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Monitoring of pesticides in river water using fully automated on-line solid-pase extraction and liquid chromatography with diode array detection with a novel filtration device

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Abstract

A modification of the SAMOS (System for the Automated Monitoring of Organic pollutants in Surface water) has been performed, which includes the attachment of four refrigerated flasks prior to the preconcentration unit, which act as sample reservoirs. River water is driven to the SAMOS, where it is pumped inside the flasks and afterwards it is preconcentrated onto C_{18} precolumns of the Prospekt (Spark Holland, Netherlands), which is coupled on-line with liquid chromatography using the HP1090 equipped with a diode array detector (Hewlett Packard, Waldbron, Germany). The system is programmed in such a way that eight samples are analyzed on each day and it can be operated unattended for at least five days. In order to prevent clogging of the equipment due to the presence of particulate matter, a novel filtering device, comprising a 50-cm stainless steel cylindrical tube with 10 μm pores, connected to a 190-mm diameter glass fiber filter with 1 μm pores was installed. This configuration permitted satisfactory performance, with the unattended monitoring of Llobregat river water and with limits of detection (LODs) of 30–100 ng/l. Terbuthylazine was detected in Llobregat river effluent at a concentration of 13 μg/l. Confirmatory analyses were performed by liquid chromatography–atmospheric pressure chemical ionization–mass spectrometry. This latter technique was also used to screen organophosphorus pesticides in the Llobregat river.

Keywords: Water analysis; Environmental analysis; Pesticides; Automated analysis; On-line solid-phase extraction

1. Introduction

Since 1970, when it was found that the presence of pesticides in environmental waters provided a risk both for human and environmental health, several monitoring programs were launched in order to improve water quality. One of the most important programs created was the Rhine Basin Program, which started in 1977, with the main objective of protecting the waters from the river Rhine from chemical pollutants. The participants of this project, which included the Netherlands, Germany, France, Luxembourg and Switzerland, agreed to install equipment and experimental stations to control and follow the evolution of the quality of the water across the Rhine basin. The specific objectives of the program and their consolidation are described in detail by van Hout and Brinkman [1]. In brief, the program focused on implementing totally automated systems for the on-line monitoring of organic contaminants in water. In the case of pesticides, such monitoring is compulsory, due to the toxicity that

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these compounds cause to the environment, even at low concentrations (0.02 to 10 μg/l in surface waters). Moreover, local accidents may pose a problem to the health of the environment [2] and the surveillance of water quality in a quick and reliable way becomes necessary. In view of the need for automated methods [3], several groups associated with the Rhine Basin Program designed the SAMOS (System for the Automated Monitoring of Organic pollutants in Surface water), which was applied to determine pesticides of different families in surface waters in different European rivers [4,5]. It consists of preconcentrating water samples on solid-phase extraction (SPE) precolumns, which are available in C_{18} or polymeric materials [6]. Using this technique, the percolation of 100 ml of water is enough to efficiently trap compounds of diverse polarities, including pesticides [7], phenols [8] and phenoxy-acids [9]. Automation of SPE is possible both with gas chromatograph (GC) [10] or liquid chromatography (LC) [11]. While the former technique permits excellent selectivity and LODs, the latter can simultaneously analyze pesticides with a larger spectrum of polarities, volatilities and also thermolabile compounds. Moreover, LC-based techniques allow one to trace pesticide conversion products in environmental waters, such as oxo analogues, sulfoxides or their isomers [12,13], which can be more toxic than their parent compounds [14]. The enumeration of the different varieties of the SAMOS is fully described by Brinkman et al. [15]. The SAMOS design is made to function without interruption for several days, but it has two weak points from the view point of routine pesticide monitoring in surface waters: The sample has to be carried to the laboratory before it is analyzed and it has to be filtered through 0.45 μm filters, to remove suspended particles. In this sense, the project EV5V-CT92-105 entitled 'The development of an automated monitoring system for the determination of pesticides and their conversion products at trace level in environmental waters' was designed to analyze waters from European rivers with different characteristics and to identify pesticides. The participants were the Department of Analytical Chemistry of the Free University (Netherlands), the Department of Agricultural Chemistry of the University of Thessaloniki (Greece), Hewlett-Packard in Waldbronn (Germany), RIZA (Netherlands) and the Department of Environmental Chemistry of the CID-CSIC, Barcelona (Spain). The objective was to develop and test a prototype that permitted to improve surface water pesticide analysis regarding automated collection and filtration of the water sample, storage of samples in reservoirs, preconcentration and chromatographic analysis. Such a configuration is mandatory when trying to analyze on-line and routinely a water sample which contains a large and variable amount of particulate river water, such as that found for the river Llobregat. This modified SAMOS is designed to be used in situations such as in water depuration plants or water management stations, where 24 h pesticide monitoring is necessary in order to assess water quality. Therefore, the main objectives of the study were: (i) to design a new, totally automated system that permitted on-line coupling of the filtration step, storage of the water samples, preconcentration and chromatographic analysis and to apply it to the direct monitoring of pesticides from surface waters, (ii) to determine the performance of the method by studying the quality parameters involved with this technique and (iii) to detect, in real-time, sporadic episodes of pollution and confirm the results by means of on-line SPE–LC–APCI-MS. To this end, the modified SAMOS was installed in the laboratory of the Water Treatment Plant (AGBAR) in Sant Joan Despí, 15 km south of Barcelona. In this plant, water from the river Llobregat is potabilized (5 m^3/s) and distributed to the Barcelona metropolitan area. The main advantages of mounting the system there were (i) the possibility of analyzing water from different depuration steps, due to the fact that water is channelled to the laboratory and (ii) the analysis of Llobregat river waters represents one of the most difficult cases, due to the high amount and variability of particulate matter.

