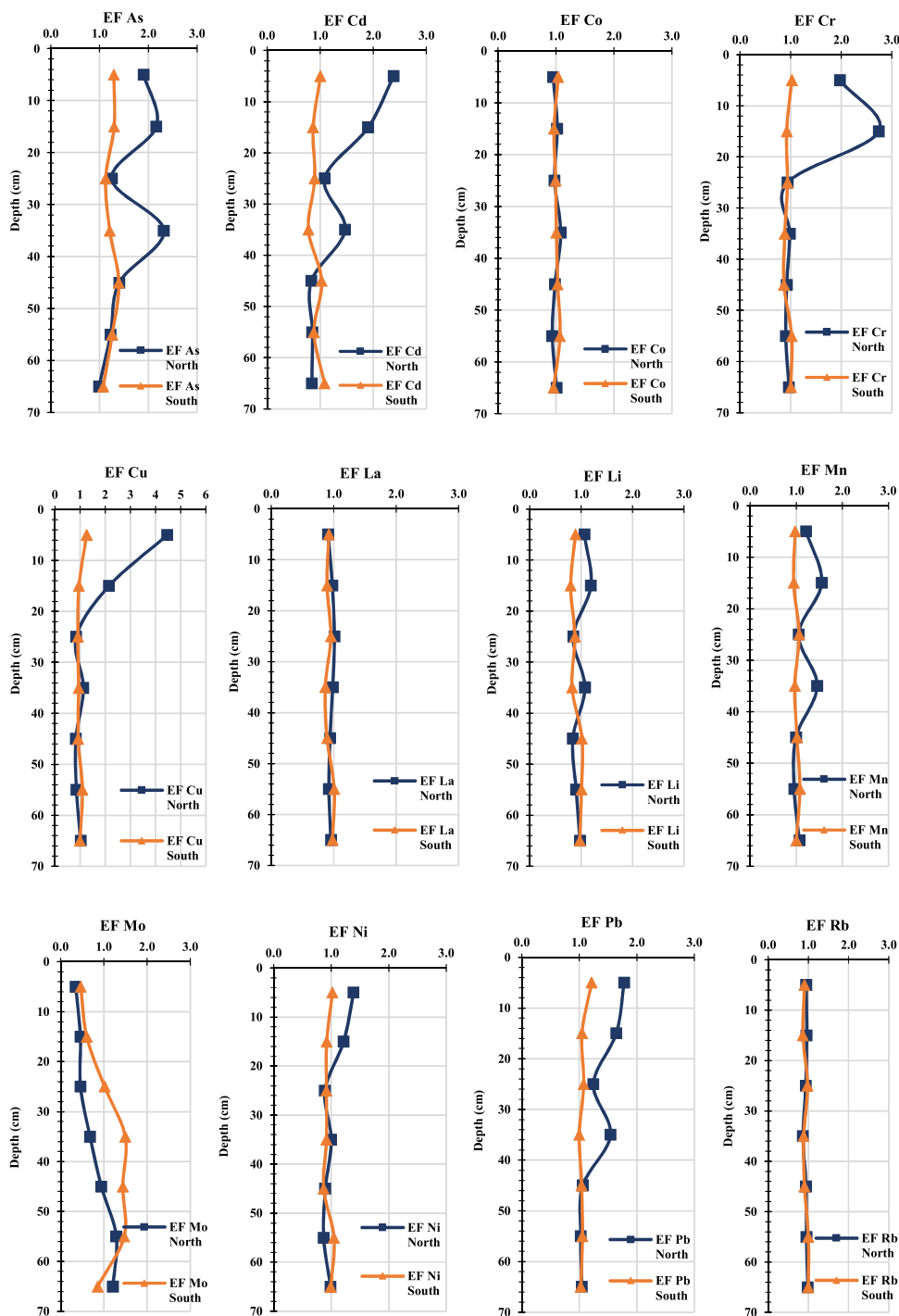


Fig. 4. Enrichment Factor (EF) in the vertical profiles at Northern and Southern sampling points in L'Albufera Lake. EF ranking class: $EF \leq 1$: no enrichment; $1 \leq EF \leq 3$: minor enrichment; $3 \leq EF \leq 5$: moderately enrichment; $5 \leq EF \leq 10$: moderately severe enrichment.

