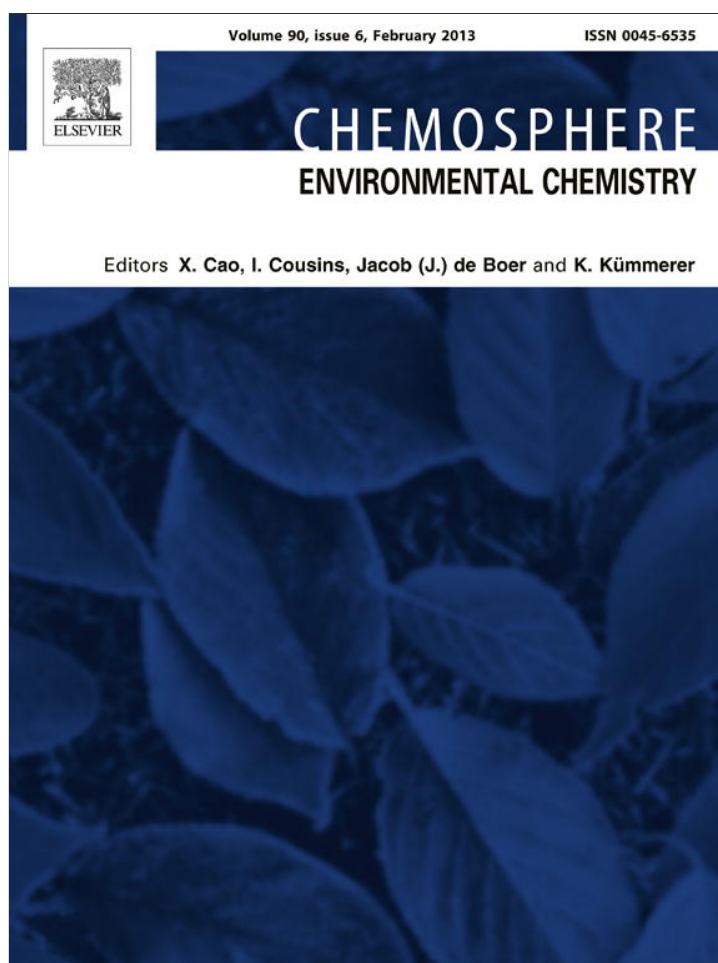


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## Determination of priority pesticides in water samples combining SPE and SPME coupled to GC–MS. A case study: Suquía River basin (Argentina)

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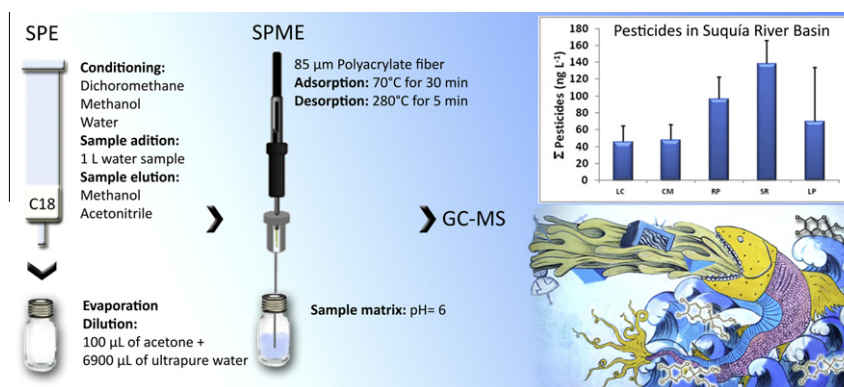
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### HIGHLIGHTS

- ▶ SPE + SPME - GC–MS is proposed for quantification of pesticides in water samples.
- ▶ Quantification of OCPs, OPPs, triazines, pyrethroids and chloroacetamides.
- ▶ Application of the method in Suquía river water samples.
- ▶ Chlorpyrifos and cypermethrine levels surpassed water quality guidelines.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This study reports a combined method using solid phase extraction (SPE), followed by solid phase microextraction (SPME) to concentrate different pesticides, including chlorinated, organophosphorus, triazines, pyrethroids and chloroacetamides, present at trace levels in water samples. Identification and quantification was carried out by gas chromatography coupled to Mass Spectrometry (GC–MS). The optimized methodology showed LOQs at ng L<sup>-1</sup> levels (ranging 0.2–3.5 ng L<sup>-1</sup>) in addition to acceptable precision and robustness (recoveries ranged 63–104%, RSD from 4% to 23%), presenting a novel method to reach trace levels, similar to that obtainable using EC detector, with structural confirmation by MS during the analysis of a wide range of environmental pollutants.

This method was applied to the study of temporal and spatial distribution of pesticides in the Suquía River basin (Córdoba-Argentina). As expected, highest levels of agrochemicals were observed in areas with intensive agricultural practices, being atrazine (max. = 433.9 ng L<sup>-1</sup>), alpha-cypermethrine (max. = 121.7 ng L<sup>-1</sup>) and endosulfan sulfate (max. = 106.7 ng L<sup>-1</sup>) predominant. In urban areas, the prevalent pesticide was alpha-cypermethrine. These results draw attention to the need of pesticide monitoring programs in rivers, considering both urban and rural sections.

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### 1. Introduction

In the last few decades, pesticides have been used on an increasingly wider scale throughout the world. Due to their large

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volumes of production and continuous use, some of these compounds have become “pseudo-persistent” substances in the environment (Barceló and Hennion, 1997). In Argentina, the agrochemicals market has been strongly expanded over recent years, with an increase in the consumption from 73 to 236 million kg per year over last 10 years (CASAFE (Cámara de Sanidad Agropecuaria y Fertilizantes), 2011).

Pesticides is a group of compounds in continuous evolution, characterized by their diversity, different physical and chemical properties as well as their low concentrations in real samples (Frenich et al., 2000). Among them, organochlorine pesticides (OCPs) are very toxic and persistent in the environment, which tend to accumulate in living organisms. Although most of them have been banned from use, they are still detected in natural ecosystems (Dong et al., 2005). Organophosphorous insecticides (OPPs) and triazine herbicides are among the most commonly used and detected pesticides in water streams around the world (Tankiewicz et al., 2010). Pyrethroids are pesticides of the last generation, very stable to light and temperature although they may suffer rapid biological degradation in the environment (Albaser et al., 2011). Finally, chloroacetamides, regarded as the safer herbicide to the environment, can be found in high-quantities in soils (Gonçalves and Alpendurada, 2005).

The determination of pesticides in environmental waters cannot be analyzed without some sample pretreatment because they are too dilute and too complex. Among extraction procedures employing different clean-up and pre-concentration techniques, it could be mentioned: liquid–liquid extraction (LLE), one of the oldest pretreatment procedure and commonly used because of its simplicity and low cost (Metcalf and Metcalf, 1997); solid-phase extraction (SPE), in which analytes can be adsorbed and extracted from complex matrices using a small amount of organic solvent (D'Archivio et al., 2007); and solid phase microextraction (SPME), a technique with less time and solvent consumption, based on the use of a coated fiber to extract traces organic compounds from the matrix, followed by the desorption of retained substances into an analytical instrument (Raposo Júnior and Ré-Poppi, 2007).

Determination of several classes of pesticides (organochlorine, organophosphorus, triazines, pyretroides and acetamides) is usually carried out by gas chromatography (GC) or high performance liquid chromatography (HPLC), depending on their polarity, volatility and the risk of decomposition at high temperature. For GC separations electron capture detector (ECD) and nitrogen phosphorous detector (NPD) are popular for the quantification of OCPs and OPPs residues, respectively. Alternatively, mass spectrometric detector (MS) is a universal detector employed not only for the quantification but for the identification of the majority of pesticides in complex matrix samples (Tahboub et al., 2005). In the full-scan MS method, all ions produced in the MS could be employed in confirmation and quantitation of the target analyte, allowing high confidence in the results (Tahboub et al., 2005). However, the detection limits of MS detectors are above from those obtainable using ECD and NPD. So far, the improvement of pre-concentration methods is absolutely necessary to reach good sensitivity using MS detectors.

