

Simultaneous determination of selected endocrine disruptors (pesticides, phenols and phthalates) in water by in-field solid-phase extraction (SPE) using the prototype PROFEXS followed by on-line SPE (PROSPEKT) and analysis by liquid chromatography-atmospheric pressure chemical ionisation-mass spectrometry.

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Abstract

In this study, a new procedure, based on on-line solid-phase extraction (SPE) and analysis by liquid-chromatography-atmospheric pressure chemical ionization-mass spectrometry (LC-APCI-MS), has been developed for the simultaneous, multianalyte determination of 21 selected pesticides, phenols and phthalates in water. SPE was carried out on polymeric PLRP-s cartridges by percolating 20 mL-samples. For sample preconcentration, the performance of a prototype programmable field extraction system (PROFEXS) was evaluated against the commercial laboratory bench Prospekt system used for method development. The Profexs is designed for the automated on-site sampling, SPE preconcentration, and storage of up to 16 samples in SPE cartridges. These cartridges are further eluted and on-line analyzed with the Prospekt coupled to the chromatographic system. In the optimized method, where completely on-line SPE-LC-MS analysis of the samples is carried out with the Prospekt in the laboratory, detection limits lower than 100 ng/L, and satisfactory precision (relative standard deviations < 25%) and accuracies (recovery percentages > 75%) were obtained for most investigated compounds from the analysis of spiked Milli-Q water. The extraction efficiency achieved with the Profexs was comparable to that of the Prospekt for most compounds and somewhat lower for the most apolar analytes, probably due to adsorption to the pump filters. The completely on-line optimized method was applied to the analysis of surface water, ground water and drinking water from a waterworks in Barcelona. Some pesticides and phenols were found in both surface water and groundwater at ng/L or µg/L levels, but not in the final drinking water. Di(2-ethylhexyl)phthalate (DEHP) was present in all samples investigated, included blanks. To the author's knowledge, this is the first work describing the application of a fully automated on-line SPE-LC-MS method to the simultaneous analysis of pesticides, phenols and phthalates in water and the second one

that examines the possibilities of the prototype Profexs for automated on-site SPE preconcentration of organic pollutants from water samples.

Keywords: pesticides, phenols, phthalates, water, in-field sampling, on-line analysis

1. Introduction

The widespread contamination of the aquatic environment, provoked by the massive use of, mostly anthropogenic, substances in different application areas such as industry and agriculture, has forced the adoption of restrictive, legislative measures to protect the environment against pollution. In the recently adopted Decision No 2455/2001/EC [i], which amends Directive 2000/60/EC [ii], a list of 33 priority substances in the field of water policy has been established. This list includes substances or groups of substances toxic, persistent, and liable to bio-accumulate, such as pesticides, and, for the first time in the field water policy, endocrine disrupters, such as nonylphenols. Endocrine disrupters are substances, either natural or synthetic, that alter the normal functioning of the endocrine system and cause important reproductive and developmental alterations, such as feminization and decreased fertility [iii]. The number of substances considered as endocrine disrupters increases hand by hand with the volume of research carried out in this field, and, among them, merit special attention, because of their extensive use, their ubiquity, and their inclusion in the various lists of priority pollutants established in the EU Directives [i,iv -vii], the groups of pesticides, phthalates, and phenolic compounds.

Due to the polarity and thermolability of many of these compounds, liquid chromatography coupled to mass spectrometry is probably the most favorable technique for their analysis. This technique provides both high sensitivity and selectivity. However, due to the very low levels at which these compounds are usually present in the environment (ppb and

ppt), and to the complexity of the environmental matrices, preconcentration of the samples previous to LC-MS analysis is normally required.

Nowadays, the technique most widely used for isolation and preconcentration of pesticides, phenols, and phthalates, and most organic pollutants, from environmental samples is solid-phase extraction (SPE), due to some well-known advantages [viii].

When performed on-line with the analysis, SPE presents additional advantages, such as automatization, time and labor saving, and improved reproducibility, accuracy, and sensitivity [ix].

These advantages of the on-line approaches have been in fact exploited for the analysis of pesticides [x -xv] and phenols [xvi,xvii] in water. However, they also present certain drawbacks as compared to off-line procedures, such as the unavailability of a final extract for parallel determinations, and the restrictions imposed, in terms of throughput, by the time necessary for the LC analysis or for the preconcentration step in the case of large sample volumes. This last aspect may be particularly problematic in extensive monitoring programs where a large number of both samples and compound classes are to be analyzed, especially if the analytes are unstable and the addition of preservatives to the sample is not recommended because they may alter its composition.

This problem, as well as that related to the transport of the water samples from the field site to the laboratory, common to both off-line and on-line methods, could be overcome by on-site SPE preconcentration. On-site SPE preconcentration avoids possible breakage in transit, facilitates transport and storage, and reduces the possibility of changes in the sample, it being unnecessary to perform the analysis immediately; and, if further desorption of the analytes is performed on-line with the analysis, the main benefits of the on-line SPE procedures remain basically the same.