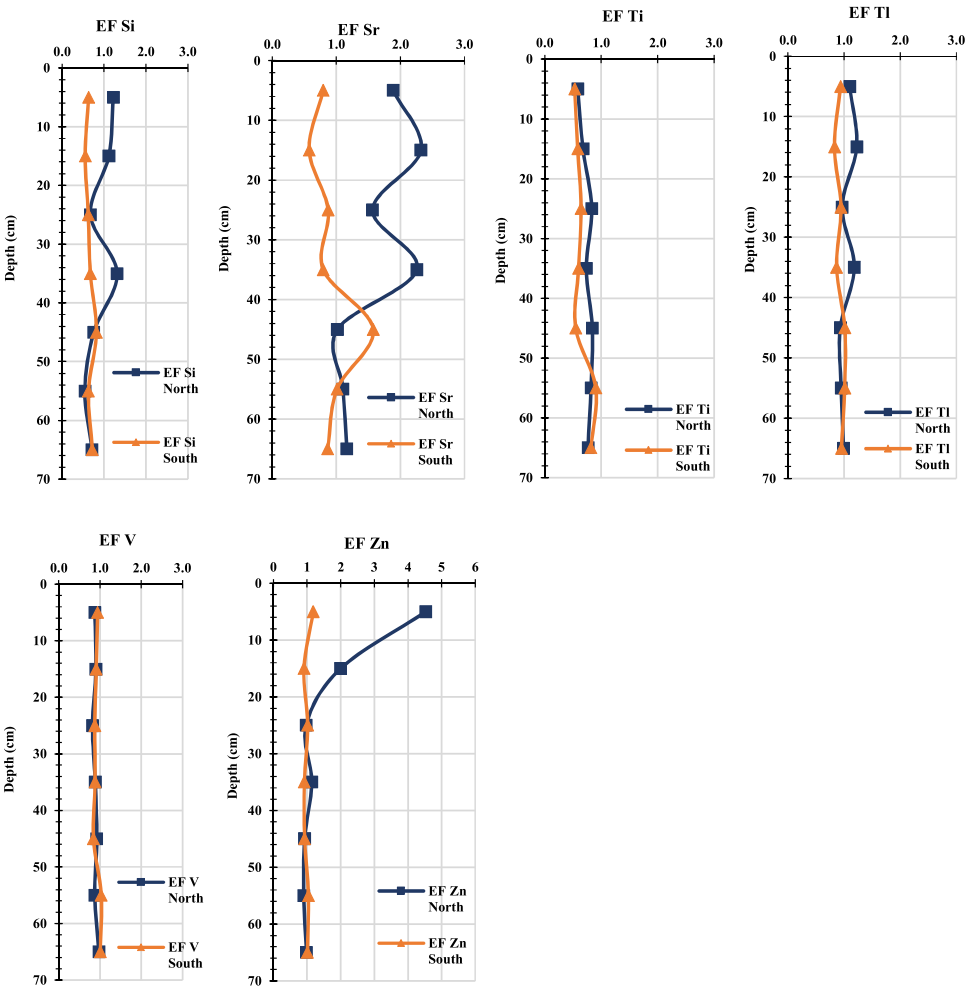


Fig. 4. Continued

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 3Mean concentrations $\pm$ 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
Azoxystrobin	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 4Mean concentrations $\pm$ 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}) $\pm$ SD						
	Sediment Depth (cm)						
Pesticides	0–10	10–20	20–30	30–40	40–50	50–60	60–70
Acetamidrid	27.7 $\pm$ 1.3	29.3 $\pm$ 4.62	30.5 $\pm$ 2.02	29.0 $\pm$ 1.41	27.9 $\pm$ 0.36	26.5 $\pm$ 2.93	24.4 $\pm$ 6.71
Azoxystrobin	0.18 $\pm$ 0.01	nd	nd	nd	nd	nd	Nd
Diazinon	nd	nd	nd	nd	nd	nd	Nd
Fluvalinate	34.2 $\pm$ 4.20	67.5 $\pm$ 2.51	56.1 $\pm$ 13.5	54.4 $\pm$ 19.9	29.1 $\pm$ 9.42	37.6 $\pm$ 3.78	34.9 $\pm$ 15.1
Imazalil	10.6 $\pm$ 1.07	nd	nd	nd	nd	nd	Nd
Molinate	nd	nd	nd	nd	nd	nd	Nd
Omethoate	nd	9.61 $\pm$ 1.10	5.12 $\pm$ 0.24	3.68 $\pm$ 0.08	nd	nd	Nd
Tebuconazole	132.8 $\pm$ 18.10	nd	nd	nd	nd	nd	Nd
Thiabendazole	9.22 $\pm$ 0.32	nd	nd	nd	nd	nd	Nd
Tricyclazol	4.75 $\pm$ 0.97	nd	nd	nd	nd	nd	Nd
PPCPs							
ButylParaben	0.33 $\pm$ 0.08	0.57 $\pm$ 0.37	0.36 $\pm$ 0.07	0.33 $\pm$ 0.11	0.32 $\pm$ 0.11	0.24 $\pm$ 0.05	0.28 $\pm$ 0.16
PropylParaben	0.60 $\pm$ 0.07	0.98 $\pm$ 0.30	0.46 $\pm$ 0.08	0.42 $\pm$ 0.11	1.04 $\pm$ 0.25	0.26 $\pm$ 0.13	0.70 $\pm$ 0.13
MethylParaben	3.39 $\pm$ 0.11	8.53 $\pm$ 2.27	3.16 $\pm$ 0.89	2.35 $\pm$ 0.64	3.63 $\pm$ 0.47	1.63 $\pm$ 0.66	3.73 $\pm$ 0.42
EthylParaben	5.22 $\pm$ 0.71	4.54 $\pm$ 1.09	7.36 $\pm$ 4.35	4.51 $\pm$ 1.02	5.11 $\pm$ 0.05	4.37 $\pm$ 1.12	5.19 $\pm$ 0.63