Up to now, combining extraction methods has scarcely been applied. Some examples are the determination of phenylurea herbicides in natural waters (Gerecke et al., 2001), the analysis of chlorobenzenes in air (Barro et al., 2004), and more recently, a successful case was reported for the enrichment of OCPs in water samples (Qiu and Cai, 2010).

Thus, the main goals of this study were: (a) develop a combined SPE and SPME extraction for the enrichment of the most widely used pesticides, overcoming the difficult detection of ultra trace environmental concentrations; (b) take advantage of the sensitive and selective Gas Chromatography tandem Mass Spectrometry (GC–MS) method for the quantification of pesticides with different chemical structure, reaching  $\text{ng L}^{-1}$  levels in addition to structural characterization; (c) test the optimized method evaluating spatial and temporal distribution of pesticides in surface waters collected from the Suquía River basin, Córdoba, Argentina.

## 2. Materials and methods

### 2.1. Chemical and reagents

All pesticides were analytical standards (pestanal grade) supplied by Sigma–Aldrich (Argentina). Individual pesticide stock standard solutions were prepared with an appropriate solvent as follows: atrazine, alpha – endosulfan, beta – endosulfan, endosulfan sulfate and alpha – cypermethrin were prepared in acetone (pesticide grade), while chlorpyrifos and acetochlor were dissolved in methanol (HPLC grade). Fresh working solutions were prepared daily by proper dilution of the stock solutions with ultra pure water and stored at 4 °C until use.

Acetone and dichloromethane used during handling of standard solutions and water extractions were of pesticide residual grade, purchased from Sintorgan (Argentina), whereas methanol and acetonitrile were HPLC grade obtained from J.T. Baker (USA). Ultra pure water (Arium 611 UV system, Sartorius, Germany) was used to prepare standard solutions, dilutions and blanks.

Following SPE cartridges were used: Lichrolut C18, 3 mL, 500 mg Merck (Germany) and Strata X, 6 mL, 200 mg, Phenomenex (USA).

Commercially available 100  $\mu\text{m}$  polydimethylsiloxane (PDMS), 85  $\mu\text{m}$  polyacrylate (PA), 75  $\mu\text{m}$  Carboxen-polydimethylsiloxane (CAR-PDMS), and 50  $\mu\text{m}$  Carboxen-polydimethylsiloxane-divinylbenzene (CAR-PDMS-DVB) were purchased from Supelco (USA). Before the analysis, fibers were conditioned in according to instructions provided by the manufacturer.

### 2.2. Study area and sampling

The Suquía River basin is located in a semi-arid region of the province of Córdoba (Argentina; Fig. 1). The river drainage area

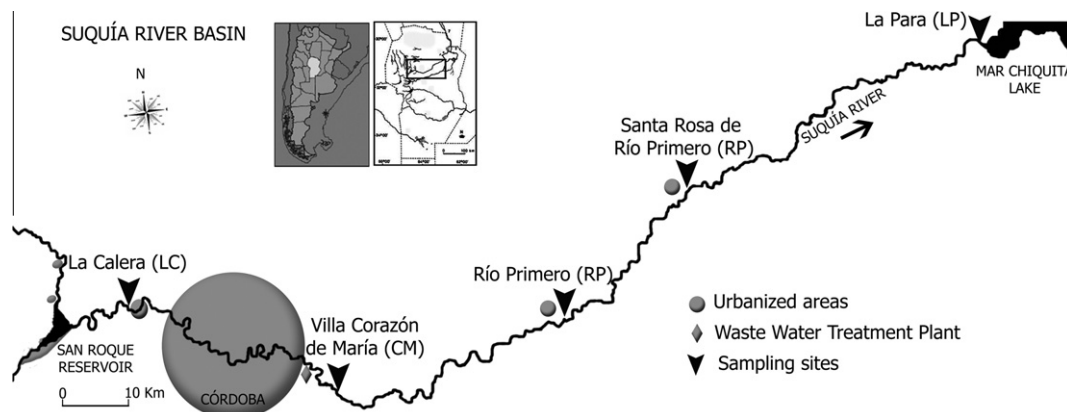


Fig. 1. Study sites in the Suquía River basin (Córdoba–Argentina).

covers approximately 7700 km<sup>2</sup>, is the main drinking water source of Córdoba city, and also serves for recreation and some sport fishing. Suquía River begins at the San Roque dam; 35 km downstream it flows for about 40 km across Córdoba city. Near the eastern edge of the city, the river receives the city sewage discharge and then continues across an agricultural production area up to Mar Chiquita Lake (150 km downstream; Fig. 1). Five sampling sites along this river were selected to evaluate the spatial distribution of pesticides concentration in river water; from the high basin, in a mountainous area (La Calera-LC), to the lower basin, first to evaluate the impact of Córdoba city monitoring immediately downstream from the city (Villa Corazón de María – CM). Then, cultivated areas downstream (Río Primero-RP; Santa Rosa de Río Primero-SR and La Para – LP; Fig. 1; Monferrán et al., 2011) were evaluated. In order to evaluate temporal trends, study sites were sampled during periods with low- and high-application of pesticides, over 2 years: July 2010 (low), November 2010 (high), April 2011 (low) and June 2011 (high).

Water samples were collected at 20–30 cm below river surface, stored in dark glass bottles filled without headspace, ice-refrigerated, and transported to the laboratory within 4 h. Then, water samples were filtered with a cellulose filter (47 mm diameter, 0.45 µm pore size, Millipore, USA) assisted by a vacuum pump, preserved by adding concentrated HCl and stored in dark glass bottles at 4 °C until analysis (Cortada et al., 2009).

Water temperature, dissolved oxygen, pH and conductivity were measured in the field using a WTW multiparametric equipment (Multiline F/Set 3; APHA, 2005).

### 2.3. Sample enrichment

Two consecutive concentration procedures (SPE and SPME) were validated to measure pesticides in water samples. For this purpose, standard water samples were prepared by spiking ultrapure water with a mixture of pesticides in order to validate the SPE step (0.035 µg L<sup>-1</sup> of atrazine, acetochlor, chlorpyrifos, alpha – endosulfan, beta – endosulfan, endosulfan sulfate and alpha – cypermethrin) and the SPME step (5 µg L<sup>-1</sup> of the same pesticides). Additionally, PCB #103 was added as internal standard.

#### 2.3.1. SPE

For SPE extraction Lichrolut C18 and Strata X cartridges were evaluated. The SPE sorbents were first conditioned by washing with 10 mL of dichloromethane, followed by 10 mL acetonitrile and finally 10 mL of Ultrapureultrapure water (procedure A). As an alternative the Lichrolut C18 cartridges were conditioned with 10 mL dichloromethane, 10 mL methanol and 10 mL of Ultrapureultrapure water (procedure B). Then, standard water samples (1 L) were applied through the SPE cartridge by employing a moderate vacuum at about 10 mL min<sup>-1</sup>. After that, SPE cartridges were air dried for 10 min under vacuum and 10 min by fluxing nitrogen to remove as much residual water as possible. Retained analytes were eluted with 5 mL of acetonitrile followed by 5 mL of methanol (for the procedure A), or exchanging the order of the eluents (5 mL of methanol followed by 5 mL of acetonitrile for the procedure B). The elutes were collected in 10 mL SPME glass vials, evaporated under nitrogen current until dryness and capped with PTFE-coated septa.

#### 2.3.2. SPME

After the SPE procedure, entirely automated SPME extractions were performed by a commercial auto-sampler Combi PAL (CTC analytics, Switzerland) mounted on the GC–MS system (Varian, USA), equipped with a cleaning station that avoids carry over contamination.