A system of these characteristics, called SAMOS (System for the Automated Monitoring of Organic pollutants in Surface water) was devised a few years ago for the on-site, completely automated analysis of organic pollutants in surface water. This system, consisting of a sample preparation unit (Prospekt), a liquid chromatograph, and a diode array detector, was successfully applied to the determination of pesticides in river water [xviii]. However, due to its design, energy consumption, number of mobile parts, and complexity, the SAMOS cannot be used as a tool for field sampling on regular basis.

Very recently, a new prototype for in field sampling of water, called Profexs (programmable field extraction system), has been developed in the frame of the European Union project “On-line Waste Water Analysis” (OWWA), which was part of the so-called Waste Water Cluster (WWC) [xix]. This prototype was built by the Mechanical Workshop of the Free Universiteit of Amsterdam (The Netherlands) in cooperation with the manufacturer of the programmable on-line solid phase extraction technique PROSPEKT (Spark Holland, Emmen, The Netherlands). The current design of the Profexs allows sampling, preconcentration and storage of up to sixteen samples in SPE cartridges. The system is robust, easy to manipulate, can handle small or large sample volumes, and has low energy consumption. After sampling, the tray containing the cartridges is removed manually, transported in a cooled container box, if necessary, to the central laboratory, and placed in a commercial system, such as the Prospekt-2 (Spark Holland, Emmen, The Netherlands), for further on-line desorption and analysis.

The Profexs has been previously tested and validated for the analysis of benzene- and naphthalene-sulfonates in environmental sewage samples [xx]. However, to our knowledge,

neither the validation of this system for the analysis of other classes of pollutants, nor the simultaneous determination of such a variety of pesticides classes, phenols and di(2-ethylhexyl)phthalate (DEHP), by means of on-line SPE-LC-MS, has ever been reported in the literature.

In this context, the main objectives of this work were as follows: (i) to develop a completely automated on-line-SPE-LC-MS method for the simultaneous multianalyte determination of pesticides, phenols and DEHP in environmental waters, (ii) to evaluate the performance of the prototype field sampler Profexs for the SPE preconcentration of the selected target analytes from water at remote locations, and (iii) to apply the developed method to selected environmental water samples.

As target analytes (see Table 1), different compounds representative of diverse classes of pesticides (triazines, organophosphates, phenylureas, and acetanilides, besides propanil and trifluralin), phenols (chlorinated and alkyl-derivatives) and DEHP, were selected based on the extent of their use, ubiquity and consideration as priority pollutants.

Table 1

2. Experimental

2.1. Chemicals and reagents

The reference substances alachlor, chlorpyrifos, diuron, linuron, dimethoate, acetochlor and propazine were purchased from Riedel-de Haën (Seelze, Germany), atrazine and simazine from Novartis (Basel, Switzerland), chlorfenvinphos, isoproturon, propanil and 4-chloro-2-methylphenol from Ehrenstorfer (Augsburg, Germany), DEHP, diazinon, 4-tert-

butylphenol and fluometuron from Supelco (Bellefonte, PA, USA), nonylphenols (mix of isomers) and para-tert-octylphenol from Aldrich Chemie GmbH & Co KG (Steinheim, Germany), trifluralin from Chem Service (West Chester, PA, USA), 2,4-dichlorophenol and 4-chloro-3-methylphenol from Merck (Darmstadt, Germany), and phenol from Sigma Chemical Co (St. Louis, MO, USA).

HPLC-grade water, acetonitrile and methanol were obtained from Merck (Darmstadt, Germany), and PA-grade acetic acid from Panreac (Barcelona, Spain).

Stock standard solutions for each of the analytes were prepared at 1000 mg/L in methanol. Working solutions of mixtures of all the analytes were prepared at various concentrations by appropriate dilution of the stock solutions in methanol and subsequent spiking of Milli-Q water. The final aqueous standard solutions did not contain more than 0.5 % of methanol. All standard solutions were stored at $-20\text{ }^{\circ}\text{C}$ in the dark.

2.2. Equipment

Preconcentration of the samples was performed on two two systems:

- the commercial automated sample preparation system Prospekt (Spark Holland, The Netherlands), consisting of a cartridge exchange module, a solvent delivery unit and a low-pressure six-port valve, which is connected on-line with the chromatographic system

- the prototype field sampler and extraction system Profexs, equipped with an external LC pump model 306 (from Gilson, Villiers-le-Bel, France) for dispensing of solvents and water samples through the SPE cartridges, and with a small microprocessor for time control of all sampling/extraction events.

The heart of the sampler is a stainless-steel 96-well micro-titre plate (with the same dimensions of those commercially available) that can hold an equivalent amount of SPE cartridges. Both SPE- and membrane-based procedures were considered at the beginning of

the OWWA project, but SPE was finally selected because of its expected greater robustness. The Profexs is basically made of stainless steel, instead of the more frequently used polymeric materials, to support the high pressures (*ca.* 2-8 MPa) applied to avoid clogging of the cartridges and/or the connecting tubing during sampling, and to allow leak-tight connections.