Bisphenol A	5.55 $\pm$ 0.98	2.24 $\pm$ 0.91	2.59 $\pm$ 0.32	2.09 $\pm$ 0.66	2.51 $\pm$ 0.85	6.27 $\pm$ 1.57	1.60 $\pm$ 0.20
Salicylic Acid	7.81 $\pm$ 0.83	9.10 $\pm$ 1.04	4.04 $\pm$ 0.72	2.72 $\pm$ 0.31	3.07 $\pm$ 0.11	2.19 $\pm$ 0.19	2.45 $\pm$ 0.19
PFASs							
HFPO-DA	nd	nd	1.05 $\pm$ 0.26	nd	nd	1.08 $\pm$ 0.15	Nd
PFDA	0.24 $\pm$ 0.06	nd	nd	nd	nd	nd	Nd
PFHxA	nd	nd	nd	nd	nd	nd	Nd
PFOA	0.55 $\pm$ 0.09	0.26 $\pm$ 0.10	0.28 $\pm$ 0.10	0.29 $\pm$ 0.11	0.27 $\pm$ 0.13	0.33 $\pm$ 0.29	0.20 $\pm$ 0.14
PFOS	5.59 $\pm$ 0.71	1.35 $\pm$ 0.74	1.11 $\pm$ 0.74	0.68 $\pm$ 0.82	0.85 $\pm$ 1.12	0.79 $\pm$ 1.10	0.77 $\pm$ 1.10
PFPeA	1.08 $\pm$ 0.35	0.13 $\pm$ 0.01	0.18 $\pm$ 0.05	0.16 $\pm$ 0.05	0.16 $\pm$ 0.01	0.19 $\pm$ 0.01	0.17 $\pm$ 0.01
PRs							
TnBP	2.02 $\pm$ 0.79	1.65 $\pm$ 0.51	2.14 $\pm$ 0.69	2.01 $\pm$ 0.14	2.06 $\pm$ 0.46	1.66 $\pm$ 0.19	2.04 $\pm$ 0.24
PAHs							
Naphthalene	156.04 $\pm$ 11.49	101.45 $\pm$ 6.24	nd	nd	nd	nd	Nd
Acenaphthylene	37.55 $\pm$ 1.96	35.52 $\pm$ 0.90	nd	nd	nd	nd	Nd
Acenaphthene	9.73 $\pm$ 0.23	10.60 $\pm$ 0.44	8.70 $\pm$ 0.44	9.17 $\pm$ 0.29	7.68 $\pm$ 0.51	8.33 $\pm$ 0.30	6.71 $\pm$ 0.18
Fluorene	13.13 $\pm$ 0.24	3.99 $\pm$ 0.11	5.27 $\pm$ 0.30	15.60 $\pm$ 0.17	4.56 $\pm$ 0.18	1.39 $\pm$ 0.18	3.77 $\pm$ 0.11
Phenanthrene	22.28 $\pm$ 1.24	11.84 $\pm$ 0.72	17.67 $\pm$ 0.37	nd	nd	nd	Nd
Fluoranthene	26.50 $\pm$ 0.27	40.92 $\pm$ 0.74	73.75 $\pm$ 0.27	23.27 $\pm$ 0.11	17.06 $\pm$ 0.51	12.37 $\pm$ 0.39	11.56 $\pm$ 0.11
Pyrene	30.32 $\pm$ 0.96	26.52 $\pm$ 1.01	27.45 $\pm$ 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 ¹⁴C dating and sediment characteristics