The SPME extractions were performed by immersing the SPME fiber in the SPE extract dissolved in 100 µL of acetone and 6900 µL of ultrapure water. During SPME runs glass vials (10 mL) having magnetic screw caps (CTC CombiPal, PN 20091405; SUPELCO, USA) and ultraclean, thin pre-marked septum (CTC CombiPal, PN 18032063; SUPELCO, USA) were used. Attempts to use different septa resulted in bending and further destruction of the needle containing the SPME fiber during the extraction.

Although the optimization of the SPME process was carried out by a multivariate optimization strategy, some previous experiments were conducted to reduce the number of factors to be included in experimental design. Thus, variables affecting the process of adsorption to the fiber (SPME fiber coatings: PDMS, PA, CAR-PDMS and CAR-PDMS-DVB) and desorption from the fiber (desorption temperature: 250 °C and 280 °C; desorption time: 5 and 10 min) were firstly evaluated (Kataoka et al., 2000).

Then, to simultaneously optimize the other experimental variables that can mainly affect the target pesticides extraction, a factorial design was run (Fernandez-Alvarez et al., 2008). Different extraction temperatures (50 and 70 °C), extraction times (20 and 30 min) and pH of the sample (pH 2 and 6) during the adsorption to the fiber were considered for this study. The design selected was (2<sup>3-1</sup>), a fractional factorial design which involves less number of experiments (four runs instead of eight runs if we would have used full factorial design) without losing too much information, meaning that the evaluation of all main effects and all two factor interactions are allowed.

### 2.4. Gas chromatography conditions

#### 2.4.1. Chromatography

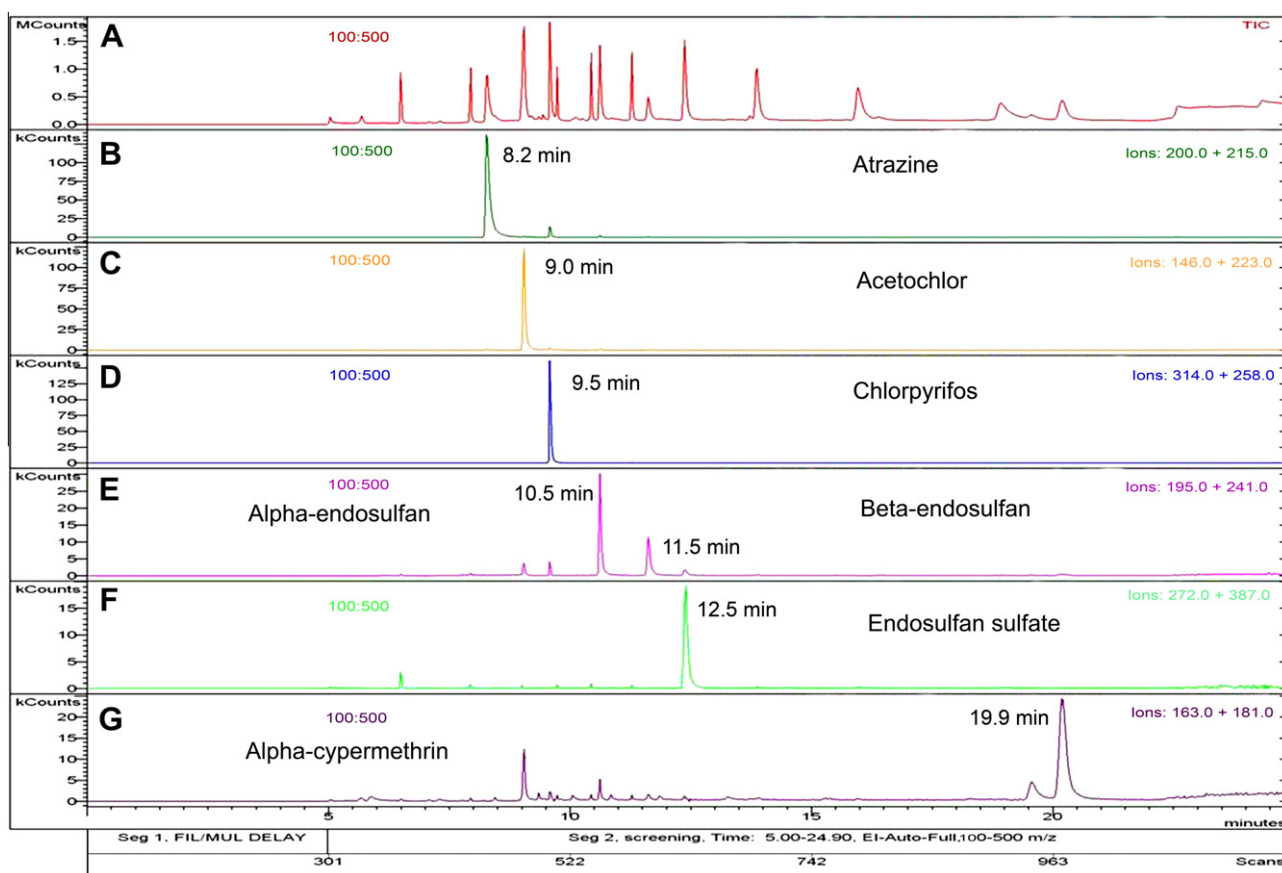
Analyses were carried out by using a Varian Saturn 2200 mass spectrometer (USA) coupled to a Varian 3800 Gas Chromatograph. The GC was equipped with a Factor Four (Varian) capillary column VF-5; 30 m × 0.25 mm ID; DF = 0.25 µm, a 1079 injector equipped with Merlin seals (USA) and working in splitless mode. High purity helium (>99.99%) at a flow rate of 1.6 mL min<sup>-1</sup> was used as the carrier gas. The oven ramp was set to initial temperature of 100 °C (hold 1 min), increased to 150 °C at 25 °C min<sup>-1</sup>, to 200 °C at 10 °C min<sup>-1</sup>, to 250 °C at 30 °C min<sup>-1</sup> (hold 10.33 min) and finally increased to 280 °C at 30 °C min<sup>-1</sup> (hold 2 min), with a total acquisition program of 25 min.

#### 2.4.2. Mass spectrometry

The instrument was operated in the full-scan mode in a range between 100 and 500 m/z. Two significant ions from each analyte were chosen for quantification: atrazine 200 and 215 m/z, acetochlor 146 and 223 m/z, chlorpyrifos 314 and 258 m/z, alpha – endosulfan and beta- endosulfan 195 and 241 m/z, endosulfan sulfate 272 and 387 m/z, alpha-cypermethrin 163 and 181 m/z. The manifold, trap and transfer line temperatures were set at 100 °C, 200 °C and 220 °C, respectively. The emission current of the ionization filament was set at 40 µA, the amplitude voltage was 200 V and the scan time 0.8 s. Fig. 2 shows a GC–MS chromatogram indicating the good resolution of the method.

### 2.5. Method validation

The method based on the combination of SPE and SPME procedure was then performed using Lichrolut C18 cartridges for SPE extraction, conditioned by washing with 10 mL of dichloromethane, followed by 10 mL acetonitrile and finally 10 mL of ultrapure water. Then, water samples (1 L) were passed through the cartridge. The retained analytes were eluted by 5 mL of acetonitrile followed by 5 mL of methanol. The eluates were evaporated under nitrogen and dissolved in 100 µL of acetone and 6900 µL of



**Fig. 2.** GC–MS ion chromatograms of  $5 \mu\text{g L}^{-1}$  standard solution for target pesticides. (A) full scan 100–500 m/z and (B–G) extracted ions and retention time for each compound.

ultrapure water. For the SPME extraction the  $85 \mu\text{m}$  Polyacrylate (PA) fiber was immersed in the solution.