Samples were preconcentrated on disposable PLRP-S cartridges (10 x 2 mm id), packed with 20 mg of a styrene-divinylbenzene copolymer (Polymer Laboratories, Church Stretton, UK) with a 100 Å pore size and 20 µm particles, supplied by Spark Holland (The Netherlands). The cartridges were used only once.

The chromatographic system consisted of an HP1100 autosampler, with the volume injection set to 20 µL, and an HP1100 LC pump connected in series with a diode array detector (DAD) model HP1100 and a mass spectrometer HP1100 MSD API-ES equipped with an orthogonal interface, all from Hewlett-Packard (Palo Alto, CA. USA). Separation was achieved on a LiChrospher 100 RP-18 analytical column (250 x 4 mm, 5 µm) preceded by a guard column (4 x 4 mm, 5 µm) of the same packing material from Merck (Darmstadt, Germany).

2.3. Sample preconcentration

As previously indicated, preconcentration of the samples was carried out with two instruments: the commercial system Prospekt, and the prototype Profexs.

In the optimized method, 20 mL of the water sample, spiked with the internal standards propazine and fluometuron at 100 ng/L, were percolated at 4 mL/min through a PLRP-s cartridge previously conditioned with 6 mL of acetonitrile and 4 mL of LC-grade water (flow-rate 2mL/min). Both propazine and fluometuron were selected as internal standards, because they are not used in Spain. After sample loading and prior to elution, 4 mL of LC-grade water were passed at a flow-rate of 2 mL/min to complete transfer of the sample

and wash the cartridge. Elution of the trapped compounds to the LC column was carried out with the chromatographic mobile phase.

When using the Prospekt for sample preconcentration, all steps of the sample preparation procedure were programmed on, and automatically controlled by, the Prospekt software, so that preconcentration of the samples was carried out on-line with the analysis by LC-APCI-MS in a completely automated, unattended way. When using the Profexs for sample preconcentration, this system was employed for cartridge conditioning, sample loading and washing of the cartridges, and further elution of the trapped compounds was performed with the Prospekt on-line with the analysis by LC-APCI-MS.

2.4. LC-DAD-MS analysis

Chromatographic separation of the target analytes was accomplished on a LiChrospher 100 RP-18 column using the gradient elution shown in Table 2. Diode array detection was performed at 215 nm, wavelength at which all analytes exhibit some absorption, to evidence eventual ion suppression effects in the mass spectrometer.

Table 2

In the optimized method, MS detection was performed with an APCI interface operating in the positive ionization (PI) mode for determination of DEHP and all pesticides except fluometuron, linuron and propanil, and in the negative ionization (NI) mode for determination of the remaining pesticides and of phenols. The various parameters influencing the MS signal in both modes of ionization were optimized by flow-injection analysis of standard solutions of the individual compounds in the scan mode (m/z 80-600), and were as follows: nebulizer gas pressure, 414 KPa; drying gas flow, 4 L/min; drying gas temperature,

300 °C; vaporizer temperature, 350 °C; capillary voltage, 4000 V, and corona current, 6 and 20 μ A in the PI and the NI modes, respectively. Nitrogen was used as both drying and nebulizing gas. Tables 3 and 4 show the time scheduled SIM conditions used in the analysis of the target analytes in the NI and the PI modes, respectively. The fragmentor voltage selected for each analyte was optimized in order to obtain moderate fragmentation while maximum sensitivity. Under the selected conditions, between 1 and 3 predominant ions are observed for each compound. In most instances, the base peak, used for quantitation, corresponded to the singly charged molecular ion, while the other, less abundant fragment ions were used for confirmation.

Table 3

Table 4

2.5. Environmental samples

Samples of river water, ground water and drinking water were collected at the Sant Joan Despi's waterworks. This plant supplies drinking water to a great part of Barcelona city and has as main source for abstraction of drinking water the Llobregat river that flows nearby, and, as second source, groundwater, for those events where the quality and/or the quantity of the surface water is poor. Samples were collected in Pyrex borosilicate amber glass containers and were filtered through a nylon filter (0.45 μ m pore size) prior to extraction. The analyses were made the same day of sample collection (February 4th, 2002).

3. Results and discussion

3.1. Breakthrough volumes

For selection of the optimal sample volume, 20 and 50 mL of Milli-Q water spiked at 1 µg/L with the target analytes were percolated through PLRP-s cartridges and analyzed by LC-APCI-MS. This experiment was performed in triplicate using the Prospekt system. Figure 1 shows the recoveries of extraction obtained for the target compounds when using both sample volumes. The recoveries were calculated from the peak areas obtained for each analyte in the analysis of the spiked water samples as percentages of the peak areas obtained from the direct injection (20 µL) of equivalent amounts of the standard mixtures in methanol. As shown in Figure 1, higher extraction recoveries were in general obtained when preconcentrating 20 mL of sample. Appreciably better recoveries through the extraction of 50 mL of sample were obtained only in the case of 4-chloro-2-methylphenol, 2,4-dichlorophenol and nonylphenols. Nevertheless, these compounds presented acceptable recoveries with 20 mL-extraction (93, 79 and 74 %, respectively), and so, this volume was finally selected for preconcentration.