2. Experimental

2.1. Description of the system

The SAMOS, available from HP, comprises a sample preparation unit (Prospekt, Netherlands) and a HP1090 liquid chromatograph equipped with a diode array detection (DAD) system. The system is

provided with unique software that controls both the preconcentration step and the chromatographic analysis [15]. In order to automate water collection and analysis, the participants of project EV5V-CT92-105 designed a sampling unit that was connected both to the water source and on-line to the SAMOS. This unit is a refrigerator that contains four flasks and two manually operated pumps, which are activated or deactivated according on whether the flasks are to be filled or not. The first pump of the sampling unit fills flasks 1 and 2 through an auxiliary 1 solenoid valve. Fig. 1 shows the design used. The system was programmed in such a way that it analyzed one sample every 4 h. Table 1 shows the 24 h sequence used. The time needed for the preconcentration step and the chromatographic analysis of each sample was 75 min. The remainder of the time was used to fill another flask for further analysis. Table 2 shows the program used. When one sample is being analyzed, the system is filling a second flask, which will be analyzed 4 h later. The system is programmed so that flasks 1 and 2 are filled in 3 h. Pump 2 exclusively fills flask 3 and was programmed in such a way that it took one water sample in 24 h, so that it gave the daily mean concentration of pesticides. Flask 4 was filled manually with a spiked water sample at a known concentration and was used for external standard quantification.

The outer side of the refrigerator was supplied with three more solenoid valves (auxiliaries 2, 3 and 4), which were responsible for emptying the flasks when necessary. These auxiliary valves were controlled from the SAMOS software. Each flask was connected to the solvent delivery unit of the Prospekt via a PTFE tube, in such a way that water from the flasks was pumped to the precolumn where the preconcentration step took place.

Table 1
Sequence (24 h) used to analyze water samples without interruption

Method	Sample description	Duration (h)
4h3	Analysis of flask 1	3
4h4	Analysis of flask 2	3
4h3b	Analysis of flask 1	4
4h5	Analysis of flask 3[a]	3
4h4	Analysis of flask 2	3
4h3	Analysis of flask 1	3
4h4b	Analysis of flask 2	4
4h6	Standard (flask 4)	1

[a] During the first day, this flask will be filled during 10 hours instead of 24 h.

In summary, the parameters that can be programmed are:

1. Water volume, which fills the flasks of the refrigerator.
2. Water flow, which fills the flasks (from 2 ml/min to 40 ml/min).
3. Time range between filling the flask and emptying it.
4. When flasks are emptied.
5. When one flask is filled again.

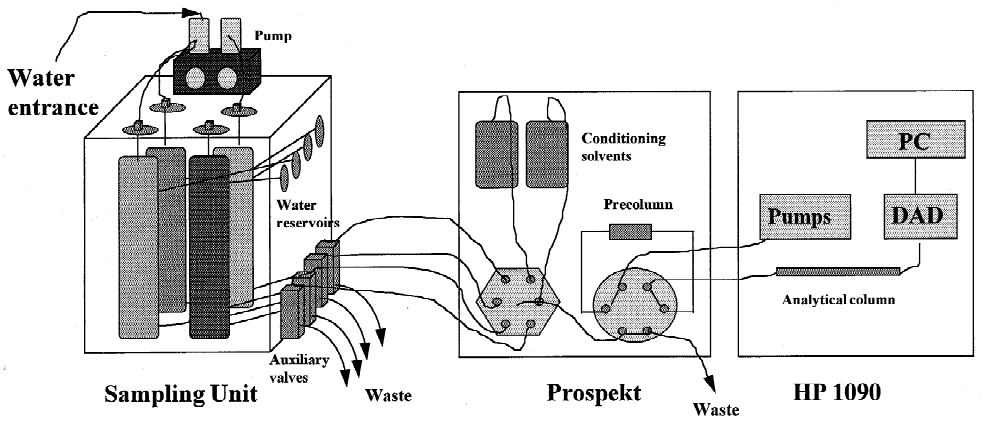

Fig. 1. Scheme of the refrigerated unit that was adapted to be used with the conventional SAMOS. It contains four flasks, and the filling and emptying is controlled by a group of valves and pumps, controlled either manually or by the PC.