Quality control (QC) and quality assurance (QA) of the developed method were performed according to Pöpke et al. (2004). Analytical quality parameters were measured using five water samples obtained from either unpolluted or polluted areas, spiked with known concentrations of target compounds (2.3) and treated as described above. Recoveries were  $\geq 60\%$  at concentrations tested. Concentrations were calculated from a linear regression plot, constructed using from peak areas, obtained monitoring from the chromatogram corresponding to the respective pesticide fragment ions (m/z). The limits of detection (LOD) and quantification (LOQ) of the method were experimentally evaluated considering a signal-to-noise ratio of 3 and 10 respectively. Precision was evaluated by calculating the relative standard deviation (RSD) from five replicates. The linearity of the method was tested over a wide range of concentrations from LOQ to  $10 \mu\text{g L}^{-1}$ .

Laboratory and instrumental blanks were frequently analyzed to ensure the absence of contaminants, carry over or interferences arising from samples or laboratory handling. Checking of the recovery from spiked water samples, calibration and verification tests as well as MS performance checks were performed before each analysis batch to check the chromatographic resolution, robustness, sensitivity and linear response.

## 2.6. Statistics

Environmental data were tested for normality and homogeneity of variance. Since the pesticides contents did not meet these assumptions, the Kruskal–Wallis test (Sokal and Rohlf, 1995) was

**Table 1**

Comparison of the retention ability using different SPE cartridges and extraction procedures. Recovery values obtained from spiked ultrapure water; pre-concentration from 1 L at  $5 \mu\text{g L}^{-1}$ .

Pesticide	Cartridge and procedure (%)		
	Strata X-procedure A	Lichrolut C-18-procedure A	Lichrolut C-18-procedure B
Atrazine	93	95	104
Acetochlor	86	85	85
Chlorpyrifos	11	68	79
Alpha-endosulfan	6	60	63
Beta-endosulfan	42	68	72
Endosulfan-sulfate	62	91	84
Alpha-cypermethrin	19	24	31

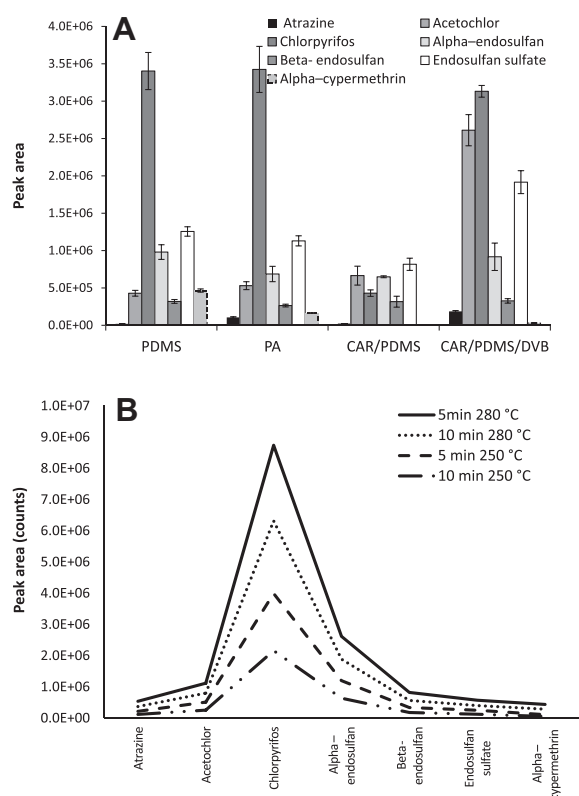
performed followed by a Dunn's multiple comparison tests. Differences were considered significant at  $p < 0.05$ . Statistical analyses were performed using the statistical package, STATISTICA 8 from StatSoft Inc.

## 3. Results and discussion

### 3.1. Extraction protocols optimized

During the optimization of sample extraction procedure, comprising two combined techniques, many factors have to be taken into account.

Table 1 shows the percentages of recovery for each studied pesticide, obtained during the optimization of the SPE step. Based on



**Fig. 3.** Chromatographic response comparison between different conditions assayed for SPME. (A) Influence of different coating fibers (polydimethylsiloxane: PDMS, polyacrylate: PA, Carboxen-polydimethylsiloxane: CAR-PDMS, and Carboxen-polydimethylsiloxane-divinylbenzene: CAR-PDMS-DVB) for the selected pesticides. (B) Influence of time and temperature of desorption from the PA fiber for the selected pesticides.

those results the C18 bonded to reversed-phase silica supporter was selected as the best SPE sorbent. All pesticides were recovered with remarkably good yields (R% being above 60%). The only exception was alpha-cypermethrin with recoveries between 24% and 31%. Since the reverse sorbent was selected, methanol and acetonitrile were evaluated as conditioning and elution solvents (procedures A and B). The recovery studies showed similar R% for both procedures (Table 1), though dichloromethane, methanol and water were selected for conditioning of the cartridges, while the elution solvents were methanol and acetonitrile, in that order (procedure B).

The optimization of the SPME step was carried out in two stages. In the first stage variables were evaluated separately. In the second, a fractional factorial design was applied seeking to assess the effect of four variables on the extraction of pesticides under study.

To evaluate the process of adsorption to the SPME fiber, four different fiber coatings were tested (Fig. 3A). CAR-PDMS-DVB fiber showed a significant improved response for atrazine, acetochlor and endosulfan sulfate. However, this fiber showed the lowest yield for alpha-cypermethrin. In contrast, PDMS fiber was the better coating for alpha-cypermethrin but the worst for atrazine. On the other hand, CAR-PDMS fiber always had the lower responses for all the pesticides while PA fiber was the best coating for chlorpyrifos, the second best suited to the extraction of the pyrethroid and showed good responses for all the other compounds (Fig. 3A). Therefore, owing to the special need to increase the response for alpha-cypermethrin (because of their low signal-to-noise ratios compared with the remaining pesticides) and to measure all other pesticides, the PA fiber was selected.

Time and temperature of desorption from the fiber were also investigated. Fig. 3B shows the response of the detector to the analytes evaluated. The better response for all the pesticides was obtained when the fiber was 5 min at 280 °C in the injector port for the desorption. Longer desorption times in the port caused lower response.

Afterward, different extraction temperatures (50 and 70 °C), extraction times (20 and 30 min) and pH of the sample (pH 2 and 6) were evaluated by applying a fractional factorial design. Pareto charts are useful graphs to illustrate the effect of the variables and their interactions. These graphs are shown in Fig. 4A and C for some representative compounds. These charts include a vertical line corresponding to the 95% confidence interval, the main effects or interactions that exceed this reference line may be considered statistically significant (Fernandez-Alvarez et al., 2008).

Fig. 4B and D shows the main interaction plots for acetochlor and endosulfan sulfate (Fernandez-Alvarez et al., 2008). For the pesticides evaluated, the temperature of extraction was the most frequent variable with a significant effect (Fig. 4A and C). The best extraction temperature was the maximum evaluated, 70 °C (Fig. 4B and D). The next most influential factor on the response was the extraction time, which was found to be statistically significant for most target pesticides. Best results were achieved with 30 min of extraction time.

The pH values was a significant variable for atrazine, chlorpyrifos, alpha-endosulfan and alpha-cypermethrin. In these cases, the better responses were registered working without acid addition.

Taking into account the factorial design results, the final proposed method for the simultaneous SPME extraction of the pesticides under study was: sample matrix pH of 6, fiber coated with PA, adsorption to the fiber at 70 °C for 30 min, desorption during 5 min at 280 °C.

### 3.2. Validation of the developed method

The whole developed method affords LODs and LOQs as follows: for atrazine = 1.1 and 3.5 ng L<sup>-1</sup>; acetochlor = 0.2 and 0.7 ng L<sup>-1</sup>; chlorpyrifos = 0.2 and 0.7 ng L<sup>-1</sup>; alpha-endosulfan = 0.14 and 0.5 ng L<sup>-1</sup>; beta-endosulfan = 0.07 and 0.2 ng L<sup>-1</sup>; endosulfan sulfate = 0.2 and 0.6 ng L<sup>-1</sup>; alpha-cypermethrin = 0.2 and 0.6 ng L<sup>-1</sup> respectively.

The relative standard deviation (RSD) ranged from 1.7% to 14% being acceptable for all the studied analytes. Good linear regressions ( $R^2 \geq 0.975$  in all cases) were obtained over the tested analytical range.