Figure 1

3.2. Analysis by LC-DAD-APCI-MS

Different mobile phases (acetonitrile-water and methanol-water), gradients, and pHs (3.5, 4, and 7) were tested for both improved chromatographic separation and MS ionization efficiency. However, even after thorough optimization of the mobile phase, baseline

resolution of all the investigated compounds could not be accomplished. Under the selected conditions the analysis time is 65 min.

For MS detection, two different interfaces, ESI and APCI, were evaluated. The LC-MS analysis of the compounds studied in this work has been addressed in numerous occasions in the literature, and therefore there is abundant information about their ionization properties in the different LC-MS interfaces available. However, due to the variety of compound classes whose determination is attempted here, and to the differences observed among instruments, especially with regards to the formation of the base peak (single-charged molecular ions, adducts, clusters, etc.), the suitability of both ESI and APCI, in both ionization modes (NI and PI), was experimentally examined. After optimization of the various parameters influencing the MS signal in each interface and ionization modes, it was found that all target compounds could be determined with the APCI interface, in either the NI mode or the PI mode. With the ESI interface, chlorpyrifos, trifluralin, and DEHP, because of their non-polar character (see log Kow in Table 1), and 2,4-dichlorophenol, could not be detected in neither ionization mode. In addition, some of the compounds that could be determined with the ESI interface in the PI mode, namely, dimethoate, isoproturon, diuron, acetochlor, alachlor, and chlorfenvinphos, presented as base peak, adducts of the corresponding analyte molecule with one sodium atom ($[M+Na]^+$), which in the quantification process normally lead to less reproducible results and to calibration curves with poor correlation coefficients, as compared to those calculated using the protonated molecular ion or fragments of this as the base peak.

Therefore, in the optimized method, APCI in the PI mode was used for determination of dimethoate, simazine, atrazine, isoproturon, diuron, propazine, alachlor, acetochlor,

chlorfenvinphos, diazinon, chlorpyrifos, trifluralin and DEHP, (see Figure 2), and the same interface in the NI mode was used for determination of phenol, fluometuron, 4-chloro-3-methylphenol, 4-chloro-2-methylphenol, 2,4-dichlorophenol, propanil, 4-tert-butylphenol, linuron, para-tert-octylphenol and nonylphenols (see Figure 3). As shown in Tables 3 and 4, for each compound between 1 and 3 characteristic ions, the most abundant for quantitation purposes and the others for confirmation, were recorded in the SIM mode.

Figure 2

Figure 3

3.3. Method performance

The performance of the fully automated on-line method developed with the Prospekt system was evaluated through determination of the linearity, sensitivity, repeatability, and accuracy. The HP LC-MSD ChemStation software application was used to assist in the quantitation, based on peak areas, of standards, samples, and blanks.

Calibration graphs were constructed, using a least-square linear regression analysis, from the on-line SPE and analysis by LC-APCI-MS of 20 mL aliquots of Milli-Q water spiked with the analytes at concentrations ranging between 1 ng/L and 10 µg/L. For quantitation in the PI and the NI modes, propazine and fluometuron (100 ng/L) were used as internal standards, respectively. The curves were linear, with correlation coefficients (R^2) higher than 0.99 for all compounds except nonylphenols ($R^2=0.98$), over the concentration ranges indicated in Table 5.

Method detection limits (DLs) were experimentally calculated from the analysis of Milli-Q water spiked at serially diluted concentrations until the signal to noise ratio reached a

value of three. DLs lower than 100 ng/L, which is the maximum admissible concentration set for pesticides in the directive 98/83/EC on the quality of water intended for human consumption [vii], were achieved for 16 of the 21 compounds investigated (see Table 5). DLs higher than 100 ng/L were obtained for acetochlor, chlorpyrifos, linuron, phenol, and 4-tert-butylphenol; however, only chlorpyrifos is included in the current list of priority substances established in the Directive 2455/2001/EC [i]. The limit of detection for DEHP is not provided because, due to their ubiquitous presence (in the ng/L or even µg/L range), it was impossible to find DEHP-free blank samples.

Table 5

The overall method repeatability and accuracy were determined from the analysis of three replicates of Milli-Q water spiked with a standard mixture of the analytes at 1 µg/L. Both the repeatability, with relative standard deviations (RSD) lower than 30% for all compounds except phenol, and the accuracy of the method, with recovery percentages higher than 70% for all compounds except phenol, 4-chloro-3-methylphenol, propanil, and linuron, were considered satisfactory (see Table 5). Precision and recovery values somewhat worse than those found in the on-line analysis of other classes of organic pollutants, such as estrogens [xxi], could have been obtained due to the rapid degradation of some of the compounds investigated. Thus, according with some studies, the half-life of propanil under real conditions is 1.2 days [xxii], whereas that of alachlor under simulated environmental conditions is 84 min [xxiii].

