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Study of the degradation of diphenyl-ether herbicides aclonifen and bifenox in different environmental waters

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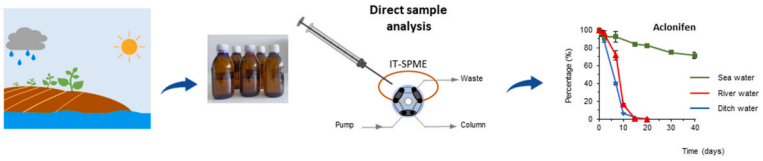
HIGHLIGHTS

- The degradation of the herbicides bifenox and aclonifen in water has been studied.
- Bifenox acid, the main degradation product of bifenox, has been also tested.
- The effects of temperature, light, pH and sample matrix is reported.
- Nanopure, ditch, river and sea water samples have been tested.
- Degradation rates and half-life times in the different waters are reported.

GRAPHICAL ABSTRACT



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ABSTRACT

The degradation of the diphenyl-ether herbicides aclonifen (ACL) and bifenox (BF) in water samples has been studied under different laboratory conditions, using in-tube solid-phase microextraction (IT-SPME) coupled to capillary liquid chromatography (capLC). The working conditions were selected in order to detect also bifenox acid (BFA), a compound formed as a result of the hydroxylation of BF. Samples (4 mL) were processed without any previous treatment, which allowed the detection of the herbicides at low ppt levels. The effects of temperature, light and pH on the degradation of ACL and BF have been tested using standard solutions prepared in nanopure water. The effect of the sample matrix has been evaluated by analysing different environmental waters spiked with the herbicides, namely ditch water, river water and seawater. The kinetics of the degradation have been studied and the half-life times ($t_{1/2}$) have been calculated. The results obtained have demonstrated that the sample matrix is the most important parameter affecting the degradation of the tested herbicides. The degradation of both ACL and BF was much faster in ditch and river water samples, where $t_{1/2}$ values of only a few days were observed. However, both compounds showed a better stability in seawater samples, where they can persist for several months. In all matrices ACL was found to be more stable than BF. In samples where BF had been substantially degraded, BFA was also detected, although the stability of this compound was also limited. Other degradation products have been detected along the study.

1. Introduction

The intensive application of herbicides in modern agriculture has been and continuous to be a major threat for the environment. After being applied, herbicides can eventually disperse to different target and non-target environmental compartments such as soils, groundwater or surface water due to different processes (mainly run off due to rainfall or irrigation practices), posing a risk to living organisms due to their

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persistence and toxicity. This problem has been addressed by the authorities, and regulations have been established not only to promote the replacement of first developed highly toxic herbicides by more selective and less persistent products, but also to monitor their presence in drinking and environmental waters (Environmental Protection US Environmental Protection Agency, 2022; European Commission, 2008; European Commission, 2013). In aquatic systems, herbicides can undergo different degradation processes that produce several known and unknown products, and some of them can be even more toxic and persistent than the parent compounds (Bottaro et al., 2008; Hensen et al., 2020; Wang et al., 2020). For this reason, there is an increasing demand of analytical methods that can be applied, not only to measure the concentration of the parent herbicides in aquatic systems, but also to obtain information about the products originated during their degradation (Hensen el at, 2020). This information would provide a better picture of the risks associated to the utilization of herbicides, as well as of the efficiency of water treatment processes.

Diphenyl-ether herbicides such as BF and ACL are in current use to control a variety of broad-leaf and grass weeds in agriculture. Both compounds were included in the list of priority substances by the European Commission in 2013 (European Commission, 2013). The usage of these compounds was authorized relatively late compared to other families of herbicides. This can explain why the number of studies that have addressed their degradation in environmental waters is rather limited in comparison with the number of papers reported for other families of herbicides such as organophosphorus, triazines, carbamates or phenylureas herbicides (Bottaro et al., 2008; Lartigues and Garrigues, 1995; Moliner-Martínez et al., 2015; Vink and Van der Zee, 1997). Some studies have been reported on the degradation of ACL in agricultural soils, examining the effect of different physical, chemical and biological variables (Abbate et al., 2007; Erguven et al., 2016; Pérez-Lucas et al., 2020; Sharipov et al., 2021). To the best of our knowledge, no similar studies have been reported for the degradation of ACL and BF in environmental waters, despite the fact that the presence of BFA, a degradation product of BF, in some samples was reported more than two decades ago (Laganà et al., 2000, 2002).

In environmental water samples, herbicides can be degraded through different abiotic and biotic mechanisms, and in many cases the processes involved remain unknown (Hensen et al., 2020). As a result, several degradation products can be originated from a single herbicide, and they are expected to be present at very low concentrations. Therefore, highly sensitive and selective analytical tools combined with efficient sample treatments are necessary to address the study of the presence of herbicides and their degradation products in environmental samples. For example, with current chromatographic instruments, ACL and BF can measured at μg/L concentration levels after applying an appropriate preconcentration treatment, and the limits of detection (LODs) reported for these compounds are in the 0.1–40 ng/L interval (Vorkamp et al., 2014; Bodur and Bakirdere, 2019; Birtek et al., 2022). Special care must be taken during the sample preparation because in some cases the extraction protocols involve conditions that may accelerate the degradation of the target herbicides, thus resulting in underestimation of the risks (Bottaro et al., 2008). For example, the degradation of the herbicide tribenuron-methyl (sulfonylurea) is accelerated in contact with acidic buffers or with organic solvents typically involved in the extraction protocols required before its analysis. In a previous study, we demonstrated that the impact of the sample preparation on the measurement of the concentration of tribenuron-methyl can be drastically minimized by using IT-SPME coupled to miniaturized liquid chromatography (LC) (Serra-Mora et al., 2020a). This approach combines the high resolution and detection capabilities of miniaturized LC (capLC, nano LC) and the possibility of introducing directly into the chromatographic system large sample volumes (of up to several mL) with no other treatment than a filtration.