Even when using a MS detector, the validation parameters for the assayed procedure afforded LODs and LOQs in the same order than those reported for other authors applying SPE or SPME or liquid-liquid extraction with electron capture detection (Tomkins and Barnard, 2002; Mmualefe et al., 2009). Passeur et al. (2010) applying SPME coupled to CG-MS detected pesticides under study in the range of 0.05 to 0.5 µg L<sup>-1</sup>. In a similar way, Claver et al. was capable to detected 0.015–0.030 µg L<sup>-1</sup> of pesticides with different chemical structures by SPE coupled to CG-MS. In contrast, better levels were reported by Qiu and Cai (2010) using a combination of SPE and SPME extraction but with electron capture detection.

The advantage of the developed method is the confidence in the identity of the compounds by mass detection at environmental relevant concentrations. Moreover, the proposed method allows the measurement of pesticides presenting different physicochemical properties including triazines, acetamides, organophosphorus, organochlorines and pyrethroids pesticides. It could also be applied to the quantification of other compounds sharing similar chemical structures.

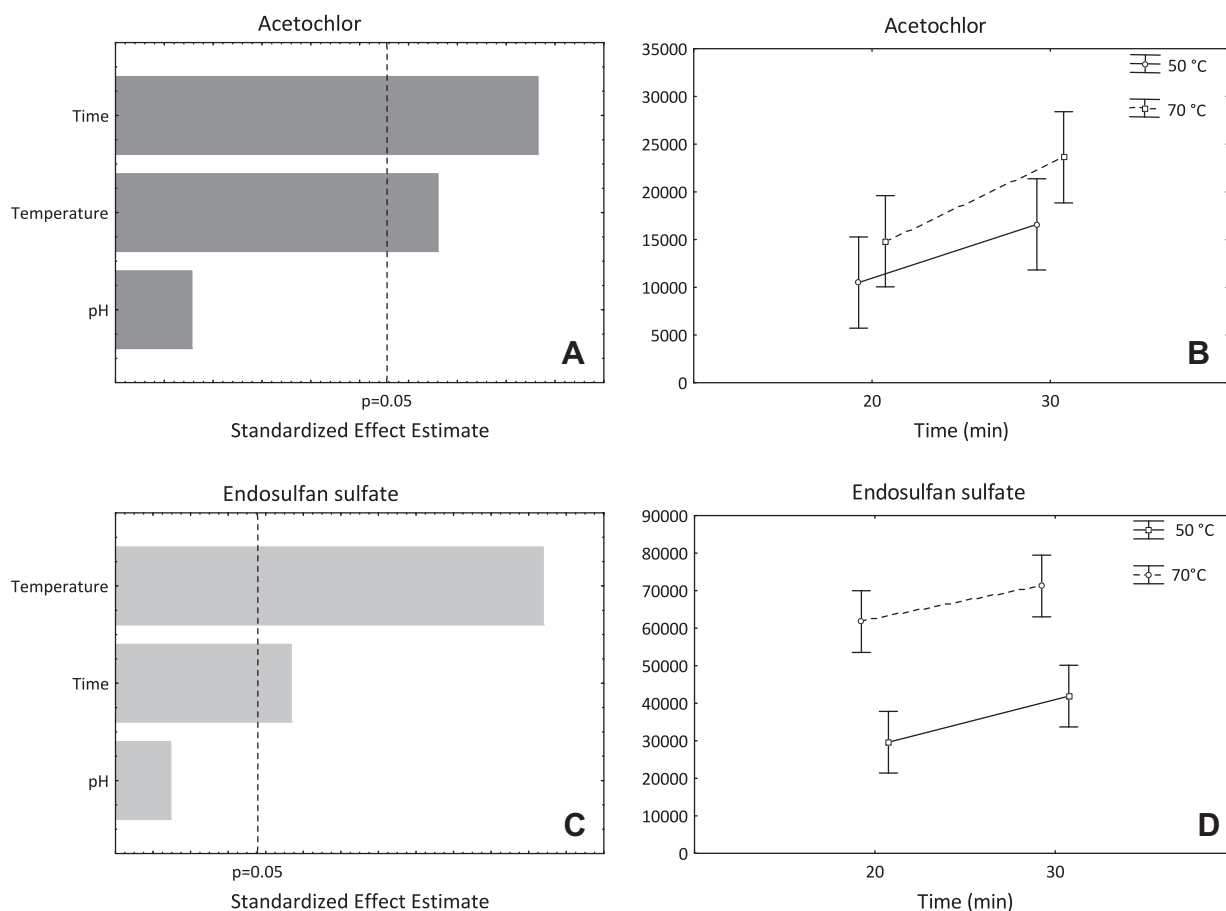


Fig. 4. Pareto charts (A and C) and interaction plots (B and D) for some selected pesticides: A and B for acetochlor; C and D for endosulfan sulfate.

### 3.3. Application of the method to water samples from the Suquía River

The developed method was applied to real freshwater samples from Suquía River basin. This monitoring program was extended over 2 years (2010–2011), sampling at five sites along the river (Fig. 1).

Water quality parameters, measured *in situ* at all sampling sites, are shown in Table 2. All analyzed parameters varied significantly among sites but did not between both sampling periods. Conductivity, dissolved oxygen and pH show that Córdoba city negatively impact on water quality. Even 50 km downstream the city (RP), the river did not recover the water quality detected at LC. Previous studies showed that the Waste Water Treatment Plant of Córdoba city would not be the only source of pollution. The runoff of the cities and cultivated fields located nearby the river would also be significant in the pollutants input (Wunderlin et al., 2001; Merlo et al., 2011; Monferrán et al., 2011).

The occurrence and concentration of the six pesticides measured in the Suquía River are given in Table 3. Results are presented as the mean, minimum and maximum values of the four sampling campaigns grouped as annual, low and high-application periods at the five samplings sites evaluated.

The presence of pollution with pesticides was revealed in all investigated samples. These results are not surprising, since these pesticides are the most widespread commercialized in Argentina (CASAFE, 2011). Atrazine exhibits the highest concentrations, at a maximum of 433.9 ng L<sup>-1</sup>. The concentration of atrazine in water samples is mainly related to their extensive use as agricultural herbicide, consumed at levels of millions of liters per year (CASAFE, 2011) and its relative persistence in surface waters, with a half-life

of 159 d (Solomon et al., 2008). Alpha-cypermethrin was the second most concentrated in the water samples with a maximum level of 121.7 ng L<sup>-1</sup>. The presence of this pyrethroid can be attributed to its use as an agricultural and urban insecticide (home and industry disinfection). The presence of endosulfan sulfate, with a maximum of 106.7 ng L<sup>-1</sup> in water samples, remarks the transformation suffered by the insecticide and acaricide endosulfan in the environment. Endosulfan has half-lives of 3–7 days in water but its toxic biological metabolite, endosulfan sulfate, has an aqueous half-life of several weeks (Leonard et al., 2000). All the other pesticides detected in the water samples were below 30.5 ng L<sup>-1</sup>.

The total amount of pesticides (calculated by totaling the concentration of identified pesticides, Table 3) reflects higher concentrations in the lower basin (downstream from Córdoba city): RP (217.3 ng L<sup>-1</sup>), SR (475.3 ng L<sup>-1</sup>) and LP (201.3 ng L<sup>-1</sup>). These sites have intensive agricultural activity surroundings the river, dedicated mainly to soybean and corn production. In RP and SR atrazine and cypermethrin were the principal pesticides found (in that order). Of the total amount of pesticides measured at LP, cypermethrin was the pesticide with higher concentration followed by atrazine and endosulfan sulfate. These results correlate well with the concentrations of endosulfan and endosulfan sulfate quantified in water samples collected in Mar Chiquita Lake (Fig. 1) by Ballesteros (2010). During that study the author also found higher endosulfan sulfate than the parental isomers (alpha and beta endosulfan). Leonard et al. (2001) proposed that the dominance of endosulfan sulfate in waterbodies, following a pesticide application, may be due to the persistence of the metabolite in cultivated soils and the following washing of the residues from these soils to the watercourses.