3.4. Profexs vs. Prospekt

After optimization of the fully automated on-line method to be performed with the Prospekt, the performance of the prototype Profexs against the Prospekt was evaluated by carrying out similar, parallel experiments with both preconcentration systems. For this purpose, 20 mL-aliquots of spiked (1 µg/L) Milli-Q water were preconcentrated using, on the one hand, the Prospekt for a totally on-line SPE-LC-MS analysis, and, on the other hand, the Profexs, for cartridge activation, sample loading, and washing of the cartridges, followed by on-line desorption and analysis using the Prospekt.

As shown in Figure 4, the extraction efficiencies achieved with both systems were comparable for most compounds. However, some bias was observed in the results obtained for the most apolar compounds analyzed in the PI mode (trifluralin, chlorpyrifos, chlorfenvinphos and DEHP) and in the NI mode (para-tert-octylphenol and nonylphenols). For these compounds, consistently lower recoveries were obtained with the Profexs. Provided that these compounds, especially the alkylphenols, are not known to be particularly unstable, their eventual adsorption to the stainless steel tubing of the Profexs, and/or, more probably, to the pumps filters attached to the Profexs, is hypothesized as the source of the observed inaccuracy.

Figure 4

On the other hand, the recoveries obtained for phenol were 0% with the Profexs and 41% with the Prospekt. Phenol is the first eluting compound in the chromatographic separation and, according with the octanol-water coefficients listed in Table 1, the second most polar compound, after dimethoate, of all the investigated analytes. Based on this, it can be assumed that, even with a low sample preconcentration volume of 20 mL, phenol experiments breakthrough, which explains the 41% recovery obtained with the Prospekt.

According with the vapor pressure values provided for each compound in Table 1, phenol is also the most volatile compound of all investigated analytes. As, when using the Profexs, the samples are first preconcentrated, and then, on-line elution and analysis of the trapped compounds is carried out some time later, evaporation of volatile compounds, such as phenol, could have occurred, even though, from extraction to analysis, the time passed never exceeded 24 hours.

3.5. Environmental samples

Samples of river water, ground water and drinking water from the Sant Joan Despi's waterworks were spiked with propazine and fluometuron at 100 ng/L and analyzed with the Prospekt system following the method developed. As shown in Table 6, simazine, atrazine, isoproturon, alachlor, diazinon, DEHP, para-tert-octylphenol, and nonylphenols, were found to be present in river water and/or ground water. All these compounds, except diazinon, are included in the list of priority substances in the field of water policy established in the Directive 2455/2001/EC [i]. The total pesticide concentration did not exceed in any case 5 µg/L, which is the maximum admissible concentration established in the Directive 75/440/EC for surface waters subjected to intensive physical and chemical treatment [iv]. Nonylphenols, para-tert-octylphenol, and DEHP were found in both river water and ground water at ng/L and µg/L levels. However, the sum of the concentrations obtained for the phenolic compounds investigated was below the phenol index limit of 100 µg/L set in the Directive 75/440/EC for the type of waters considered in this study. For DEHP no concentration limit in water has been established yet. In the final drinking water, none of the compounds investigated, with the exception of DEHP (it is even present in the blank samples), were found. These data demonstrate the good removal efficiency of the water treatment process applied, which is

based on prechlorination, sand filtration, ozonization, activated carbon filtration, and chlorination.

Table 6

4. Conclusions

The presence of pesticides, phthalates and phenols in the aquatic environment is regulated through various European Union Directives and therefore requires regular monitoring. In this work, a completely automated method, based on on-line SPE-LC-APCI-MS analysis, has been developed for the simultaneous, multianalyte determination of some selected pesticides, phthalates and phenols. With this method most of the selected compounds can be determined with acceptable precision and accuracy, according to the method performance evaluation carried out with spiked Milli-Q water, at concentrations lower than 100 ng/L, and in up to 16 samples in a completely automated, unattended way. However, as analyses are carried out in the laboratory using the commercial bench Prospekt system, samples still have to be collected and transported to the laboratory, with the corresponding risk of breakage in transit, and of changes in the sample composition. To minimize these risks, an alternative protocol based on the use of the prototype in-field sampler Profexs, for sample SPE preconcentration at remote locations, followed by on-line desorption and analysis using the Prospekt, has been proposed and tested. This analytical scheme facilitates transport and storage of the samples preconcentrated in the SPE cartridges, eliminates the need for carrying out the analyses immediately after collection, and yet, exploits the benefits of on-line protocols regarding minimal manipulation, and improved sensitivity, precision and accuracy. This prototype represents a step forward to the in-field preconcentration of samples. However, its current design still lacks autonomy and easy portability, features that should be addressed

in future, potentially commercial, designs of the system through miniaturization and integration of the currently separate parts. On the other hand, according to the tests carried out, adsorption of some of the most apolar compounds investigated to the Profexs tubing and/or the pump filters could be occurring. This aspect, along with the study of the stability of the analytes in the PLRP-s cartridges for longer periods of time, and the use of tandem mass spectrometry, instead of single mass spectrometry, for improved sensitivity and selectivity, will be subject of future research.