The Accelerator Mass Spectrometry (AMS) measurement is performed on graphite produced by the reduction of a carbon dioxide (CO₂) sample over cobalt catalysis [6,7]. CO₂ is obtained from the combustion of the sample at more than 800 °C in an atmosphere with 100 % oxygen. The CO₂ 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 C¹⁴/C¹³ ratio of the sample relative to C¹⁴/C¹³ in oxalic acid II (NIST-4990C) in one of the many own particle accelerators and using a $\delta^{13}\text{C}$ ion source. The AMS dating result is corrected as a function of total fractionation using the $\delta^{13}\text{C}$ 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 (%)
Acetamidrid	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 $\delta^{13}\text{C}$ values were measured separately on an IRMS (Isotope Ratio Mass Spectrometer). They are NOT $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ values are for the material itself (not the d13C value obtained by AMS). The $\delta^{13}\text{C}$ and $\delta^{15}\text{C}$ 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).

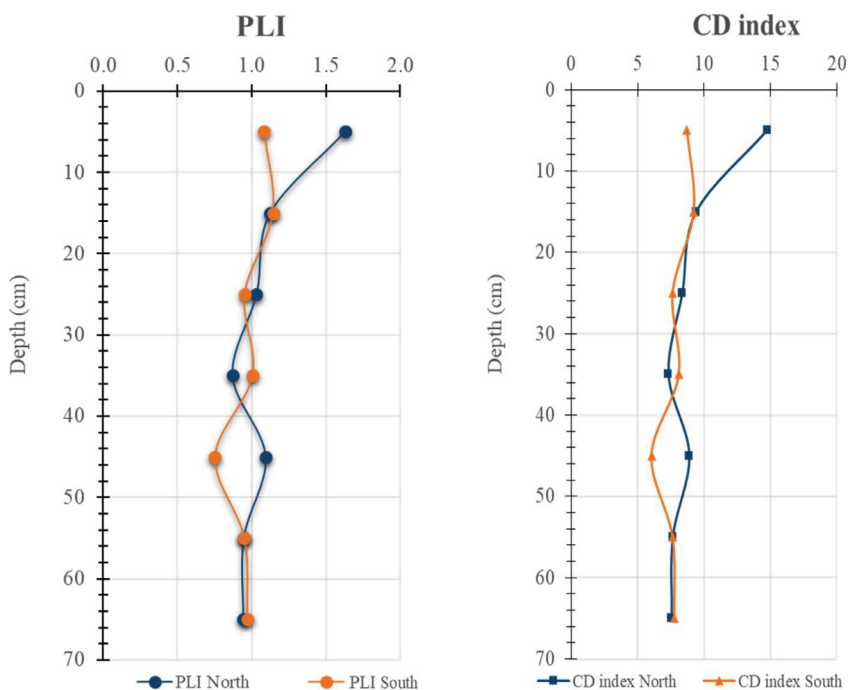


Fig. 5. Left side: Contamination Load Index (PLI): $PLI > 1$ indicates that the site is polluted, $PLI \leq 1$ indicates no contamination [10]. Right side: Contamination Degree (CD) classify the contamination status in: $CD < 6$ low; $6 < CD < 12$ moderate; $12 < CD < 24$ considerable; $CD > 24$ very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