**Table 2** Water quality parameters measured at each sampling site in the Suquia River basin. Different letters, when shown, indicate significant differences between monitoring stations. Asterisk indicates differences between monitoring stations ( $p < 0.05$ ).

Parameter	Season	Site																			
		LC				CM				RP				SR				LP			
		Mean	Minimum	Maximum	Significance	Mean	Minimum	Maximum	Significance	Mean	Minimum	Maximum	Significance	Mean	Minimum	Maximum	Significance	Mean	Minimum	Maximum	Significance
Conductivity ( $\mu\text{S cm}^{-1}$ )	Annual	<sup>A</sup> 268	243	308	<sup>C</sup> 1388	1155	1555		<sup>B</sup> 1253	1177	1350		<sup>B</sup> 1106	725	1345		<sup>B,C</sup> 992	517	1253		
	Low	<sup>A</sup> 1422	1412	1431	<sup>C</sup> 1177	1139	1215		<sup>B,C</sup> 1098	1065	1131		<sup>A,B</sup> 1264	1177	1350		<sup>B,C</sup> 1422	1412	1431		
	High	<sup>A</sup> 1355	1155	1555	<sup>B</sup> 1035	725	1345		<sup>B</sup> 885	517	1253		<sup>A,B</sup> 1243	1216	1269		<sup>B</sup> 1355	1155	1555		
Dissolved oxygen ( $\text{mg L}^{-1}$ )	Annual	<sup>C</sup> 10.1	6.3	12.5	<sup>A</sup> 3.2	1.6	5.0		<sup>B</sup> 6.9	5.2	8.7		<sup>B,C</sup> 8.8	6.4	10.7		<sup>B,C</sup> 8.7	7.0	10.6		
	Low	<sup>B</sup> 8.8	6.3	11.3	<sup>A</sup> 3.4	1.7	5.1		<sup>A,B</sup> 6.2	5.2	7.2		<sup>B</sup> 7.1*	6.4	7.7		<sup>B</sup> 7.4*	7.0	7.7		
	High	<sup>C</sup> 11.5	10.6	12.5	<sup>A</sup> 3.1	1.6	4.6		<sup>A,B</sup> 7.6	6.6	8.7		<sup>B,C</sup> 10.6	10.5	10.7		<sup>B,C</sup> 10.1	9.7	10.6		
pH	Annual	<sup>B</sup> 8.1	7.8	8.4	<sup>A</sup> 7.5	7.2	7.8		<sup>A,B</sup> 7.7	7.5	7.9		<sup>A</sup> 8.0	7.6	8.4		<sup>C</sup> 8.5	8.4	8.8		
	Low	<sup>A,B</sup> 7.9*	7.8	8.0	<sup>A</sup> 7.5	7.2	7.8		<sup>A</sup> 7.9*	7.8	7.9		<sup>A</sup> 8.0	7.6	8.3		<sup>B</sup> 8.6	8.4	8.8		
	High	<sup>A</sup> 8.3	8.1	8.4	<sup>A</sup> 7.6	7.4	7.7		<sup>A</sup> 7.6	7.5	7.7		<sup>A</sup> 8.0	7.6	8.4		<sup>B</sup> 8.5	8.4	8.5		
Temperature ( $^{\circ}\text{C}$ )	Annual	17.2	9.9	25.6	20.7	11.0	30.9		20.5	10.7	30.9		20.4	12.2	29.4		20.1	13.5	26.9		
	Low	15.7	9.9	21.4	18.0	11.0	25.0		18.8	10.7	26.8		18.7	12.2	25.2		19.9	13.5	26.2		
	High	18.7	11.8	25.6	23.4	15.8	30.9		22.2	13.5	30.9		22.0	14.6	29.4		20.4	13.9	26.9		

The total amount of pesticides measured at CM ( $153.8 \text{ ng L}^{-1}$ ) reflects pesticides coming from runoff from agricultural fields (situated close to the river at this site) and the contribution of the wastewater from Córdoba city. The combined source of pesticides (urban and agricultural) is reflected by the similar proportion of all the measured compounds on the total detected. In LC, upstream from Córdoba city, pesticides are present at much lower concentrations ( $131.6 \text{ ng L}^{-1}$ ) than in agricultural sites downstream, being alpha-cypermethrin the most contributing at this site, which evidence the urban use of this compound. Chlorpyrifos was the only pesticide showing significant differences among sampling sites (Table 3). The use of chlorpyrifos can be either associated to urban or agricultural uses (Wielgomas and Krechniak, 2007). This compound was present along the complete basin with maximum values at CM and RP (Table 3). A similar pattern was observed for acetochlor, though differences between sampling sites were not significant (Table 3). Acetochlor is used for pre-emergence control of annual grasses and small seeded broadleaf weeds in corn and soybean. It is a common herbicide used worldwide and, due to low adsorption coefficients, is a rather mobile pollutant of the soil, posing a potential danger to the aquatic environment (Lengyel and Földényi, 2003). The presence of this compound out of the agricultural areas (e.g. at LC) demonstrate its intensive use in the basin, but also its distribution and mobility throughout the Suquia River basin.

With regard to temporal distribution, it is known that pesticides used in agricultural practices are generally applied at a specific time of the year. During the present study no significant differences were found between periods of high or low application analyzing either each individual pesticides or the accumulative amount. However, higher pesticides content in water samples was observed during high application periods at SR and LP (both sites with intensive agricultural use of the land). This difference was not observed at CM and RP, where the input of pesticides might be also coming from wastewater discharged by the Waste Water Treatment Plant of Córdoba city. LC showed a slight increasing trend during high-application period but without significant differences.

Concentrations of atrazine similar than those found in the Suquia River were observed in the Ebro River basin ( $62 \text{ ng L}^{-1}$ , Navarro et al., 2010). Conversely, higher concentrations of chlorpyrifos ( $31 \text{ ng L}^{-1}$ , Navarro et al., 2010) and lower levels of cypermethrin were reported in the Ebro River ( $0.73\text{--}57.2 \text{ ng L}^{-1}$ , Feo et al., 2010). Higher concentrations of chlorpyrifos ( $450\text{--}10.8 \mu\text{g L}^{-1}$ ) and cypermethrin ( $710\text{--}194 \mu\text{g L}^{-1}$ ) were measured in other Argentinean rivers (Jergentz et al., 2005; Marino and Ronco, 2005).

In African basins, the concentration of endosulfan and endosulfan sulfate were higher than those detected in the Suquia River ( $40 \text{ ng L}^{-1}$ ,  $185 \text{ ng L}^{-1}$ , respectively; Kuranchie-Mensah et al., 2012). On the other hand, Gómez et al. (2012) found similar amounts of endosulfan ( $3 \text{ ng L}^{-1}$ ) in water samples of Henares River basin (Spain), while in Quequén Grande River (Argentina) Gonzalez et al. (2012) reported this pesticide in the same order of magnitude than in Suquia River water ( $3\text{--}8.5 \text{ ng L}^{-1}$ ).

Chlorpyrifos concentrations surpassed the Canadian Water Quality Guidelines (CCME, 2002) established for the protection of the aquatic biota in freshwaters ( $3.5 \text{ ng L}^{-1}$ ). Higher values were measured at CM and RP during low and high-application periods. On the other hand, the CCME has not established guideline values for cypermethrin. According to Argentinean Environmental Water Quality Guidelines (Niveles Guía Nacionales de Calidad de Agua Ambiente) (2003), alpha-cypermethrin in the Suquia River water exceeded the limit of  $0.6 \text{ ng L}^{-1}$  established for the protection of the aquatic biota at the five sampling sites and during both seasons.