Today, the detection and quantification of herbicides such as ACL and BF at concentration levels amenable for monitoring purposes is possible, but intensive sample treatments are often involved (Birtek et al., 2022; Stang et al., 2016; Vorkamp et al., 2014). This is because reaching the required sensitivity relies on achieving high preconcentration factors, typically by processing large sample volumes (up to 1 L) by solid-phase extraction (SPE). Sample treatments can be somewhat simplified using some forms of microextraction, although this option has not been tested for degradation products (Bodur and Bakirdere, 2019; Li et al., 2018; Perreau and Einhorn, 2006; Serra-Mora et al., 2018; Sheu et al., 2006). The analysis of ACL and BF in water samples by electrochemical methods is possible without any previous treatment of the samples, but neither the sensitivity nor the selectivity would be suitable for the analysis of possible degradation products (Morawski et al., 2021; Shetti et al., 2019).

In the present study we have evaluated the possibility of using IT-SPME coupled to capLC with UV (DAD) for the study of the degradation of the diphenyl-ether herbicides ACL and BF. The chromatographic and detection conditions have been selected to obtain information also about the levels of BFA originated during the dissipation of BF. The chemical structures of the compounds tested are shown as supplementary content (Fig. S1). The effect of different experimental variables such as the temperature, the sample pH or the effect of natural sunlight on the degradation of the parent herbicides has been systematically evaluated. Results obtained for the degradation of ACL and BF in different environmental waters are also reported.

2. Materials and methods

2.1. Chemicals and solutions

All reagents used throughout out the study were of analytical grade. BF was purchased from Chemservice (West Chester, PA, USA), BFA was obtained from LGC Standards (Teddington, UK and ACL was acquired from Sigma-Aldrich (Steinheim, Germany). Methanol and acetonitrile, both HPLC grade, were purchased from VWR Chemicals (Randnor, PA, USA).

Stock solutions of the BF, BFA and ACL (50 μg mL^{-1}) were prepared by dissolving the appropriate amounts of the commercial standards in methanol and kept at 4 °C until use. Working solutions of the analytes and their mixtures were prepared by diluting the stock solutions with ultrapure water obtained from an Adrona system (Riga, Latvia). *Ortho*-phosphoric acid was obtained from Panreac (Barcelona, Spain) and sodium hydroxide was purchased from VWR Chemicals (Randnor, PA, USA).

2.2. Apparatus and chromatographic conditions

The chromatographic assays were carried out with a chromatograph consisting of a capillary pump (Agilent 1100 Series, Waldbronn, Germany), a Rheodyne model 7725 six-port injection valve, and a photodiode array detector (DAD) equipped with an 80 nL flow cell (Agilent 1200 Series). An Agilent HPLC ChemStation system was used for data acquisition and calculation. The analytical signal was recorded between 190 and 400 nm and monitored at 205 nm. A Zorbax SB C18 (150 mm × 0.5 mm id, 5 μm) column (Agilent) was used for the separation. The mobile phase was a mixture water-acetonitrile in gradient elution mode; the percentage of acetonitrile was increased from 25% at 0 min to 100% at 14 min, and then kept constant until the end of the run; the mobile phase flow rate was 6 μL min^{-1}.

All the solvents were filtered through 0.22 μm nylon membranes purchased from GVS (Sandfor, ME, USA) before use.

2.3. IT-SPME conditions

For IT-SPME, segments of 30 cm of a TRB-35 (35% diphenyl-65% dimethyl polysilioxane) column of 0.32 mm i. d. and 3 μm coating thickness (Teknokroma, Barcelona Spain) were used as extractive

capillaries in replacement of the inner loop of the injection valve. Samples were manually loaded into the capillaries using a 500 μL high precision syringe, and then 25 μL of nanopure water were flushed through the capillary to remove unwanted matrix compounds. Next, the position of the valve was switched, so the extractive capillary was inserted into the chromatographic flow scheme, and the analytes were desorbed and transferred to the analytical column for separation and detection by the mobile phase. For connecting the extractive capillaries to the valves 2.5 cm sleeve of 1/6 i. n. polyether ether ketone (PEEK) tubing, and 1/6 i. n. PEEK nuts and ferrules (Teknokroma) were used.

2.4. Degradation experiments

To study the stability ACL, BF and BFA in nanopure water, standard solutions of these compounds were introduced into glass flasks and then kept in dark at 4 °C (refrigerated). Unless otherwise stated, the concentrations assayed were 50 μg/L for ACL and BF, and 200 μg/L for BFA. Portions of 4 mL of these solutions were removed from the flasks at different times within the 0–40 days time interval, and then processed. In order to evaluate the effect of the temperature, similar studies were carried out in parallel with solutions kept in dark at ambient temperature. To study the effect of the light, solutions exposed to ambient conditions (dark and natural sunlight and ambient temperature) were also assayed. The ambient temperature ranged from 19 to 24 °C throughout the study.