Table 2
Analytical method, including the preconcentration of the water sample and chromatographic analysis

Sequence	Function	Fixed at	Comment
Part I. Program used for sample preconcentration (as an example, the preconcentration of flask 1 is given and flask 2 is being filled simultaneously)			
00:00:00	Auxiliary 1	Closed	Electrovalve fill flasks
00:00:00	Auxiliary 2	Closed	Electrovalve empty flask 1
00:00:00	Auxiliary 3	Closed	Electrovalve empty flask 2
00:00:00	Auxiliary 4	Closed	Electrovalve empty flask 3
00:00:00	BCD output	Closed	Water not pumped into flasks
00:00:01	Valve 1	Purge	Position of preconcentration
00:00:01	Valve 2	1>2	Position of preconcentration
00:00:01	Valve 3	1>6	Residues to waste
00:00:02	Precolumn		Change precolumn
00:00:03	Solvent line	1	Methanol selected
00:00:04	Flow	2 ml/min	Conditioning of precolumn
00:00:05	Auxiliary 1	On	Electrovalve fill flask 1
00:00:05	BCD output	On	Flask 1 is being filled
00:02:34	Solvent line	2	Select HPLC water
00:05:04	Flow	4 ml/min	Conditioning of precolumn
00:05:04	Solvent line	3	Selection of sample
00:07:04	Flow	4 ml/min	Preconcentration of 100 ml
00:07:04	Valve 2	1>2	Position of preconcentration
00:07:04	Valve 3	1>2	Collection in calibrated flask
00:32:04	Flow	0 ml/min	Stop preconcentration
00.32:05	Stop		
Part II: Program for the elution of the samples (in this case, sample 2 is being eluted)			
00:00:01	BCD output	On	Fill flask 2
00:00:01	Start chromatogram		Start acquisition
00:00:01	Valve 1	Elution	Elution of the analytes
00:00:02	Solvent line	1	Selection of methanol
00:00:02	Flow	2 ml/min	Rinse system
00:00:02	Valve 3	1>6	Elimination of residues
00:02:32	Solvent line	0	Rinse system stopped
00:30:01	Valve 1	Purge	Position of preconcentration
01:00:00	Auxiliary 2	On	Empty flask 1
02:00:00	Auxiliary 2	Off	Stop emptying flask 1
03:24:59	BCD output	Off	Flask 2 is filled
03:25:00	Stop program		

6. Water volume that can be preconcentrated in the precolumns of the Prospekt.
7. Parameters related to the preconcentration: Flow-rate, elution mode (normal or backflush) and type of precolumn.
8. Parameters related to the chromatographic system: Gradient elution, chromatographic separation and detection.

The conditions used in all cases were the preconcentration of 100 ml of water in C_{18} precolumns, and the analyses were done by LC–DAD. This system was used to analyze waters from the river Llobregat. The Llobregat comes from the north west of Catalonia and flows into the Mediterranean sea, 10 km south of Barcelona. The physico-chemical parameters of these waters are listed in Table 3. One of the characteristics of the river Llobregat is the amount and variability of particulate matter, which oscillate depending on rainfall. The highest flow in 1994 was around 750 m^3/s (May and September–October), while the minimum was around 0.7 m^3/s. The distribution of particles and their abundance in the river Llobregat is variable, but the mean size is 7 μm and, as a whole, 72.6% of the particles are below

Table 3
Physico-chemical properties of the river Llobregat during 1994

	Mean	Maximum	Minimum
Flow, m^3/s	18.3	740	0.7
Color, mg Pt/l	21	50	1
Turbidity, NTU	25	101	24
Temperature, °C	16.4	28.0	4.0
pH	8.1	12.0	7.4
Alkalinity, mg $CaCO_3$/l	210	322	105
Conductivity, 20°C μS/cm	1555	2970	604
Cl, mg Cl/l	364	1844	70
Br, mg Br/l	0.6	1.2	<0.1
Sulfates, mg SO_4/l	181	254	99
Si, mg $Si0_2$/l	3.0	6.8	3.1
Dry residue, mg/l	1101	1555	556
Oxygen, mg O_2/l	6.4	13.4	0.4
Total organic carbon, mg C/l	7.8	150	2.9

10 μm in diameter. The amount of particulate matter is one of the most important issues to be taken into account when analyzing organic compounds in river waters. Particulate matter will influence the adsorption of the more lipophilic compounds and will affect filtration and preconcentration of river water samples. Moreover, the performance of the method for the analysis of river water will depend on the presence of particulate matter and humic material. Even though it has been reported that the SAMOS (in its original form) clogged twice in every 1000 analyses of river Rhine water [15], it has to be taken into consideration that the method used for analyzing one type of water will not work when the matrix of the water is changed.