The high concentration of pesticides found in Suquia River, plus the elevated frequency on their occurrence, indicates the intensive



**Table 3**  
Pesticides in water samples collected from Suquia River basin. Different letters, when shown, indicate significant differences between monitoring stations ( $p < 0.05$ ).

Pesticide (ng L <sup>-1</sup> )	Season	Site	LC			CM			RP			SR			LP		
			Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
			Atrazine	Annual	0.6	<LOD	4.8	8.0	<LOD	63.7	47.4	<LOD	189.7	95.6	<LOD	433.9	15.2
	Low	<LOD	<LOD	<LOD	15.9	<LOD	63.7	59.3	<LOD	189.7	1.3	<LOD	5.4	<LOD	<LOD	<LOD	
	High	1.2	<LOD	4.8	<LOD	<LOD	<LOD	35.4	<LOD	75.8	189.9	<LOD	433.9	30.4	4.8	69.6	
Acetochlor	Annual	2.0	<LOD	12.4	4.3	<LOD	17.0	7.2	<LOD	15.8	6.3	<LOD	30.5	3.8	0.5	2.0	
	Low	3.4	0.1	12.4	6.2	1.26	17.0	8.8	3.4	15.8	4.9	0.81	8.8	2.2	1.3	3.2	
	High	0.7	<LOD	1.4	2.4	<LOD	6.4	5.6	<LOD	10.6	7.8	<LOD	30.5	5.4	0.5	9.6	
Chlorpyrifos	Annual	0.6	<LOD	2.6	B,C,2.8	<LOD	5.5	C 3.5	2.5	5.6	A,B,1.3	<LOD	3.1	A 0.7	<LOD	2.6	
	Low	<LOD	<LOD	<LOD	A,B,2.2	<LOD	5.5	B,3.2	2.7	3.6	A,B,1.4	<LOD	3.1	A < LOD	<LOD	<LOD	
	High	A,B 1.3	<LOD	2.6	C,3.3	2.6	5.1	B,C 3.9	2.5	5.6	B 1.2	<LOD	2.5	A,B 1.3	<LOD	2.6	
Alpha-endosulfan	Annual	0.6	<LOD	4.6	0.4	<LOD	2.0	0.3	<LOD	2.0	0.2	<LOD	1.5	1.2	<LOD	6.4	
	Low	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1.6	<LOD	6.4	
	High	1.2	<LOD	4.6	0.9	<LOD	2.0	0.6	<LOD	2.0	0.4	<LOD	1.5	0.7	<LOD	2.7	
Beta-endosulfan	Annual	<LOD	<LOD	<LOD	0.7	<LOD	4.9	1.8	<LOD	9.2	0.1	<LOD	0.7	<LOD	<LOD	<LOD	
	Low	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.3	<LOD	9.2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	
	High	<LOD	<LOD	<LOD	1.4	<LOD	4.9	1.2	<LOD	3.7	0.3	<LOD	0.7	<LOD	<LOD	<LOD	
Endosulfan-sulfate	Annual	5.0	<LOD	17.8	5.1	<LOD	18.6	7.4	<LOD	41.7	1.6	<LOD	3.8	15.5	<LOD	106.7	
	Low	2.8	<LOD	8.7	4.0	<LOD	8.2	2.6	<LOD	9.6	1.0	<LOD	3.2	0.8	<LOD	3.2	
	High	7.3	1.6	17.8	6.3	<LOD	18.6	12.2	0.65	41.7	2.2	<LOD	3.8	30.2	<LOD	106.7	
Alpha-cypermethrin	Annual	36.4	<LOD	121.7	26.0	<LOD	93.0	28.4	<LOD	105.0	33.1	<LOD	112.4	33.6	<LOD	106.6	
	Low	23.1	<LOD	91.6	20.2	<LOD	80.8	19.4	<LOD	77.6	21.7	<LOD	84.6	22.3	<LOD	89.2	
	High	49.7	<LOD	121.7	31.9	<LOD	93.0	37.5	<LOD	105.0	45.1	<LOD	112.4	44.9	<LOD	106.6	
Σ Pesticides	Annual	45.3	0.9	131.6	47.3	1.3	153.8	96.0	7.1	217.3	138.4	4.0	475.3	69.9	1.3	201.3	
	Low	29.3	0.9	112.7	48.5	1.3	153.8	95.7	7.1	217.3	29.8	4.0	98.1	26.9	1.3	92.3	
	High	61.3	12.4	131.6	46.1	4.4	102.2	96.3	11.3	138.2	246.9	18.1	475.3	112.8	18.7	201.3	

use of these compounds in the adjacent area of the watercourse. This is the first report of temporal and spatial distribution of pesticides in Córdoba province. Distant from being only of local interest, the present results alerts about the input of pesticides, not only by extensive agricultural activities but also by urban wastewaters. This research intends to draw attention to the necessity of planning pesticide monitoring programs in rivers, both in their urban and rural sections.

#### 4. Conclusions

The monitoring and control of pesticides in rivers and streams are an important practical problem to be solved in many areas and countries. The validation of methods that allowed the accurate identification and quantification of pesticides with different chemical structures is a significant contribution to resolving this problem. The SPE–SPME–GC–MS method developed in the present study accomplishes this aim and could be also applied to the identification and quantification of other pesticides with similar characteristics.

The implementation of effective measures that prevent and/or reduce the losses of pesticides from non-point sources, in detriment of natural environments, is a challenge for agricultural and water management.