2.5. Samples

The proposed conditions were applied to the analysis of river, sea and ditch water samples collected at different points of the Comunitat Valenciana region (East Spain). Stability assays in river water were carried out using a composite sample prepared by mixing equal volumes of a sample collected at Magro river and two samples collected at Júcar river. Similarly, a composite seawater sample was prepared by mixing four samples collected at Las Cañas, Almassora, Puerto de Sagunto and El Saler beaches, respectively. A ditch water sample was collected from an agricultural area located in the outskirts of the city of Valencia was also tested. The coordinates of the sample sites are given in Table S1. After their arrival to the lab, the samples were kept in the dark at 4 °C until analysis.

For analysis, the samples were manually homogenized and then, aliquots of 4 mL were directly loaded into the IT-SPME device and processed as described above. All assays were carried out at ambient temperature by triplicate.

3. Results and discussion

3.1. IT-SPME and chromatographic conditions

Assays for the optimization of the chromatographic conditions were carried out with standard solutions of the analytes (or their mixtures) prepared in nanopure water (pH = 7.9). Under the selected chromatographic conditions, the retention times (t_r) were 9.7 min, 16.3 min and 17.0 min for BFA, ACL and BF, respectively. As observed, the retention time (t_r) of BFA was much lower despite of having similar octanol/water partition coefficients (K_{ow}) (see Fig. S1). This can be attributed to the deprotonation of BFA at the working pH.

The effect of the sample volume on the analyte responses (peak areas measured at 205 nm) was evaluated. Different volumes of the working solutions were loaded in the capillary of the IT-SPME device. Before inserting the extractive capillary into the mobile-phase stream, 100 μL of nanopure water were flushed through it in order to eliminate the remaining sample. For ACL and BF, nearly linear increments of their responses were found up to sample volumes of 15 mL, and then the increment was more moderate (Fig. S2). However, for BFA the responses were approximately constant for sample volumes larger than 4 mL, and they were much lower than those measured for BF. These results suggested that BFA was not significantly retained in the extractive capillary. Next, solutions of BF and BFA were processed using a sample volume equivalent to the internal volume of the extractive capillary (≈25 μL), so that the whole sample aliquot introduced in the capillary was transferred to the analytical column (no preconcentration was effected). It was observed that solutions of BF and BFA of the same concentrations led to peaks of similar areas. This confirmed that unlike BF, BFA was not significantly retained in the extractive capillary when using sample volumes ≫ 25 μL. As stated earlier, BFA was expected to be deprotonated at the working pH, which could explain its low extraction efficiency considering that the extractive capillary of the IT-SPME was coated with an apolar polymer (section 2.3).

As a compromise, between the sensitivity and the time required to load the samples into the IT-SPME device, the sample volume selected for further studies was 4 mL. Under the selected conditions, the LODs estimated as the concentration of the analytes which resulted in a signal-to-noise ratio of 3 were 10 ng/L for ACL and BF, whereas the LOD found for BFA was 500 ng/L. The limits of quantification (LOQs) were established as the concentration of the analytes which resulted in a signal-to-noise ratio of 10; the values obtained were 10, 35 and 1550 ng/L for ACL, BF and BFA, respectively. The maximum allowable concentrations established in the European legislation for ACL are 120 ng/L and 12 ng/L in freshwater and seawater, respectively; for BF the values are 40 ng/L and 4 ng/L, respectively (European Commission, 2013). The LODs obtained under the proposed conditions were below the legislated values except for BF in seawater. If required, a higher sample volume could be processed to reduce the LOD for this compound (Fig. S2). A second capillary with an extractive phase more appropriate for polar compounds could be coupled in series to the capillary used in the present work to improve the overall recovery of BFA (Serra-Mora et al., 2020b).

3.2. Effect of the temperature, light and pH

First, the stability of solutions of ACL and BF prepared in nanopure water was studied. Illustrative examples of the chromatograms obtained for solutions containing a mixture of the analytes freshly prepared, and 15 and 30 days after are depicted in Fig. S3.

The chromatograms obtained for ACL were rather similar under all conditions assayed, and minor changes in the peak areas were observed throughout the study. The chromatograms also showed some minor peaks that could not be related to the tested pesticide, as most of them were also found for in blanks. Thus, those peaks were most probably due to the solvents and materials used along the analysis. For BF, a decrement on the peak areas was observed a few days after the preparation of the solutions, especially for solutions exposed to ambient conditions (natural sunlight and ambient temperature). As expected, BFA was found in the working solutions in which a significant degradation of BF had occurred. Since with the chromatographic system used mass spectrometry detection was not available, for the positive identification of BFA in those solutions the concordance of both the retention times and UV spectra of the suspected peak and the peak obtained for a standard solution of BFA were examined. Examples of the similarity between the spectra and the retention times of BFA and the peaks attributed to BFA in the solutions of BF are shown in Fig. S3 and Fig. S4A, respectively.

The percentages of undegraded herbicides over the time were calculated as the ratios between the peak areas obtained for the analytes in the working solutions and those obtained for solutions freshly prepared. The results obtained under the three conditions assayed for ACL and BF are depicted in Fig. 1A and B, respectively.