Finally, the application of the method developed to the determination of the target pollutants in various waters from a waterworks demonstrates both the suitability of the optimized technique for the analysis of real samples and the efficiency of the treatment processes applied at the studied waterworks.

Acknowledgements

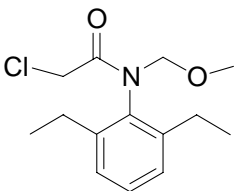
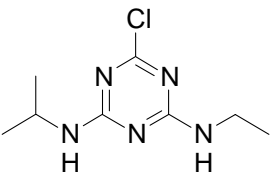
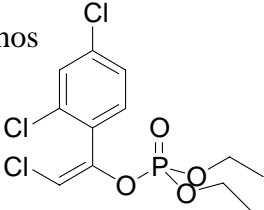
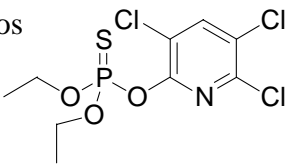
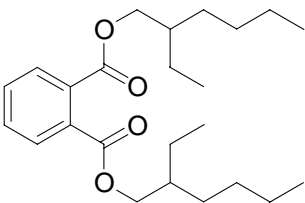
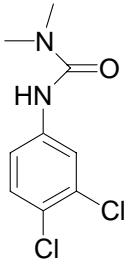
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Table 1. Structure, molecular weight (M.W.), octanol-water partition coefficient (log Kow), and vapor pressure (Pv) of the investigated pesticides, phenols and phthalates.

Compound	Structure	M _w	Log K _{ow} ¹	Vapor Pressure 25°C (mmHg)
Alachlor		269.77	3.52	2.2 E-005
Atrazine		215.69	2.61	2.89 E-007
Chlorfenvinphos		359.58	3.81	4 E-006 (20°C)
Chlorpyrifos		350.59	4.96	2.02 E-005
DEHP		390.57	7.6	1.42 E-007
Diuron		233.1	2.68	6.9 E-008

¹ <http://esc.syrres.com>

Table 1 (cont.)

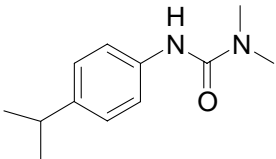
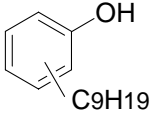
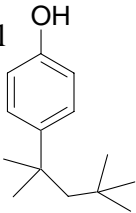
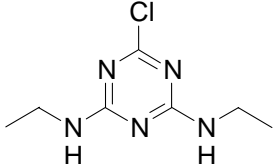
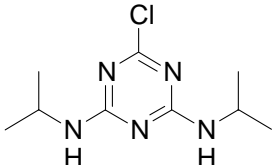
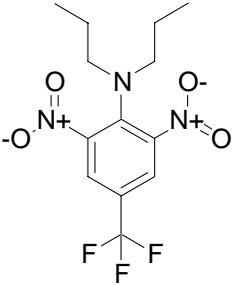
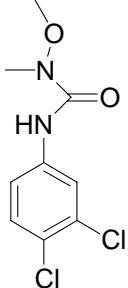
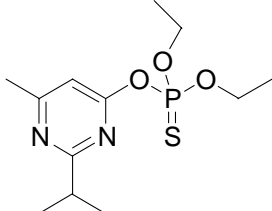
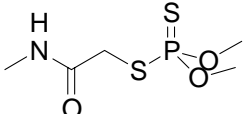
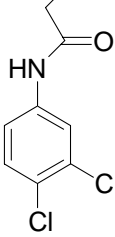
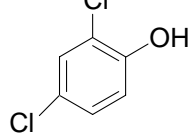
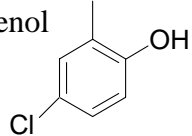
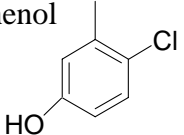
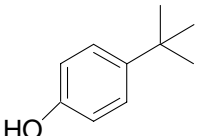
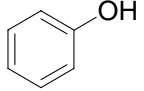
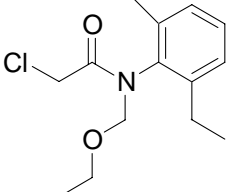
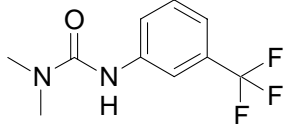
Isoproturon		206.29	2.87	2.47 E-008
Nonylphenols		220.36	5.99	9.416 E-005
Para-tert-octylphenol		206.33	5.28	0.000478
Simazine		201.66	2.18	2.21 E-008
Propazine		229.71	2.93	1.31 E-007
Trifluralin		335.29	5.34	4.58 E-005
Linuron		249.1	3.2	1.43 E-006
Diazinon		304.35	3.81	9.01 E-005

Table 1 (cont.)

Dimethoate		229.26	0.78	8.25 E-006
Propanil		218.08	3.07	9.08 E-006
2,4-dichlorophenol		163	3.06	0.1155
4-chloro-2-methylphenol		142.59	2.63	0.024
4-chloro-3-methylphenol		142.59	3.1	0.05 (20°C)
4-tert-butylphenol		150.22	3.31	0.03807
Phenol		94.114	1.46	0.35
Acetochlor		269.77	3.03	n.a.
Fluometuron		232.21	2.42	9.38 E-007

n.a.: not available

Table 2. LC gradient elution conditions used for separation of selected pesticides, phthalates and phenols in a LiChrospher 100 RP-18 column after on-line SPE. Mobile phase components: A = Acetonitrile, B = Water. Flow rate 1 mL/min.