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#### References

- Albaseer, S.S., Mukkanti, K., Rao, R.N., Swamy, Y.V., 2011. Analytical artifacts, sample handling and preservation methods of environmental samples of synthetic pyrethroids. *Trends Anal. Chem.* 30, 1771–1780.
- American Public Health Association [APHA], American Water Works Association [AWWA], Water Environment Federation [WEF], 2005. Standard methods for the examination of water and wastewater. In: Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.H. (Eds.), 21st ed. Baltimore.
- Argentinean Environmental Water Quality Guidelines (Niveles Guía Nacionales de Calidad de Agua Ambiente), 2003. Subsecretaría de Recursos Hídricos de la Nación, República Argentina. <<http://www.hidricosargentina.gov.ar/NivelCalidad1.html>>.
- Ballesteros, M.L., 2010. Acumulación y efectos fisiológicos, histomorfológicos y conductuales del pesticida endosulfán en peces de cuenca del Río Suquia, Doctoral Thesis. Facultad de Ciencias Exactas, Físicas y Naturales. Universidad Nacional de Córdoba, Argentina.
- Barceló, D., Hennion, M.C., 1997. Trace Determination of Pesticides and Their Degradation Products in Water. *Techniques and Instrumentation in Analytical Chemistry*. Elsevier, Amsterdam.
- Barro, R., Ares, S., García-Jares, C., Llompart, M., Cela, R., 2004. Development of a sensitive methodology for the analysis of chlorobenzenes in air by combination of solid-phase extraction and headspace solid-phase microextraction. *J. Chromatogr., A* 1045, 189–196.
- CASAFE (Cámara de Sanidad Agropecuaria y Fertilizantes), 2011. Mercado Argentino 2011 de Productos Fitosanitarios. <<http://www.casafe.org/>>.
- CCME (Canadian Council of Ministers of the Environment), 2002. Canadian water quality guidelines for the protection of aquatic life. In: Canadian Environmental Quality, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- Cortada, C., Vidal, L., Tejada, S., Romo, A., Canals, A., 2009. Determination of organochlorine pesticides in complex matrices by single-drop microextraction coupled to gas chromatography–mass spectrometry. *Anal. Chim. Acta* 638, 29–35.
- D'Archivio, A.A., Fanelli, M., Mazzeo, P., Ruggieri, F., 2007. Comparison of different sorbents for multiresidue solid-phase extraction of 16 pesticides from groundwater coupled with high-performance liquid chromatography. *Talanta* 71, 25–30.
- Dong, C., Zeng, Z., Li, X., 2005. Determination of organochlorine pesticides and their metabolites in radish after head space solid-phase microextraction using calix[4]arene fiber. *Talanta* 66, 721–727.
- Feo, M.L., Ginebreda, A., Eljarrat, E., Barceló, D., 2010. Presence of pyrethroid pesticides in water and sediments of Ebro River Delta. *J. Hydrol.* 393, 156–162.
- Fernandez-Alvarez, M., Llompart, M., Lamas, J.P., Lores, M., García-Jares, C., Cela, R., Dagnac, T., 2008. Simultaneous determination of traces of pyrethroids, organochlorines and other main plant protection agents in agricultural soils by headspace solid-phase microextraction–gas chromatography. *J. Chromatogr., A* 1188, 154–163.
- Frenich, A.G., Martínez Vidal, J.L., Pablos Espada, M.C., Gil García, M.D., Arrebola, F.J., 2000. Comparison of gas chromatography with NPD, MS, and tandem MS–MS in the multiresidue analysis of pesticides in environmental waters. *Chromatographia* 52, 614–620.
- Gerecke, A.C., Tixier, C., Bartels, T., Schwarzenbach, R.P., Müller, S.R., 2001. Determination of phenylurea herbicides in natural waters at concentrations below 1 ng L<sup>-1</sup> using solid-phase extraction, derivatization, and solid-phase microextraction–gas chromatography–mass spectrometry. *J. Chromatogr., A* 930, 9–19.
- Gómez, M.J., Herrera, S., Solé, D., García-Calvo, E., Fernández-Alba, A.R., 2012. Spatio-temporal evaluation of organic contaminants and their transformation products along a river basin affected by urban, agricultural and industrial pollution. *Sci. Total Environ.* 420, 134–145.
- Gonçalves, C., Alpendurada, M.F., 2005. Assessment of pesticide contamination in soil samples from an intensive horticulture area, using ultrasonic extraction and gas chromatography–mass spectrometry. *Talanta* 65, 1179–1189.
- Gonzalez, M., Miglioranza, K.S.B., Shimabukuro, V.M., Londoño, O.M.Q., Martínez, D.E., Aizpún, J.E., Moreno, V.J., 2012. Surface and groundwater pollution by organochlorine compounds in a typical soybean system from the south Pampa, Argentina. *Environ. Earth Sci.* 65, 481–491.
- Jergentz, S., Mugni, H., Bonetto, C., Schulz, R., 2005. Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina. *Chemosphere* 61, 817–826.
- Kataoka, H., Lord, H.L., Pawliszyn, P., 2000. Applications of solid-phase microextraction in food analysis. *J. Chromatogr., A* 880, 35–62.
- Kuranchie-Mensah, H., Atiemo, S.M., Palm, L.M.N.D., Blankson-Arthur, S., Tutu, A.O., Fosu, P., 2012. Determination of organochlorine pesticide residue in sediment and water from the Densu River basin, Ghana. *Chemosphere* 86, 286–292.
- Lengyel, Z., Földényi, R., 2003. Acetochlor as a soil pollutant. *Environ. Sci. Pollut. Res.* 10, 13–18.
- Leonard, A.W., Hyne, R.V., Lim, R.P., Pablo, F., Van den Brink, P.J., 2000. Riverine endosulfan concentrations in the Namoi River, Australia: link to cotton field runoff and macroinvertebrate population densities. *Environ. Toxicol. Chem.* 19, 1540–1551.
- Leonard, A.W., Hyne, R.V., Lim, R.P., Leigh, K.A., Le, J., Beckett, R., 2001. Fate and toxicity of endosulfan in Namoi River water and bottom sediment. *J. Environ. Qual.* 30, 750–759.
- Marino, D., Ronco, A., 2005. Cypermethrin and chlorpyrifos concentration levels in surface water bodies of the Pampa Ondulada, Argentina. *Bull. Environ. Contam. Toxicol.* 75, 820–826.
- Merlo, C., Abril, A., Amé, M.V., Argüello, G.A., Carreras, H.A., Chiappero, M.S., Hued, A.C., Wannaz, E., Galanti, L.N., Monferrán, M.V., González, C.M., Solís, V.M., 2011. Integral assessment of pollution in the Suquia River (Córdoba, Argentina) as a contribution to lotic ecosystem restoration programs. *Sci. Total Environ.* 409, 5034–5045.
- Metcalf, T.L., Metcalfe, C.D., 1997. The trophodynamics of PCBs including mono and non-ortho congeners in the food web of north-central Lake Ontario. *Sci. Total Environ.* 201, 245–272.
- Mmuallefe, L.C., Torto, N., Huntsman-Mapila, P., Mbongwe, B., 2009. Headspace solid phase microextraction in the determination of pesticides in water samples from the Okavango Delta with gas chromatography–electron capture detection and time-of-flight mass spectrometry. *Microchem. J.* 91, 239–244.
- Monferrán, M.V., Galanti, L.N., Bonansea, R.I., Amé, M.V., Wunderlin, D.A., 2011. Integrated survey of water pollution in the Suquia River basin (Córdoba, Argentina). *J. Environ. Monitor.* 20, 1–13.
- Navarro, A., Tauler, R., Lacorte, S., Barceló, D., 2010. Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro River Basin. *J. Hydrol.* 383, 18–29.
- Päpke, O., Fürst, P., Herrmann, T., 2004. Determination of polybrominated diphenylethers (PBDEs) in biological tissues with special emphasis on QC/QA measures. *Talanta* 63, 1203–1211.
- Passeport, E., Guenne, A., Culhaoglu, T., Moreau, S., Bouyé, J.-M., Tournèze, J., 2010. Design of experiments and detailed uncertainty analysis to develop and validate a solid-phase microextraction/gas chromatography–mass spectrometry method for the simultaneous analysis of 16 pesticides in water. *J. Chromatogr., A* 1217, 5317–5327.
- Qiu, C., Cai, M., 2010. Ultra trace analysis of 17 organochlorine pesticides in water samples from the Arctic based on the combination of solid-phase extraction and headspace solid-phase microextraction–gas chromatography–electron-capture detector. *J. Chromatogr., A* 1217, 1191–1202.
- Raposo Júnior, J.L., Ré-Poppi, N., 2007. Determination of organochlorine pesticides in ground water samples using solid-phase microextraction by gas chromatography–electron capture detection. *Talanta* 72, 1833–1841.
- Sokal, R.R., Rohlf, F.J., 1995. *Biometry: The Principles and Practice of Statistics in Biological Research*, third ed. WH Freeman, New York.
- Solomon, K.R., Carr, J.A., Du Preez, L.H., Giesy, J.P., Kendall, R.J., Smith, E.E., Van Der Kraak, G.J., 2008. Effects of atrazine on fish, amphibians, and aquatic reptiles: a critical review. *Crit. Rev. Toxicol.* 38, 721–772.
- Tahboub, Y.R., Zaater, M.F., Al-Talla, Z.A., 2005. Determination of the limits of identification and quantitation of selected organochlorine and

- organophosphorous pesticide residues in surface water by full-scan gas chromatography/mass spectrometry. *J. Chromatogr., A* 1098, 150–155.
- Tankiewicz, M., Fenik, J., Biziuk, M., 2010. Determination of organophosphorus and organonitrogen pesticides in water samples. *Trends Anal. Chem.* 29, 1050–1063.
- Tomkins, B.A., Barnard, A.R., 2002. Determination of organochlorine pesticides in ground water using solid-phase microextraction followed by dual-column gas chromatography with electron-capture detection. *J. Chromatogr., A* 964, 21–33.
- Wielgomas, B., Krechniak, J., 2007. Effect of  $\alpha$ -cypermethrin and chlorpyrifos in a 28-day study on free radical parameters and cholinesterase activity in wistar rats. *Polish J. Environ. Stud.* 16, 91–95.
- Wunderlin, D.A., Díaz, M.P., Amé, M.V., Pesce, S.F., Hued, A.C., Bistoni, M.A., 2001. Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia River basin (Córdoba-Argentina). *Water Res.* 35, 2881–2894.