For solutions of ACL kept at 4 °C and in the dark, a slight decrement of the signals was observed during the first week, and then the percentage of undegraded compound remained approximately constant (≈90%), as it can be seen in Fig. 1A. According to this figure, both temperature and light had minor impact on the degradation of this herbicide.

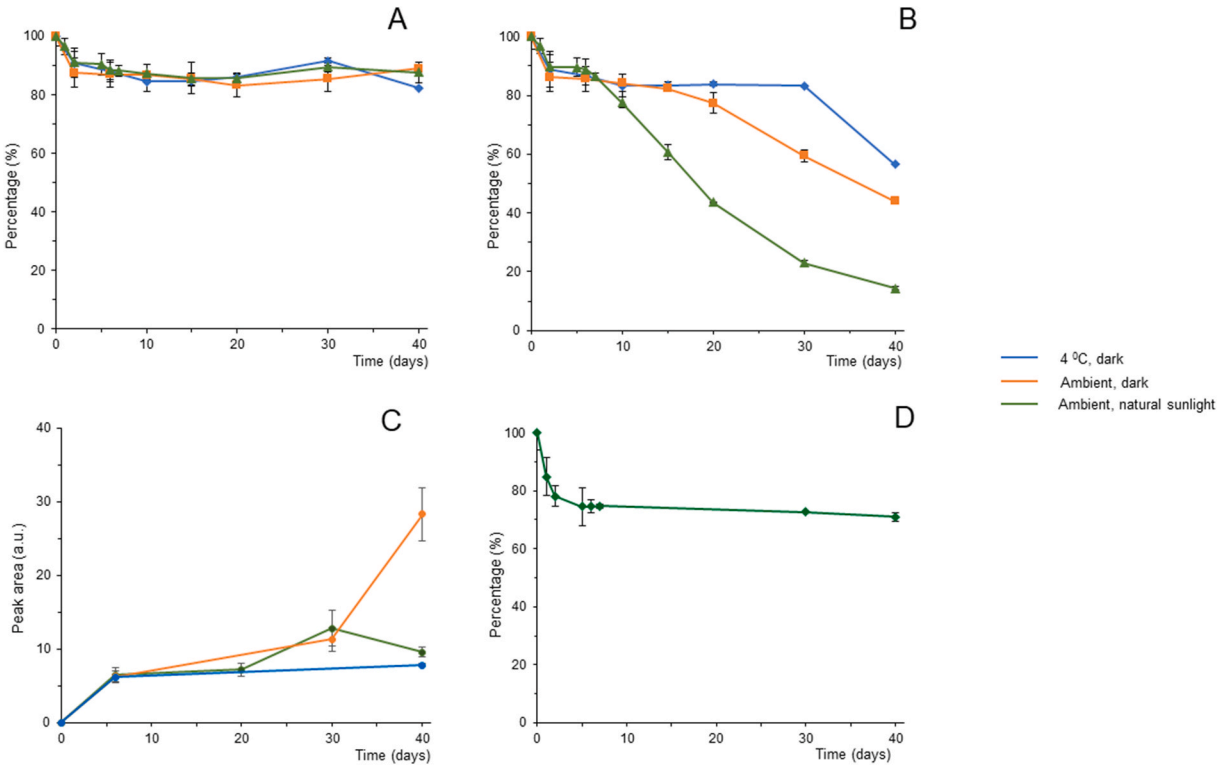

Fig. 1. Percentage of (A) ACL and (B) BF remaining in nanopure water over the time under the three conditions assayed; (C) peak areas of BFA over the time in standard solutions of BF under the three conditions assayed; (D) percentage of undegraded BFA in a standard solution of this compound exposed to ambient temperature and natural sunlight. Initial concentration of the parent herbicides in (A), (B) and (C), 50 μg/L; initial concentration of BFA in (D), 200 μg/L. For other experimental conditions, see text.

A similar behavior was observed for solutions of BF kept at 4 °C and in the dark up to day 30, and around the 85% of the analyte remained in solution (Fig. 1B). This percentage declined to 57% at day 40. A more pronounced decrement in the percentage of undegraded BF was observed under the other two conditions tested (Fig. 1B). In solutions kept in the dark at ambient temperature, the percentage of undegraded BF remained approximately constant up to day 15, and then started to decline. In solutions exposed to ambient conditions, the degradation of BF was observed from the beginning of the experiment.

The variation of the peak areas of BFA in the solutions of BF with the time is depicted in Fig. 1C. As expected, the peak of BFA was not detected in fresh solutions of BF (day 0). At day 6 the peak of BFA was detected, being its intensity very similar under the three conditions assayed. The latter observation can be explained by the fact that at day 6 the percentages of degraded BF were also very similar under the three conditions (Fig. 1B). For longer times, an inverse relationship between the percentage of degraded BF and the peak areas of BFA was observed when the solutions were kept in the dark. For example, a slight increment of the peak areas of FBA was found in solutions kept at 4 °C in the dark within the 6–40 days interval, which is consistent with the fact that under such conditions BF degraded very slowly. At ambient temperature, a moderate increment in signals of BFA occurred between days 6 and 30, and then the peak areas increased considerably at day 40; under the same conditions, the degradation of BF was moderated at first and progressed more rapidly at the end of the experiment (Fig. 1B). In contrast, in solutions of BF exposed to natural sunlight at ambient temperature a decrement of the peak areas of BFA occurred between days 30 and 40, even though BF degraded within this period. These results suggested that BFA was also degraded by sunlight. The hypothesis was further confirmed by analysing solutions of BFA exposed to natural sunlight and ambient temperature, as it can be seen in Fig. 1D.