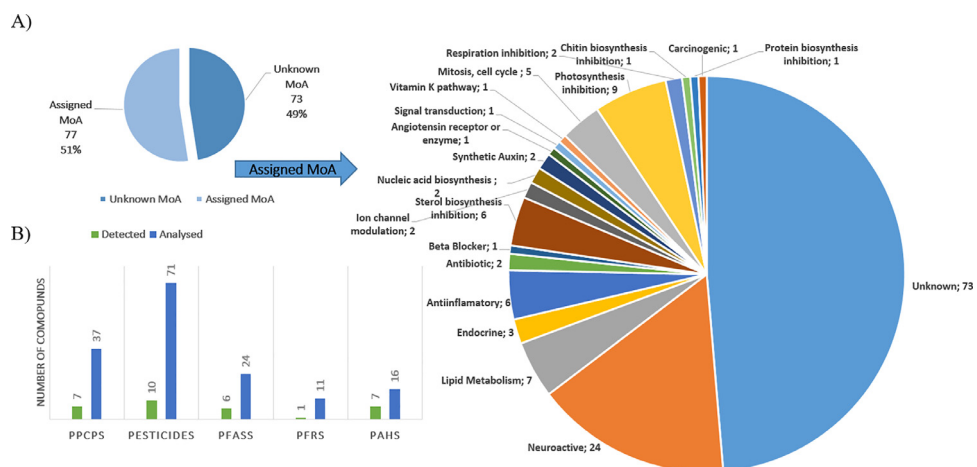


Fig. 6. A) Mode of action information for detected compounds. Left: fraction of assigned and unknown MOAs. Right: pie-chart MOA information of the detected target compounds. B) Quantitative LC-HRMS screening results. Left: number of analysed (blue colored bar) versus detected (green colored bar) target 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 µg·kg ⁻¹	PNEC _{fresh water} µg·L ⁻¹	k _p no units	PNEC _{sediment} µg·kg ⁻¹	RQ _{sediment} no units
Acetamidrid	28.581	0.024	20.1	386.3	7.40·10 ⁻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	9.85·10 ⁻⁸
Imazalil	–	0.870	21,066.5	14,662,257.3	–
Molinate	7.780	3.800	5171.2	15,720,457.5	4.95·10 ⁻⁷
Omethoate	–	0.004	0.6	1.9	–
Tebuconazole	4.485	0.240	15,980.5	3,068,264.7	1.46·10 ⁻⁶
Thiabendazole	2.455	1.200	941.0	903,364.1	2.72·10 ⁻⁶
Tricyclazole	0.136	0.470	80.1	30,114.8	4.53·10 ⁻⁶
Bisphenol A	9.735	0.240	6661.8	1,279,065.6	7.61·10 ⁻⁶
ButylParaben	0.376	5.060	11,846.5	47,954,801.9	7.85·10 ⁻⁶
Codeine	0.946	7.190	49.4	284,060.3	3.33·10 ⁻⁶
EthylParaben	7.564	13.300	941.0	10,012,285.5	7.55·10 ⁻⁷
MethylParaben	2.530	5.000	290.8	1,163,192.5	2.18·10 ⁻⁷
PropylParaben	0.690	12.300	3496.2	34,402,238.0	2.00·10 ⁻⁸
Salicylic Acid	5.800	18.000	580.2	8,355,146.9	6.94·10 ⁻⁷
HFPO-DA	1.020	–	31,885.4	0.0	–
PFDA	0.272	0.170	10,083,042.5	1,371,293,778.1	1.98·10 ⁻¹⁰
PFHxA	0.161	140.000	9629.2	1,078,473,851.7	1.49·10 ⁻¹⁰
PFOA	0.690	0.180	205,869.3	29,645,179.8	2.33·10 ⁻⁸
PFOS	8.787	0.002	98,535.2	157,656.4	5.57·10 ⁻⁵
PFPeA	0.222	3.910	8009.2	25,052,919.4	8.87·10 ⁻⁹
TnBP	1.838	37.000	21,066.5	623,567,264.9	2.95·10 ⁻⁹
Naphthalene	286.834	–	7474.7	0.0	–
Acenaphthylene	33.900	0.530	31,885.4	13,519,401.1	2.51·10 ⁻⁶
Acenaphthene	31.680	3.700	26,521.1	78,502,467.6	4.04·10 ⁻⁷
Fluorene	20.700	0.250	48,260.5	9,652,095.1	2.14·10 ⁻⁶
Phenanthrene	186.903	–	118,465.4	0.0	–
Fluoranthene	20.100	0.006	529,165.6	2,666,994.6	7.54E·10 ⁻⁶
Pyrene	–	0.028	482,604.8	10,810,346.5	–
RQ _{sediment} = ∑ MEC / PNEC _{sediment}					7.41·10 ⁻²