To avoid clogging of the system, a laboratory-made design was used, which consisted of setting two filters on-line with the SAMOS, before the water was pumped to the sampler unit. Fig. 2 shows a schematic of the design. The first filter consisted of a stainless steel cylindrical filter (50 cm long, 10 μm pore size), which was placed inside a closed cylindrical support and was connected to tap water (consisting of water at different stages of depuration). Circulation of water through the 10 μm filter and to waste was done using the pressure of the tap water. This filter was connected to another one by a PTFE tube. The second filter was a glass filter (190 mm in diameter, 1 μm pore size; Whatman) placed on a disk support (Millipore, USA), which was connected

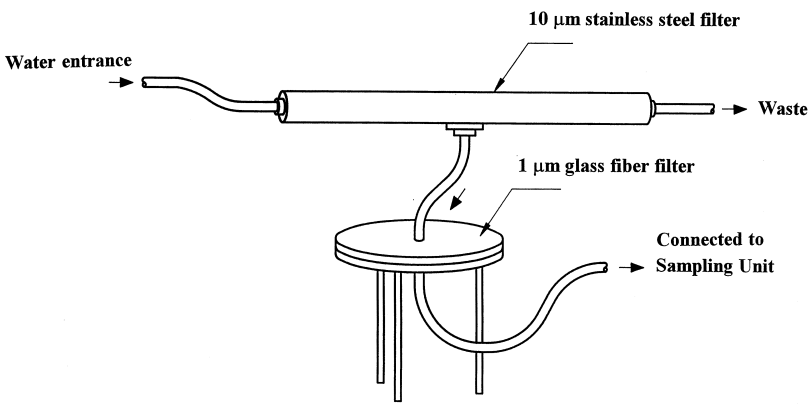

Fig. 2. Filtration system design. It consists of a 50-cm long stainless steel cylindrical tube with a 10-μm pore size connected on-line to a 1-μm glass fiber disk, which is connected to the flasks.

to the pumps of the sampler unit. The arrangement was such that water circulated through the 10 μm filter as long as the tap was opened. Only in the case where the sampler unit pumps were activated, water circulated through the disc filter to fill the flasks. Thus, when the sampler pumps were stopped, water circulated through the cylindrical filter and to waste. This simple two-stage process fulfilled the requirement for on-line monitoring, with regard to filtrate quality as well as easy use, and provided a sufficiently wide operating time-span for unattended application.

2.2. Chemicals and reagents

The pesticides, desethylatrazine, atrazine, terbuthylazine, simazine, propazine, parathionmethyl, fenitrothion, diazinon and chlorpyrifos were obtained from Promochem (Wesel, Germany). Pesticide grade acetonitrile, methanol and water were purchased from Merck (Darmstadt, Germany) and were filtered through 0.45 μm filters before use.

2.3. Sample preparation

A stock solution was prepared in acetonitrile at a concentration of 800 ng/ml. This solution was used to spike different types of water, e.g. water from the river Llobregat and Milli-Q water. Prior to the spiking process, the water from the Llobregat river was filtered through the two-step filtering device. A 100-ml volume of water was preconcentrated on 10×2 mm I.D. disposable precolumns packed with 40 μm octadecylsilica (C_{18}) (Spark Holland) at a flow-rate of 4 ml/min. Before the extraction process, the precolumns were conditioned with 10 ml of methanol and 10 ml of water, at a flow-rate of 2 ml/min. The elution step was carried out by coupling the column on-line with the analytical column and starting the gradient.

2.4. Chromatographic analysis

2.4.1. On-line SPE–LC–DAD

The on-line SPE–LC–DAD analyses were performed with the SAMOS described above. A 150×4.6 mm Zorbax column packed with 4 μm C_{18} was used. The gradient elution consisted of setting the initial conditions to 5% acetonitrile and 95% HPLC-grade water at a flow-rate of 0.1 ml/min, then increasing the flow to 1 ml/min over 1 min, and from these conditions, to 95% acetonitrile and 5% water in 31 min, with these conditions being maintained for 5 min. The flow-rate was set at 1 ml/min and the total run time was 36 min.

Quantification was carried out at 215, 250 and 275 nm, depending on the compound, using external standard calibration.

2.5. SPE–LC–APCI-MS

Confirmatory analyses were carried out by LC–APCI-MS. The procedure consisted of preconcentrating Llobregat river water onto both C_{18} and polymeric sorbent PLRPs precolumns of the Prospekt using the SAMOS. The purpose of using two SPE precolumns was to increase the probability of trapping analytes of different polarity that might be present in the water sample. For this reason, and on different days, Llobregat river water was preconcentrated onto two precolumns of C_{18} and two of PLRPs in such a way that each sample was analyzed with both positive (PI) and negative (NI) ionization modes. These precolumns were removed from the holder without performing any drying treatment and were stored at 4°C for a maximum of one month following the procedure reported by Lacorte et al. [16]. Afterwards, they were placed in a holder that was coupled on-line with the LC–APCI-MS system. The analytical column was as described above, and the analytes were desorbed with methanol and water using the same gradient as for LC–DAD analysis. These water samples were not analyzed simultaneously by LC–DAD.