For solutions of BF kept at ambient temperature both in the dark and exposed to sunlight, the representation of the Ln of the percentages of remaining BF against the time led to linear relationships, which indicates that the degradation followed a pseudo-first order mechanism. The corresponding equations are listed in Table 1. By comparing the slopes of both lines, it can be concluded that at ambient temperature, the degradation of BF in samples kept in the dark is about 2.7 times slower than in samples exposed to natural light. The equations of Table 1 were also used to estimate the half-life time ($t_{1/2}$) of BF, which were 33.83 days and 16.12 days in the dark and exposed to the light, respectively. It must be noted that a pseudo-first order degradation mechanism was also found for solutions of ACL exposed to ambient conditions up to day 7 days (Table 1); however, the $t_{1/2}$ value could not be established from the corresponding equation because, as stated earlier, the percentage of undegraded ACL remained approximately constant between days 7 and 40 (Fig. 1A). For the other conditions assayed, a clear tendency was not found.

The effect of the concentration of the tested herbicides on their degradation was evaluated by processing over the time solutions containing 130 μg/L of ACL or 10 μg/L of BF exposed to ambient conditions. No significant differences in their respective degradation patterns were observed with respect to the results obtained for 50 μg/L solutions (Fig. S5). Thus, solutions containing initial concentrations of 50 μg/L of the herbicides were used in further assays.

Finally, the effect of the pH of the working solution on the stability of the herbicides was studied. In order to promote the degradation of the parent pesticides, thus facilitating the detection of possible degradation products, strong acidic (pH = 3.0) and basic (pH = 10.0) media were tested, even though the pHs expected in environmental waters were 6–8. The results of this study are depicted in Fig. 2. As observed, the peak areas of undegraded ACL and BF at pH 3.0 and 7.9 were similar within experimental variations. At pH 10.0 a moderate degradation of ACL was observed, although no peaks corresponding to possible degradation products were detected. A more intense degradation was observed for BF at pH 10. At this pH no peaks other than that of BFA were found in the

Table 1
Degradation equations obtained for ACL and BF in the different types of water tested. All values were obtained from solutions kept to ambient temperature and natural sunlight; solutions of BF in nanopure kept in the dark at ambient temperature were also tested.

Analyte	Time of water	Time interval used in calculation (days)	Linear regression equation[a]	$t_{1/2}$ (days)
ACL	Nanopure	0–7	$y = -0.0178x + 4.5961$ $R^2 = 0.98$, n = 5	–
	Ditch	0–7	$y = -0.1378x + 4.6691$ $R^2 = 0.98$, n = 4	5.43
	River	0–10	$y = -0.0907x + 4.7203$ $R^2 = 0.98$, n = 4	8.81
	Sea	0–50	$y = -0.0135x + 4.6467$ $R^2 = 0.97$, n = 5	53.75
BF	Nanopure (kept in the dark)	0–40	$y = -0.0187x + 4.5537$ $R^2 = 0.98$, n = 5	33.83
	Nanopure (exposed to natural sunlight)	0–40	$y = -0.0507x + 4.7384$ $R^2 = 0.98$, n = 9	16.12
	Sea	0–40	$y = -0.0245x + 4.5685$ $R^2 = 0.995$, n = 7	26.43
	Ditch	1–2	$y = -37.65x + 132.1$ $R^2 = 0.990$, n = 5	2.18
	River	0–7	$y = -13.588x + 108.63$ $R^2 = 0.98$, n = 5	4.31

[a] - values obtained by plotting the Ln of the percentage of undegraded herbicide against time, except for BF in ditch and river water, which were calculated by plotting the percentage of undegraded herbicide against time.

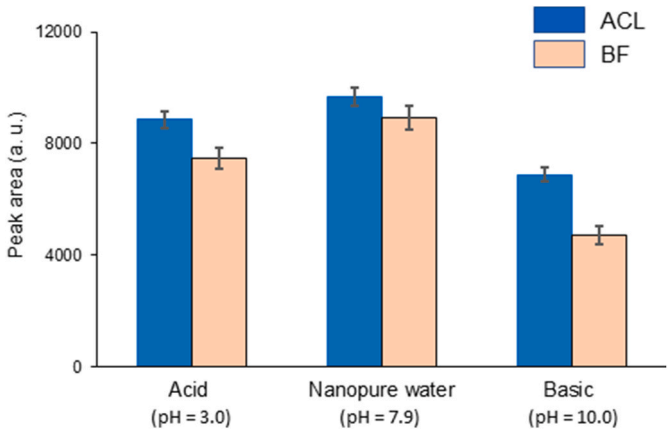

Fig. 2. Peak areas of ACL and BF in nanopure water (pH 7.9), and under acid (pH 3.0) and basic (pH 10.0) conditions. For other experimental details, see text.

corresponding chromatograms.