Time (min)	A%	B%
0	30	70
1	30	70
16	35	65
25	40	60
35	50	50
45	70	30
55	100	0
65	100	0

Table 3. Retention time, time schedule, ion mode, fragmentor voltage and selected masses used for the APCI-PI-MS determination of the studied compounds.

Compound	Time (min)	Window (min)	Polarity	Fragm. (V)	MW	Ions*	m/z (abundance %)
Dimethoate	6.35	0	PI	80	229	[M+H-CH ₃ NH ₂] ⁺ [M+H-C ₂ H ₅ NO] ⁺	199(100) 171(33)
Simazine	12.44		PI	120	201	[M+H] ⁺ [M+1] ⁺ [M+3] ⁺ [M+1-C ₄ H ₈ N] ⁺	230(27) 202(100) 204(28) 132(27)
Atrazine	20.83	16	PI	100	215	[M+1] ⁺ [M+3] ⁺ [M+1-C ₃ H ₆] ⁺	216(100) 218(34) 174(26)
Isoproturon	23.37		PI	80	206	[M+H] ⁺	207(100)
Diuron	24.35		PI	80	232	[M+1] ⁺ [M+3] ⁺	233(100) 235(56)
Propazine	31.21	28	PI	110	229	[M+1] ⁺ [M+3] ⁺ [M+1-C ₃ H ₆] ⁺	230(100) 232(36) 188(22)
Alachlor	42.69		PI	80	269	[M+1-CH ₃ OH] ⁺ [M+1-C ₄ H ₁₁ OCl] ⁺ [M+3-CH ₃ OH] ⁺	238(77) 162(65) 240(27)
Acetochlor	42.75	39	PI	80	269	[M+1-C ₅ H ₁₁ OCl] ⁺ [M+1-C ₂ H ₆ O] ⁺ [M+3-C ₂ H ₆ O] ⁺	148(100) 224(96) 226(51)
Chlorfenvinphos	44.83		PI	80	358	[M+1] ⁺ [M+3] ⁺ [H ₂ PO ₄ C ₄ H ₁₀] ⁺	359(100) 361(97) 155(91)
Diazinon	47.40		PI	120	304	[M+H] ⁺ [M+H-PS(OC ₂ H ₅) ₂] ⁺ [M+H-C ₂ H ₄] ⁺	305(100) 153(35) 277(26)
Trifluralin	52.48		PI	80	335	[M+H] ⁺	336(100)
Chlorpyrifos	52.61		PI	80	349	[M+1] ⁺ [M+3] ⁺ [M+5] ⁺	350(100) 352(70) 354(37)
DEHP	60.59	57	PI	80	390	[M+H] ⁺ [M+H-C ₈ H ₁₆] ⁺ [C ₈ H ₁₇] ⁺	391(100) 279(35) 113(20)

*[M+1]⁺=molecule³⁵Cl+H; [M+3]⁺=molecule³⁷Cl+H; [M+5]⁺=molecule³⁹Cl+H

Table 4. Retention time, time schedule, ion mode, fragmentor voltage and selected masses used for the APCI-NI-MS determination of the studied compounds.

Compound	Time (min)	Window (min)	Polarity	Fragm. (V)	MW	Ions*	<i>m/z</i> abundance (%)
Phenol	7.51	0	NI	100	94	[M-H] ⁻	93(100)
Fluometuron	20.64		NI	120	232	[M-H] ⁻	231(100)
						[M-H-C ₂ H ₇ N] ⁻	186(19)
4-chloro-3-methylphenol	23.95		NI	100	142	[M-1] ⁻	141(100)
						[M+1] ⁻	143(41)
4-chloro-2-methylphenol	26.62		NI	100	142	[M-1] ⁻	141(100)
						[M+1] ⁻	143(62)
2,4-dichlorophenol	27.93		NI	100	162	[M-1] ⁻	161(100)
						[M+1] ⁻	163(52)
Propanil	31.94	30	NI	110	217	[M-1] ⁻	216(100)
						[M+1] ⁻	218(62)
						[M-1-C ₃ H ₄ O] ⁻	160(25)
tert-butylphenol	33.79		NI	100	150	[M-H] ⁻	149(100)
						[M-H-C ₂ H ₅] ⁻	120(38)
Linuron	35.80		NI	110	248	[M-1-C ₃ H ₅ NO ₂] ⁻	160(100)
						[M-1] ⁻	247(32)
						[M+1] ⁻	249(19)
para-tert-octylphenol	49.85	45	NI	100	206	[M-H] ⁻	205(100)
Nonylphenols	52.62		NI	100	220	[M-H] ⁻	219(100)

*[M-1]⁻ = molecule³⁵Cl-H; [M+1]⁻ = molecule³⁷Cl-H;

Table 5. Analytical data corresponding to the on-line SPE and analysis by LC-APCI-MS of selected pesticides, phenols, and phthalates in water.