4.2. Reagents and chemicals

HPLC grade MeOH ≥ 99.8 % purity was purchased from VWR Chemicals® (Radnor, PA, USA) and ammonium formate (NH₄HCO₂), formic acid (CH₂O₂), ammonium fluoride (NH₄F) and acetone (CH₃COCH₃) 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, Na₂HPO₄ and EDTA were purchased from Alfa Aesar (Karlsruhe, Germany). Octadecylsilica (C18) and primary-secondaryamine (PSA) were purchased from Análisis Vínicos (Tomelloso, Spain). Magnesium sulfate (MgSO₄) and sodium sesquihydrate citrate [HOC(COOH) (CH₂COONa)₂ · 1.5 H₂O] from Alfa Aesar (Karlsruhe, Germany) and sodium chloride (NaCl) and trisodium citrate dihydrate (C₆H₅Na₃O₇ · 2 H₂O) 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 μg.kg ⁻¹	PNEC _{freshwater} μg.L ⁻¹	k _p no units	PNEC _{sediment} μg.kg ⁻¹	RQ _{sediment} no units
Acetamiprid	27.736	0.024	14.1	271.2	1.02.10 ⁻¹
Azoxystrobin	0.179	0.200	708.1	113,288.6	1.58.10 ⁻⁶
Diazinon	–	0.010	4467.5	35,740.1	–
Fluvalinate	34.224	0.003	23,445,859.9	61,897,070.2	5.53.10 ⁻⁷
Imazalil	10.649	0.870	14,793.3	10,296,162.9	1.03.10 ⁻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	6.16.10 ⁻⁵
Thiabendazole	9.223	1.200	660.8	634,362.3	1.45.10 ⁻⁵
Tricyclazole	4.753	0.470	56.2	21,147.3	2.25.10 ⁻⁴
Bisphenol A	5.547	0.240	4678.1	898,188.3	6.18.10 ⁻⁶
ButylParaben	0.328	5.060	8318.9	33,674,927.5	9.75.10 ⁻⁹
Codeina	–	7.190	34.7	199,473.4	–
EthylParaben	5.221	13.300	660.8	7,030,849.4	7.43.10 ⁻⁷
MethylParaben	3.394	5.000	204.2	816,819.6	4.16.10 ⁻⁶
PropylParaben	0.595	12.300	2455.1	24,158,016.0	2.46.10 ⁻⁸
Salicylic Acid	7.815	18.000	407.4	5,867,169.8	1.33.10 ⁻⁶
HFPO-DA	–	–	22,390.6	–	–
PFDA	0.244	0.170	7,080,536.5	962,952,964.2	2.53.10 ⁻¹⁰
PFHxA	–	140.000	6761.9	757,328,304.7	–
PFOA	0.550	0.180	144,566.0	20,817,504.1	2.64.10 ⁻⁸
PFOS	5.589	0.002	69,193.6	110,709.8	5.05.10 ⁻⁵
PFPeA	1.081	3.910	5624.3	17,592,716.7	6.15.10 ⁻⁸
TnBP	2.015	37.000	14,793.3	437,882,790.5	4.60.10 ⁻⁹
Naphthalene	156.800	–	5248.9	–	–
Acenaphthylene	37.500	0.530	22,390.6	9,493,623.9	3.95.10 ⁻⁶
Acenaphthene	9.870	3.700	18,623.7	55,126,177.2	1.79.10 ⁻⁷
Fluorene	13.007	0.250	33,889.6	6,777,915.7	1.92.10 ⁻⁶
Phenanthrene	22.170	–	83,189.1	–	–
Fluoranthene	26.451	0.006	371,591.838	1,872,822.863	1.41.10 ⁻⁵
Pyrene	30.240	0.028	338,895.784	7,591,265.560	3.98.10 ⁻⁶
RQ _{sediment} = ∑ MEC/ PNEC _{sediment}					1.03.10 ⁻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 MgSO₄, 1.5 g NaCl, 1.5 g C₆H₅Na₃O₇ · 2 H₂O, and 0.75 g [HOC(COOH) (CH₂COONa)₂ and 1.5 H₂O] 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 mL Na₂HPO₄ 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 Milestone® 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 limit of 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.