2.6. Instrument calibration

Calibration plots were constructed by percolating 100 ml of Llobregat river water spiked from 0.3 to 1.5 ng/ml. The repeatability of the method was tested using Milli-Q water and Llobregat river water. The procedure consisted of preconcentrating 5×100 ml of water spiked at 1 ng/ml onto the C_{18} precolumns. Moreover, the long-term reproducibility was tested by analyzing 100 ml of Milli-Q water and Llobregat river water spiked at 1 ng/ml over five

consecutive days. Quantitation was performed by the external standard method using spiked tap water as the reference.

3. Results

3.1. Filtrating process

On-line systems described to date only used automated SPE trace enrichment followed by multiresidue analysis. When analyzing river waters with the characteristics of the Llobregat, filtration of the water samples is an obligatory step if the system is to perform optimally. This tedious step is performed off-line, prior to analysis of the pesticides. However, the modified SAMOS was designed so that sampling, filtering, extraction and analysis were coupled on-line and could be fully automated. The sampling process is based on pumping water samples to a refrigerated reservoir, where they are kept until extraction. Coupling the filtration step on-line with the chromatographic analysis is important, as it avoids the need for sample manipulation and facilitates unattended sampling and analysis, with the additional advantage that human intervention is reduced. The filtration mechanism proposed is a laboratory design, the advantage of which is that percolation of the water through the 1 μm disk filter is done by using the pumps of the sampling unit, so that only the amount of water required for analysis will pass through the disk. However, the amount of water that can be percolated depends on the characteristics of the river. In the river Llobregat, where the common turbidity is around 60 to 100 NTU (Nephalometric Turbidity Units), glass filter disks allowed the filtration of 25 l. Translated to days, the system was suitable for unattended sampling over at least five consecutive days, without changing the filter. With that procedure, 98% of the particles were removed using the 1 μm filter. After this process, the turbidity decreased to 0.33 NTU for waters that had an initial value of 66 NTU and, thereafter, it was possible to run the SAMOS for sample preconcentration and analysis. However, in cases where the turbidity of the river was increased to 2000 NTU, the 1 μm filter collapsed after filtering 4–5 l and further analysis was not possible. Therefore, for rivers of variable flow, the measurement of the turbidity is an important parameter to consider before on-line sampling.

3.2. Screening of pesticides in Llobregat river water

The SAMOS described here was evaluated in first instance by using river water from the depuration plant that had undergone an intermediate depuration step with flocculation with alumina followed by filtration through sand. With these two treatments, all of the organic material was removed but it was thought that the more polar compounds could still be monitored. These waters were analyzed directly without filtering them through 10 and 1 μm filters, however, removal of all of the organic content avoided the detection of any pesticide, as could be seen from the similarity of the chromatographic profiles obtained at different times. This indicates that this stage of depuration was too efficient to be of use in gaining information regarding possible pollutants that might be present in river waters.

In order to monitor pesticides from river water and to gain a general overview of the presence of pollutants in water, direct sampling and preconcentration of Llobregat river water was done. Analysis of unfiltered Llobregat river water lead to the obstruction of the SAMOS after four runs, due to the presence of particles. However, installation of the filtering device described above allowed full automation and analysis over several days. Fig. 3 shows the chromatographic profiles obtained for Llobregat river water that was sampled on different days. In contrast to the results obtained with Llobregat river water that was prefiltered with sand, the elution profiles of untreated river water samples are different each time, indicating on one hand that different pollutants might be present and on the other, that the method is capable of detecting potential contaminants in water samples. At this stage of development and during the time that the system was running, no pesticide was unequivocally identified through retention time data and library searches. In general, the procedure used to increase identification capability and determine the nature of such pollutants in the river of study was the application of LC–MS with an APCI source. It is advisable to prescreen the river water using a

