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Study of the distribution of dichlorobenzenes in sediment and water of Suquía River basin (Córdoba-Argentina) by an optimised SPME-GC-MS procedure

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Abstract: Three dichlorobenzene isomers (DCBs) were monitored in water and sediment from the Suquía River basin by Solid Phase Microextraction (HS-SPME), coupled to Gas Chromatography–Mass Spectrometry (GC–MS). DCBs were not detected in water or sediments corresponding to the upper basin. Pollution with DCBs became evident when the river flows through small cities. As expected, Córdoba city causes the most severe pollution, presenting up to 764.7 μg kg^{-1} DW DCBs in the sediment of urban areas. Results show that DCBs mainly originate in domestic activities, reaching the river by non-point sources such as urban run-off or sewage discharge, resulting in a widespread distribution in the basin. The high level of DCBs found in sediments involves absorption of these xenobiotics in the natural organic matter of sediments. This organic layer could be responsible for transporting DCBs downstream from their discharge, thus spreading the pollution throughout the basin.

Keywords: dichlorobenzene; Argentina; SPME; river monitoring; water quality; Suquía River.

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1 Introduction

Dichlorobenzene isomers (DCBs) can be introduced into the environment following their use as solvents in deodorants or as intermediates in the manufacture of pesticides and other chemicals (Beurskens et al., 1994). DCBs are found in water (He et al., 2000; Meharg et al., 2000), soil (Wang et al., 1995), sediment (Beck et al., 1996), sewage sludge (McPherson et al., 2002) and aquatic biota (Wezel and Opperhuizen, 1995), demonstrating their widespread distribution among all the components of the aquatic environment.

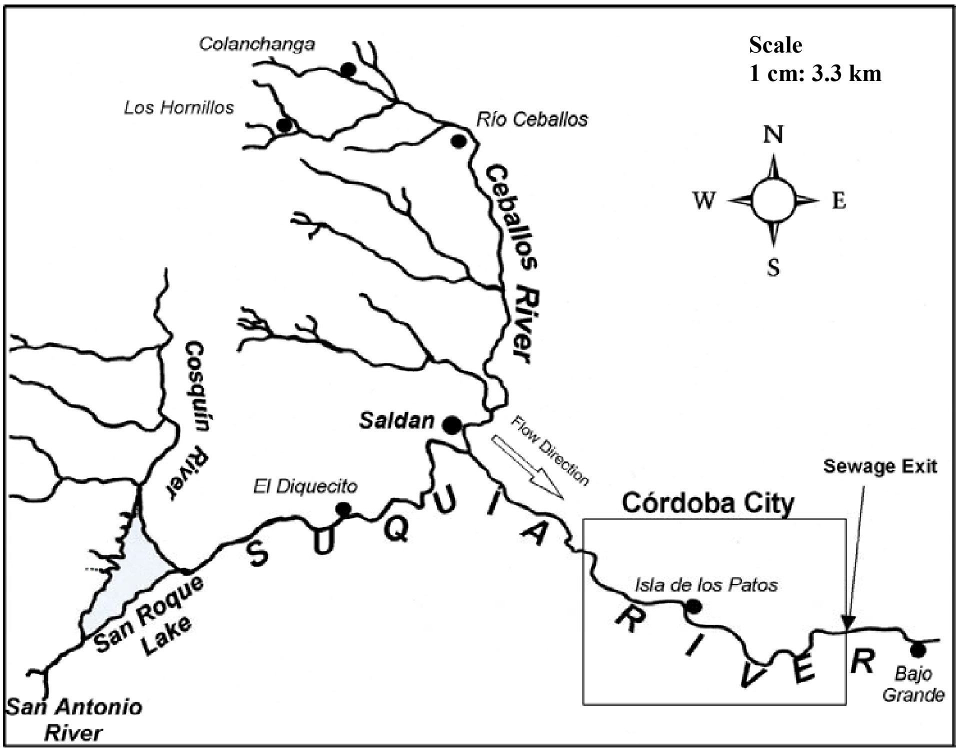
DCBs are hazardous to health and have been ranked as priority pollutants by the US-EPA. These compounds have high octanol-water partition coefficients (3.38 for 1,2-DCB and 1,4-DCB; 3.48 for 1,3-DCB) (Wang and Lee, 1998; Malcolm et al., 2004), so accumulation can be expected in the aquatic ecosystem. Because of their acute toxicity and potential harmfulness to the aquatic environment (Belfroid et al., 1993; Wang and Lee, 1998; Malcolm et al., 2004), it is important to examine levels of DCBs in aquatic systems. Their physicochemical properties, such as water solubility (91.1 mg L^{-1} for 1,2-DCB, 123 mg L^{-1} for 1,3-DCB and 30.9 mg L^{-1} for 1,4-DCB) and Henry's Law constants (0.198 for 1,2-DCB, 0.366 for 1,2-DCB and 0.160 for 1,4-DCB) suggest that they have low water solubility and are volatile compounds. However, DCBs released into water may also be absorbed onto sediment, especially if it is rich in organic matter (constant soil sorption K_{oc}, 987 for 1,2-DCB, 1070 for 1,2-DCB and 1470 for 1,4-DCB) (Malcolm et al., 2004).