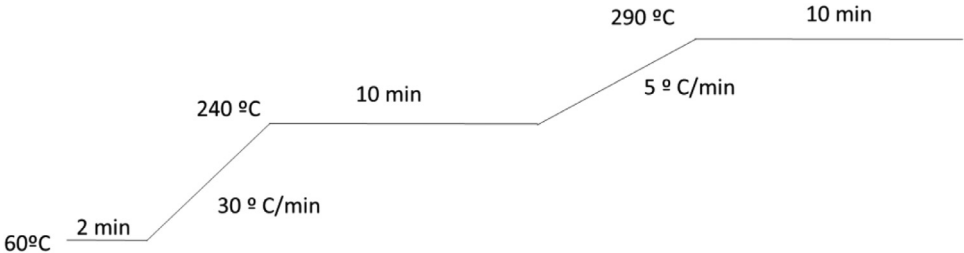
GC Conditions	
Analytical column	Capillary column Zebron ZB-5MS of 30 m × 0.25 mm i.d. with 0.25 µm film thickness
Injector temperature	280 °C
Splitless time	1.2 min
He flow rate	1 mL min ⁻¹
Ionizing energy	70 eV
Oven Programme	

Table 10

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

LC Conditions	
Analytical column	<i>Pesticides</i> : Luna C18 (15.0 cm × 0.21 cm) with a 3 µm particle size (Phenomenex, USA) <i>PFASs and OPFRs</i> : Kinetex XB-C18: 50.0 × 4.6 mm, 1.7 µm (Phenomenex, USA) <i>PPCPs</i> : Kinetex 1.7 µm Biphenyl, 1.7 µm. 50 × 2.1 mm, (Phenomenex, USA)
Column temperature	30 °C
Volume injected	5 µL
Mobile phase	<i>Pesticides</i> : (A) Water – (B) MeOH both with 0.1 % Formic Acid and 5 mM Ammonium formate <i>PFASs</i> : (A) Water – (B) MeOH both with 10 mM Ammonium formate <i>OPFRs and PPCPs (for positive mode)</i> : (A) Water – (B) MeOH both with 0.1 % Formic Acid <i>PPCPs (for negative mode)</i> : (A) Water – (B) MeOH both with 2.4 mM Ammonium fluoride
Flow rate	<i>PPCPs</i> : 0.2 mL min ⁻¹ <i>PFASs and pesticides</i> : 0.3 mL min ⁻¹ <i>OPFRs</i> : 0.2 mL min ⁻¹
Linear gradient	<i>Pesticides</i> : 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). <i>PFASs</i> : 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). <i>OPFRs</i> : 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). <i>PPCPs</i> : 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.

$$EF = \frac{\frac{C_{\text{metal sample}}}{C_{\text{normalizer sample}}}}{\frac{C_{\text{metal background}}}{C_{\text{normalizer background}}}} \quad (3)$$

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:

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

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:

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

$$K_p = OM \cdot 0.411 \cdot K_{ow} \quad (6)$$

$$RQ_{\text{sediment}} = \sum_{i=1}^n \frac{MEC_i}{PNEC_{\text{sediment } i}} \quad (7)$$

Where Lowest Predicted No Effect Concentrations ($PNEC_{\text{water}}$) ($\mu\text{g L}^{-1}$) values were extracted from the NORMAN Ecotoxicology Database (<https://www.norman-network.com/nds/ecotox/lowestPnecsIndex.php>) and $PNEC_{\text{sediment}}$ ($\mu\text{g kg}^{-1}$) 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 m³) [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 $PNEC_{\text{sediment}}$ 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.

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

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

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).

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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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