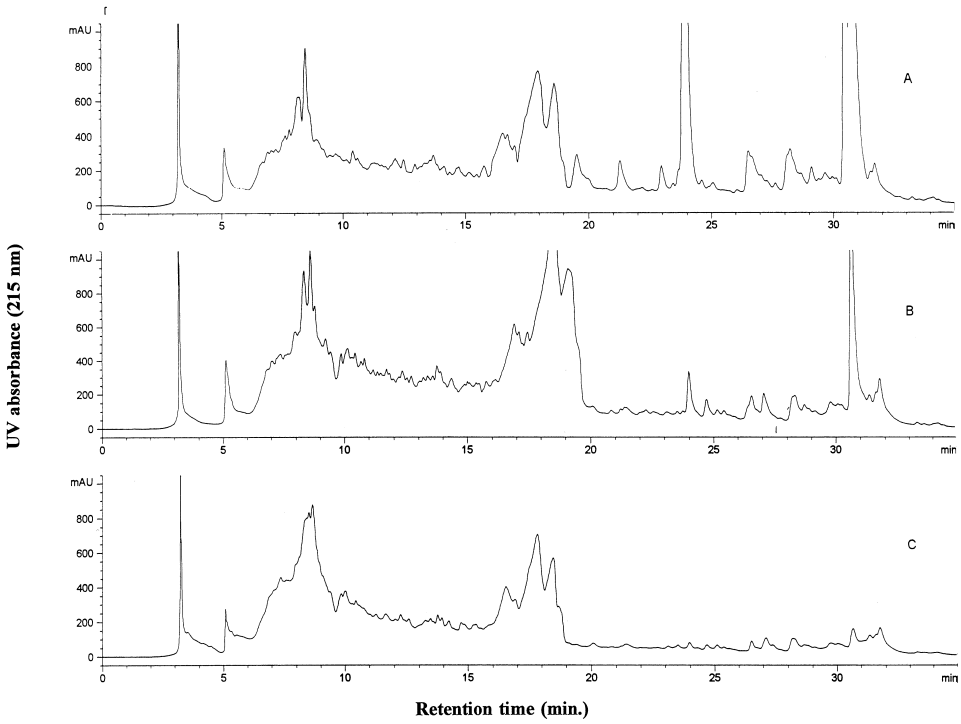

Fig. 3. On-line SPE–LC–DAD chromatogram at 215 nm of 100 ml of an untreated Llobregat river water sample that was filtered through the 10- and 1 μm filters. Samples were taken at different times on a single day: A=time 0, B=8 h after A and C=16 h after A.

technique that renders structural information and when pollutants are detected, to establish a LC–DAD method that would include the detected pesticides in the spectral library. Afterwards, one can attempt to perform on-line LC–DAD monitoring of environmental waters, which would be manageable, as one would be checking for target compounds. To accomplish that, water samples were preconcentrated over several days and afterwards they were coupled on-line with APCI–MS to record potential contaminants.

3.3. Confirmatory analysis

For most of the LC–DAD analyses, the tendency was to obtain a chromatographic profile with many peaks but without any final confirmation on their characterization. To solve this problem, C_{18} and PLRPs precolumns of the Prospekt were loaded with Llobregat river water and eluted on-line with LC–APCI–MS. In this case, the chromatograms confirmed the presence of phthalates and organic phosphates and the absence of pesticides. Tentative identification of the compounds found and the main ions formed is reported in Table 4.

3.4. Calibration data

In Table 5, the calibration data for eight pesticides are reported. Linearity was observed for all of the compounds studied over a range of concentrations from 0.3 to 1.5 ng/ml. Coefficients of correlation were around 0.99, which is acceptable if one takes into consideration that river water was used. The worst values were for diazinon and chlorpyrifos, which eluted at high percentages of acetonitrile, together with the more lipophilic components in the water matrix. The high LOD of diazinon contributes to the low coefficient of correlation of this compound. Desethylatrazine and simazine were the most polar compounds studied, and they eluted at the beginning of the chromatogram, in the interval where

Table 4
Retention time, ions (m/z and relative abundance) and compounds identified by LC–APCI-MS in positive ionization mode in water from the river Llobregat

Time	Principal ions [m/z, abundance (%)]	Compound
5.2	232(100), 106(35), 233(21), 214(16), 106(32)	
7.8	163(100)	Dimethyl phthalate
8.3	139(100)	
9.5	194(100), 195(10)	Phthalate
12.5	177(100), 178(10), 149(10)	Phthalate
14.8	288(100), 289(20), 270(20)	
18.7	155(100), 211(76), 267(39)	Tri-iso-buthylphosphate
19.1	297(100), 268(10), 211(67), 155(60)	Phosphate
22.6	205(100), 206(10), 149(88), 150(10)	

humic and fulvic substances abound. In the present case, neither of them could be detected. Moreover, it is demonstrated that desethylatrazine has a breakthrough volume of 40 ml, therefore, losses of this compound were expected on percolating 100 ml of sample [17]. Simazine was not detected due to interferences present in the chromatogram which coeluted with this analyte. The chromatogram shown in Fig. 4 represents a Llobregat river water blank and a spiked sample at 0.7 ng/ml, which were analyzed with the SAMOS. It can be observed that even though several interferences are present, the method is capable of detecting these pesticides at a low concentration level. It has to be mentioned that the chromatographic profile can be different each day, therefore, the problem of coelution and interferences in the calibration data will vary from one day to another. The LODs were calculated in Llobregat river water by the standard method, assuming a S/N ratio of three. Results are reported in Table 5. These limits can be lowered when using drinking water, since matrix interferences will not be present. Table 6 compares the repeatability values of the method with both Llobregat- and Milli-Q water. It can be seen that the overall values have an error of less than 10% and, therefore, they are within the EU regulations [18]. As expected, better results are obtained with Milli-Q water, since interferences are not present, but a river water sample is more realistic, as the complexity of the determination of pesticides is increased due to the water matrix, the presence of particles and of humic and fulvic material. From Table 6 it can be seen that even with Llobregat river water, the precision of the SAMOS is very good. Simazine has a higher error, due to a co-eluting peak from the matrix at that interval. Regarding long-term reproducibility, which provides information on the day-to-day reliability of the results, in most cases,

Table 5
Calibration data obtained after the preconcentration of 100 ml of Llobregat river water spiked with a mixture of triazines and organophosphorus pesticides at levels from 0.3 to 1.5 ng/ml