3.3. Effect of the sample matrix

One of the most relevant features of IT-SPME is that, when applied to the analysis of organic pollutants in environmental waters, the off-line sample treatment required is significantly reduced with respect to other forms of (micro)extraction, and in most instances only a filtration of the sample before loading it into the extractive capillary is necessary. During our study, we observed that the chromatograms obtained for filtered solutions showed different additional peaks, one of them eluting at a retention time close to BF. The presence of those minor peaks could be related to the materials of the filters as they were also observed for blanks (nanopure water). In order to avoid the presence of such peaks, the direct introduction of untreated water samples was the option selected for the analysis of real waters, assuming that possible particulate matter of the samples would be flushed out of the IT-SPME capillary with the 25 μL-portion of nanopure water used during the washing step.

Three different types of water were tested, seawater (pH = 7.1), river water (pH = 7.8) and ditch water collected from an area of intensive agricultural activity (pH = 7.3). None of the tested compounds was found in the water samples. Then, the samples were spiked with the tested herbicides at a concentration of 50 μg/L and immediately processed. At the pHs of the samples, no significant variation in the responses of the analytes were expected with respect to those obtained for the standard solutions, according to the results found in the above section.

The recoveries of the analytes in the spiked samples were calculated with respect to those obtained for standard solutions (also freshly prepared in nanopure water). These values were calculated by comparing the peak areas obtained for the spiked samples with those obtained for standard solutions containing the same concentration of herbicide. The results obtained are listed in Table 2. This table shows that for the parent herbicides the recoveries ranged from 89% to 97% and were not dependent on the sample matrix. It was concluded that the effect of matrix on the analytical responses was negligible. In all cases, the relative standard deviations were <4% (n = 3).

To evaluate the effect of the sample matrix, the samples were spiked with the tested herbicides and kept in glass flasks under ambient conditions (ambient temperature and natural light). The study was simultaneously performed for the three matrices, so that the samples were exposed to identical conditions. Aliquots of the samples were removed from the vials at different times and analysed directly (without filtration) with the proposed method. Examples of the chromatograms obtained for the three matrices at different times are shown in Fig. 3. As for the standard solutions, the identification of BFA in some of the samples was possible considering the similarity between the spectra of the suspected peak and that registered from a standard solution of BFA, as well as the concordance of the corresponding retention times. Additionally, the real samples were fortified with BFA for more reliable identification. The similarity between the spectra registered for the peak attributed to BFA in the samples and for a standard solution of this compound can be seen in Fig. 3. As an illustrative example, the concordance between the retention times of the peaks of suspected BFA in seawater spiked with BF, the same sample spiked with BFA and a standard solution of BFA is shown in Fig. S4B.

The chromatograms obtained revealed that the sample matrix had a

Table 2
Extraction efficiency found for the spiked water samples (n = 3).

Type of water	Extraction recovery, (%)	
	ACL	BF
Ditch	94 ± 3	90 ± 2
River	93 ± 3	97 ± 4
Sea	90 ± 3	89 ± 3