Compound	Polarity	R^2	Calibration range (ng/L)	DL (ng/L)	RSD	Recovery (%)
Dimethoate	PI	0.9999	10-10000	6.2	0.4	101
Simazine	PI	0.9998	5-10000	2.4	5.0	100
Atrazine	PI	0.9997	5-10000	1.8	1.3	94
Isoproturon	PI	0.9989	10-10000	2.5	3.3	93
Diuron	PI	0.9999	50-10000	11.7	4.5	106
Propazine	PI	-	-	-	0.4	99
Acetochlor	PI	0.9999	500-10000	228.3	1.6	98
Alachlor	PI	0.9995	100-10000	72.4	10.6	87
Chlorfenvinphos	PI	0.9984	50-10000	20.4	1.6	100
Diazinon	PI	0.9998	5-10000	1.7	0.9	100
Chloropyrifos	PI	0.9960	500-10000	150	13.1	95
Trifluralin	PI	0.9997	100-10000	71.4	12.4	113
DEHP	PI	0.9954	500-10000	n.c.	7.3	149
Phenol	NI	0.9904	1000-10000	1216.2	60.6	41
Fluometuron	NI	-	-	-	6.5	84
4-chloro-3-methylphenol	NI	0.9983	50-10000	38.5	14.7	64
4-chloro-2-methylphenol	NI	0.9988	50-10000	34.9	9.4	93
2,4-dichlorophenol	NI	0.9994	100-10000	87.7	1.5	79
Propanil	NI	0.9998	50-10000	16.1	25.7	58
Tert-butylphenol	NI	0.9990	500-10000	264.7	7.9	87
Linuron	NI	0.9999	500-10000	266.7	27.4	64
Para-tert-octylphenol	NI	0.9996	100-10000	65.2	29.1	93
Nonylphenoles	NI	0.9809	100-10000	52.9	28.0	74

n.c.: not calculated

Table 6. Concentrations (ng/L) of selected pesticides, phenols and phthalates found in water samples from Sant Joan Despi waterworks.

	River water (ng/L)	Ground water (ng/L)	Potable water (ng/L)
dimethoate	nd	nd	nd
simazine*	4.2	18.4	nd
atrazine*	2.9	3.7	nd
isoproturon*	239.1	2.7	nd
diuron*	39.1	nd	nd
acetochlor	nd	nd	nd
alachlor*	127.4	nd	nd
chlorfenvinphos*	nd	nd	nd
diazinon	24.3	nd	nd
chloropyrifos*	nd	nd	nd
trifluralin*	nd	nd	nd
DEHP*	1671.0	5661.5	**
4-chloro-3-methylphenol	nd	nd	nd
4-chloro-2-methylphenol	nd	nd	nd
2,4-dichlorophenol	nd	nd	nd
propanil	nd	nd	nd
4-tert-butylphenol	nd	nd	nd
linuron	nd	nd	nd
para-tert-octylphenol*	988.0	374.2	nd
nonylphenols*	3286.0	1612.7	nd

n.d.: non detected, * Included in the list of priority substances in the field of water policy established in Directive 2455/2001/EC, ** present in all samples (included blanks).

Figure captions

Figure 1. Recovery percentages obtained from the on-line SPE of 50 mL (□) and 20 mL (■) of Milli-Q water spiked at 1 µg/L with the target analytes. Preconcentration system: Prospekt. Compounds analysed by (A) LC-APCI(PI)-MS, (B) LC-APCI(NI)-MS.

Figure 2. Total ion current LC-APCI(PI)-MS chromatogram obtained in the SIM mode from the on-line analysis of 20 mL Milli-Q water spiked with a mixture of the analytes at 1 µg/L (propazine used as internal standard at 100 ng/L). Peak identification: dimethoate (1), simazine (2), atrazine (3), isoproturon (4), diuron (5), propazine (6), alachlor (7), acetochlor (8), chlorfenvinphos (9), diazinon (10), trifluralin (11), chlorpyrifos (12), DEHP (13).

Figure 3. Total ion current LC-APCI(NI)-MS chromatogram obtained in the SIM mode from the on-line analysis of 20 mL Milli-Q water spiked with a mixture of the analytes at 1 µg/l (fluometuron used as internal standard at 100 ng/l). Peak identification: phenol (1); fluometuron (2); 4-chloro-3-methylphenol (3); 4-chloro-2-methylphenol (4); 2,4-

dichlorophenol (5); propanil (6); 4-tert-butylphenol (7); linuron (8); para-tert-octylphenol (9); nonylphenols (10).

Figure 4. Comparison between the recoveries of extraction (%) obtained with the Prospekt (□) and the Profexs (■) in the on-line SPE of 20 mL of Milli-Q water spiked at 1µg/L with the target analytes. Compounds analysed by (A) LC-APCI(PI)-MS, (B) LC-APCI(NI)-MS.