Compound	Wavelength (nm)	Calibration curve	R^2	LOD (ng/l)
Desethylatrazine	215	n.d.	n.d.	n.d.
Simazine	215	n.d.	n.d.	n.d.
Atrazine	215	$y=485\,603x-14\,495$	0.997	10
Propazine	215	$y=657\,625x+16\,098$	0.996	10
Parathion-methyl	275	$y=177\,910x-4062$	0.994	13
Fenitrothion	275	$y=168\,103x+23\,745$	0.987	18
Diazinon	250	$y=831\,59x+11\,072$	0.972	105
Chlorpyrifos	215	$y=92\,692x+16\,050$	0.974	22

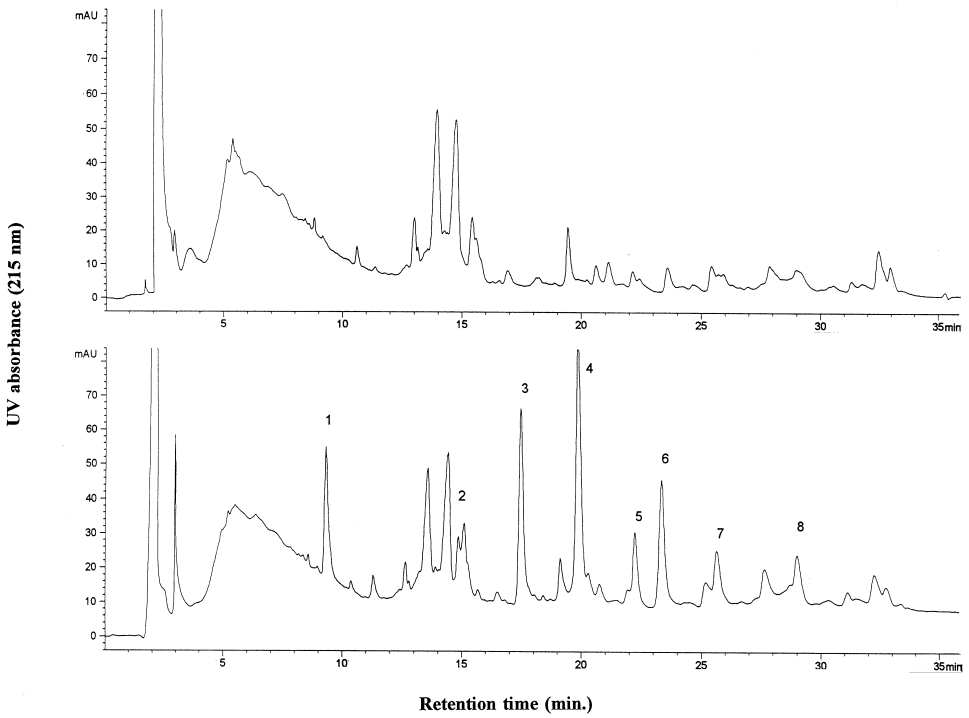

Fig. 4. On-line SPE–LC–DAD chromatogram at 215 nm of 100 ml of Llobregat river water spiked with a mixture of triazine and organophosphorus pesticides at 1 ng/ml. Peak numbers 1=desethylatrazine, 2=simazine, 3=atrazine, 4=propazine, 5=parathion-methyl, 6=fenitrothion, 7=diazinon and 8=chlorpyrifos.

the percentage of error was below 10%. The higher values observed in Llobregat river water samples were due to matrix interferences.

3.5. Environmental levels

The described on-line method was applied to the monitoring of effluent waters located upstream of the river Llobregat. Terbuthylazine was detected in one sample and corresponded to an industrial waste water effluent. This herbicide is commonly used on maize, vines, fruit trees, citrus, coffee and potatoes, but it is also used as an algicide. Fig. 5 shows the LC–DAD chromatogram of this water sample. Identification

Table 6
Repeatability and reproducibility (expressed as the coefficient of variation) of the method using 100 ml of HPLC-grade water and Llobregat river water spiked at 1 ng/ml (n=5)

Compound	Milli-Q water		Llobregat river water	
	Repeatability	Reproducibility	Repeatability	Reproducibility
Desethylatrazine	1.1	9.7	10.0	2.3
Simazine	0.7	12.9	23.8	49
Atrazine	2.1	10.1	3.8	3.5
Propazine	3.1	6.3	8.9	13.1
Parathion-methyl	0.1	2.5	4.0	5.2
Fenitrothion	7.7	1.4	4.6	6.3
Diazinon	n.c.	2.4	4.7	10.2
Chlorpyrifos	2.6	14.2	4.1	12.2

n.c.=not calculated.

was by retention time and spectral comparison with a library search. The SAMOS permitted its confirmation at a concentration of 13 μg/l. The same water was qualitatively analyzed by LC–APCI-MS for confirmation of the results. The presence of this compound in this river water sample was a consequence of a local spill produced by a company that uses terbuthylazine as an algicide for their refrigerating circuit. In this sense, it is worth mentioning that the SAMOS is a powerful tool to get an early warning of the presence of pesticides in river water at levels in the μg/l range, and the results can be confirmed by spectral comparison, without the need to use more sophisticated equipment, such as LC–