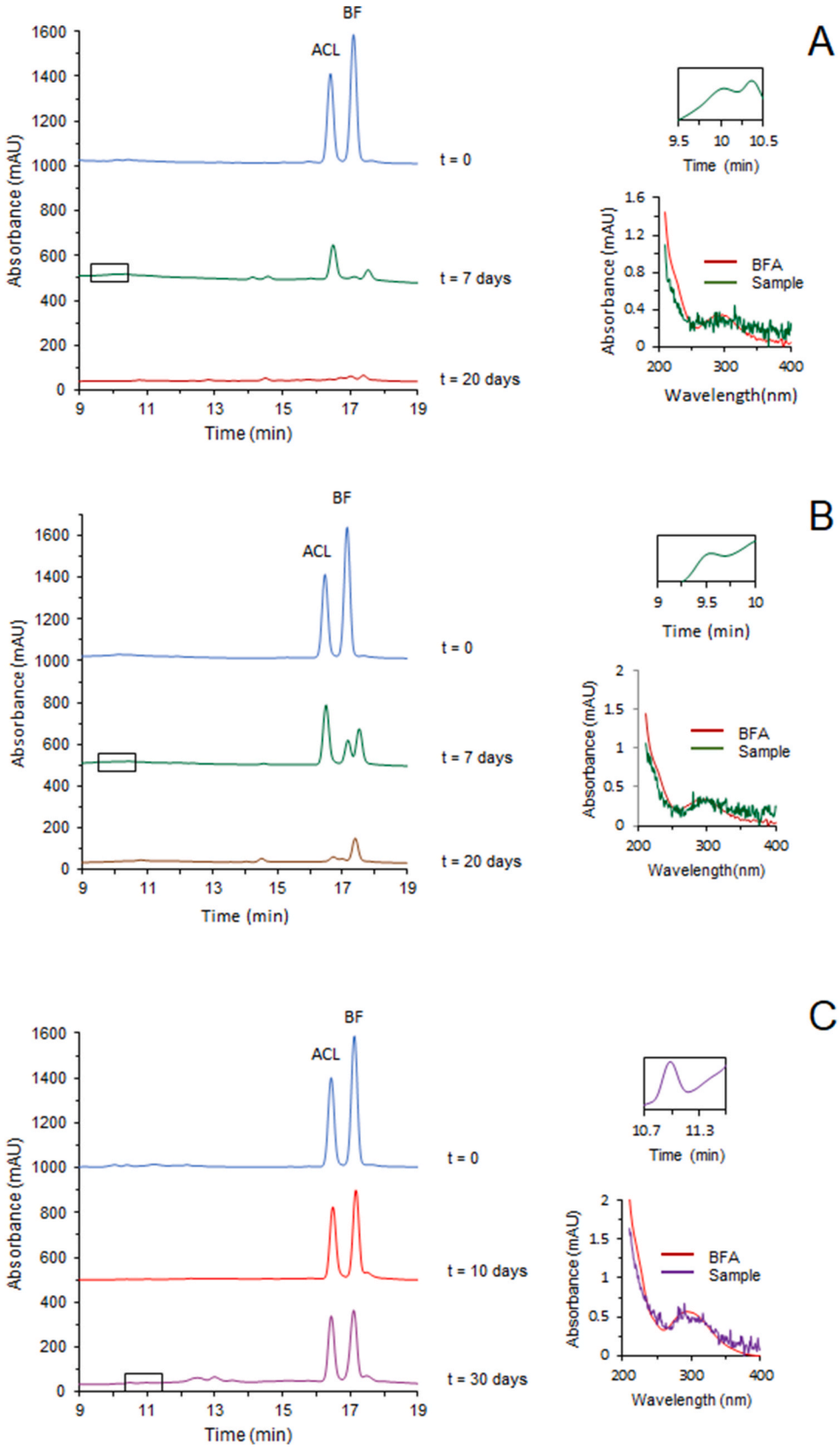

Fig. 3. Chromatograms obtained for real water samples spiked with ACL and BF (50 μg/L each) kept at ambient conditions: (A) ditch water freshly prepared, and 7 and 20 days after, (B) river water freshly prepared, and 7 and 20 days after, and (C) seawater freshly prepared, and 10 and 30 days after. Insert: zoomed area for the peak identified as BFA, and comparison of the spectra of such peak and the spectrum of a standard solution of BFA. For other experimental conditions, see text.

significant impact on the degradation of both analytes, which was much faster in the ditch and river waters. In some of the chromatograms obtained for the samples spiked with ACL, an additional peak was observed at 14.4 min (Fig. 4A); the area of this peak increased with the time. No similar peak was detected during the study with standard solutions. The peak of BFA was observed in some samples spiked with BF, but its intensity was much lower than an additional the peak observed at 17.3 min (Fig. 4B). The intensity of this unknown peak was much higher in river water that in the other two matrices. To the best of our knowledge, apart from BFA, aminobiphenox is the only degradation that has been reported to be present in environmental waters (Reemtsma et al., 2013). However, with the CapLC UV(DAD) system used along the study, we could not confirm that the peak observed at 17.3 in corresponded to this compound. It has to be noted that, besides the peaks of the analytes and their degradation products, the chromatograms also showed other minor peaks, especially in those corresponding to the river samples; the number and intensity of those peaks increased with the time of exposure of the samples. The analysis of unspiked water samples confirmed that such peaks were originated by substances present in the samples.

The percentages of herbicides remaining in the spiked environmental water samples were calculated as explained for the solutions prepared in nanopure water. The results are depicted in Fig. 5. As observed in this figure, the degradation of the two herbicides in ditch and river water was much faster than in seawater. The concentration of ACL was below its LOD after 15 days in ditch water and after 20 days in river water (Fig. 5A). The degradation of ACL in seawater was slower, and about 71% of the initial ACL was found in this samples after 40 days, vs the 87% present in nanopure water exposed to similar conditions. In the three matrices, the variation of the percentages of undergraded ACL vs time fitted to a pseudo-first order degradation mechanism, as it can be seen in Table 1. According to the slopes of the corresponding equations, the degradation in dich and in river samples was around 8 times and 5 times faster than the degradation in standard solutions, respectively. The equations of Table 1 were used to estimate the $t_{1/2}$ for this compound, being the values obtained 5.43 days and 8.81 days, for the ditch and river water samples, respectively. The stability of ACL in seawater was slightly lower than that found in nanopure water, being $t_{1/2}$ 53.75 days.

The sample matrix also had a considerable impact of the degradation of BF (Fig. 5B). The degradation of this herbicide was much faster in the ditch and river samples. In fact, the variation of the peak intensity with time during the first days of the study was nearly linear (Table 1). The estimated $t_{1/2}$ were 2.18 days and 4.31 days, in the ditch and river waters, respectively. Neither BF nor BFA were detected in the chromatogram obtained for the river sample spiked with BF after 40 days. Interestingly, BF was clearly stabilized in seawater, being the degradation velocity constant about half of the value found for solutions prepared in nanopure water (Table 1). Similar behavior has been reported for the sulfonyl urea herbicide tribenuron-methyl (Bottaro et al., 2008; Serra-Mora et al., 2020a). The results of Fig. 5B are consistent with the signals measured for BFA, which increased with the time of exposure in seawater. However, the peak of BFA could not be detected after 10 days in the ditch water sample, and after 20 days in the river sample. This indicates that BFA also suffered a faster degradation in these matrices. In all the chromatograms obtained for river samples, the intensity of the degradation compound eluted at 17.3 min was much higher than the peak of BFA.

The above findings support the importance of including the degradation products of herbicides to get a better picture of their real impact on ecosystems. The products to be targeted should be selected according to the sample matrix. The information derived from this type of assays can be considered of interest in biomonitoring studies, and to elucidate the final fate of these pollutants (-). The development of analytical methods for degradation compounds can be also useful to investigate the efficiency of treatments applied to water (Ribeiro et al., 2015).