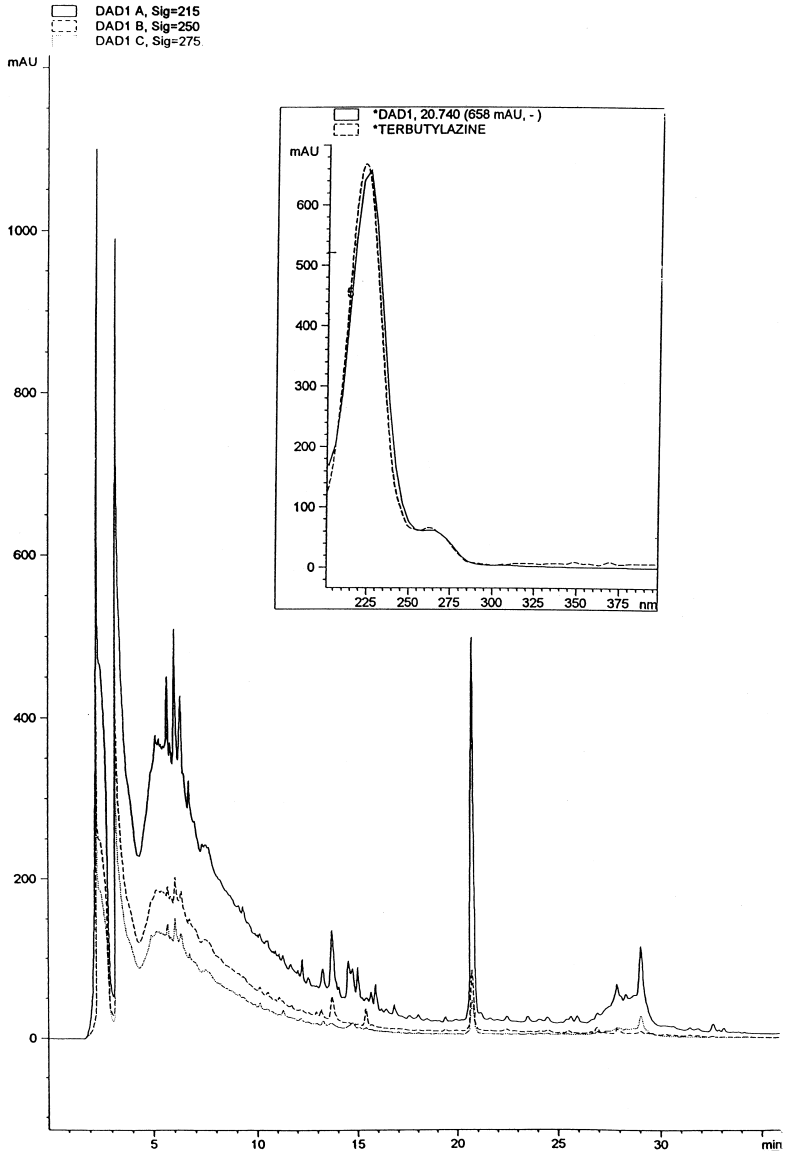

Fig. 5. On-line SPE–LC–DAD chromatogram of a 100-ml Llobregat effluent water sample that contained terbuthylazine at 13 μg/l.

MS, to report the unequivocal identification of pesticides in water.

4. Conclusions

A fully automated technique for determining pesticides in water has been discussed. It includes a laboratory-made filtering device coupled on-line with the sampling unit and the SAMOS. The filtering system consists of a 10-μm stainless-steel filter and a 1-μm glass fiber filter, which eliminates 98% of the suspended particles in river water samples where turbidity has a usual value of 100 NTU, and where the most abundant particle size is 10 μm. This approach allowed the direct sampling of river waters and HPLC–DAD analysis, which could be run, unattended, for five days. The modified SAMOS presented in this paper was used for screening pesticides in Llobregat river water. Terbuthylazine was found in one sample at a level of 13 μg/l, indicating the suitability of the technique as an alarm system for pesticides in water. One of the main advantages of the system is that it has a DAD system, which allows the results to be confirmed by retention time and by comparison with data in a library, without having to use more sophisticated techniques such as MS. LC–APCI-MS was used for confirmation of the presence of terbuthylazine in river water.

On-line SPE–LC–APCI-MS was also used as a pre-screening technique for identifying pollutants that might be present in this river water. Coupling the C_{18} and PLRPs precolumns to LC–APCI-MS allowed the determination of some phthalates and organic phosphates, which could not be identified by means of LC–DAD.

Calibration of the system using Llobregat river water spiked with a mixture of triazines and organophosphorus pesticides revealed a good linearity within the 0.3 to 1.5 ng/ml range, with a LOD of around 15 ng/l when 100 ml of water was preconcentrated. Problems encountered were due to matrix dependent interferences at high percentages of acetonitrile, which coeluted with some of the pesticides.

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