4. Conclusions

In the present work we have developed a method for monitoring the concentration of the diphenyl-ether herbicides ACL and BF, as well as BFA, the main degradation product of BF. The method has been applied to study the effect of different variables on the degradation of the parent herbicides. In nanopure water, ACL was relatively unaffected by the temperature and natural light, at least up to 40 days. In contrast, increasing the temperature an exposing the solution to the light accelerated significantly the degradation BF. As regards environmental waters spiked with the herbicides, the type of sample was the main parameter affecting the degradation of sample matrix had a parameter affecting the stability of the tested herbicides. The degradation of both compounds was drastically accelerated in ditch and river and stabilized in seawater, which means that both ACL and BF are more persistent in the later matrix. Although a significant degradation was also observed for BFA, this compound could be detected after the dissipation of the parent herbicide BF. In some of the samples unknown degradation products were also observed for ACL and BF. These results stress the need for analytical tools applicable to the degradation products of herbicides, being IT-SPME coupled to capLC a useful option.

Credit author statement

C. E. Rodríguez-Palma: Conceptualization, Methodology, Data curation, Formal analysis, Funding acquisition, Investigation, Validation, Visualization, Writing – review & editing. R. Herráez-Hernández: Conceptualization, Methodology, Data curation, Formal analysis, Funding acquisition, Investigation, Validation, Visualization, Writing. P. Campíns-Falcó;: Conceptualization, Methodology, Data curation,

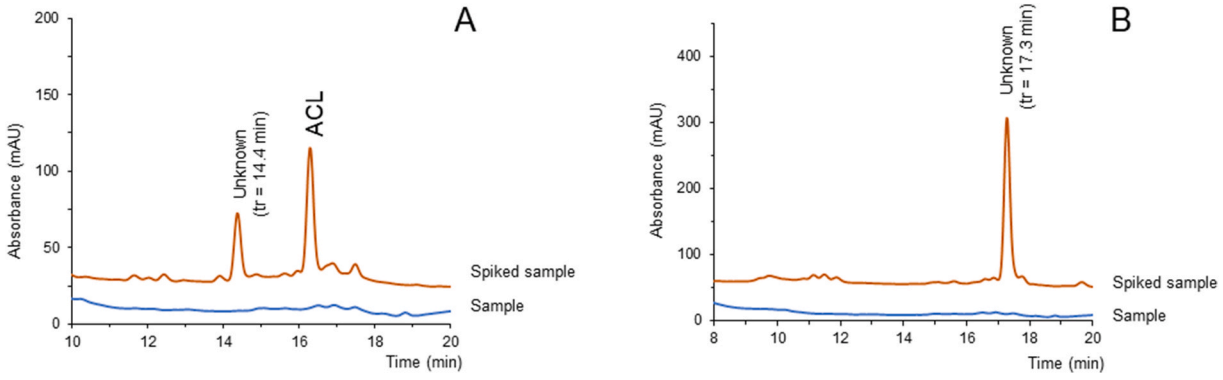

Fig. 4. Chromatograms obtained for a river water sample, and for the same sample 40 days after being spiked with (A) ACL and (B) BF. Concentration of herbicide in the spiked samples, 50 μg/L. For other experimental conditions, see text.

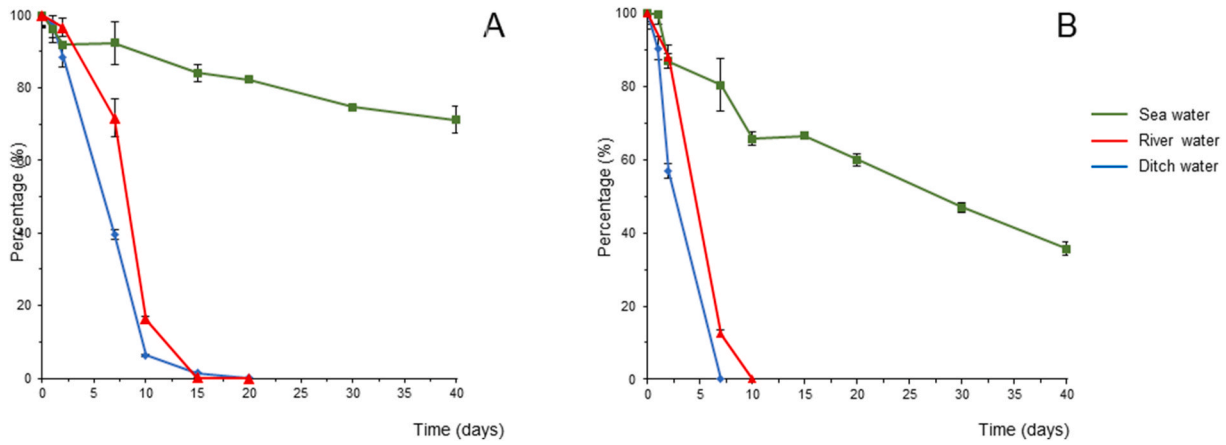

Fig. 5. Variation of the percentage of undegraded analytes under ambient conditions (ambient temperature and natural sunlight) for the three environmental waters tested: (A) ACL, (B) BF. Initial concentration of the analytes, 50 μg/L. For other experimental conditions, see text.

Formal analysis, Funding acquisition, Investigation, Validation, Visualization, Supervision, Project administration, Writing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139238.

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