Monitoring of Volatile Organic Compounds (VOCs) in environmental samples requires the use of highly sensitive techniques to ensure low detection limits as well as an accurate quantification of contaminants. Solid Phase Microextraction (SPME) was developed by Pawliszyn and co-workers (Arthur and Pawliszyn, 1990; Louch et al., 1992). It is a rapid, less expensive, solvent-free and easily automated technique for the isolation of organic compounds from gaseous and liquid samples. The analysis of organic compounds using SPME in soils and sludge is not as common as in water and is generally based on the analysis of water soil dispersions, as long as the soil matrix dose not significantly interfere in the extraction (Santos et al., 1997).

Zhang and Pawliszyn (1993) demonstrated that extraction times can be substantially reduced by using Headspace (HS) technique, mainly because the diffusion of analytes is significantly greater in the vapour phase than in the aqueous phase. A further advantage of the HS-SPME approach is that samples from virtually any matrix can be analysed since the fibre is not in direct contact with the sample, although care should be taken to release analytes efficiently into the headspace (Liu and Hara, 1999). Thus, optimisation of pre-analytical procedure for HS-SPME is mandatory to achieve good results with this technique, especially when analysing low levels of environmentally relevant chemicals.

The Suquía River basin is located in the Province of Córdoba (Argentina), belonging to a semi-arid region (Figure 1). The river is the main drinking water source for Córdoba city, and receives its sewage effluents downstream from the city centre. Previous works have demonstrated the presence of diverse pollution sources along the middle section of Suquía River basin, showing severe pollution, evidenced by low dissolved oxygen (2.8 ± 7.5 mg L^{-1}), high ammonia (22.5 ± 7.5 mg L^{-1}), nitrates (25.5 ± 8.5 mg L^{-1}) and nitrites (2.0 ± 0.5 mg L^{-1}), high BOD (19.4 ± 5.8 mg L^{-1}) as well as the presence of lindane in the sediment downstream from the city sewage discharge (Pesce and Wunderlin, 2000; Wunderlin et al., 2001). The presence of heavy metals distributed in sediments throughout the basin has also been reported (Nimptsch et al., 2005), evidencing high values of Al (≤23 mg g^{-1} DW), Pb (≤25 mg g^{-1} DW), etc. Finally, the eutrophication of the San Roque reservoir has been reported (Amé et al., 2003), showing high values of nitrite (≤0.53 mg L^{-1}), nitrates (≤27.9 mg L^{-1}), total phosphorous (≤2.39 mg L^{-1}), iron (≤0.54 mg L^{-1}), ammonia (≤3.23 mg L^{-1}). Several of the parameters measured are above levels considered as hazardous for human health and aquatic life, exceeding EPA guidelines (http://www.epa.gov/waterscience/criteria/library/goldbook.pdf).

Figure 1 Schematic plan of Suquía river basin with indication of monitoring stations. The box represents Córdoba City



Considering these previous results, a study was initiated to evaluate the presence of organic pollution in the Suquía River basin, specially the presence of xenobiotics. Among xenobiotics, chlorinated compounds have high persistence in water and sediments being translocated for aquatic biota. The main goal of this work was to assess the presence of DCBs, as representatives of chlorinated xenobiotics, in the Suquía River basin. To do that, an analytical procedure was optimised using HS-SPME equipped to GC-MS analysis for determination of DCBs concentration in water and sediment.

2 Materials and methods

2.1 Standards and reagents

Chromatographic standards were prepared from 1,2-, 1,3- and 1,4- dichlorobenzene (1,2-DCB; 1,3-DCB and 1,4-DCB) of analytical grade (Sigma-Aldrich, USA). 3-chloro-1-bromobenzene of analytical grade was used as the internal standard during HS-SPME/GC-MS analysis (Sigma-Aldrich, USA). Stock solutions were prepared by diluting the corresponding reagent with methanol (HPLC grade) to afford a final concentration of 200 $\mu g\ mL^{-1}$. The water used was from a Milli-Q system (Millipore-USA). Assays were carried out using a Polydimethylsiloxane (PDMS) SPME fibre with 100 μm film thickness (Supelco, USA).

2.2 Equipment

Gas chromatographic analyses were performed on a Shimadzu QP5050A equipment (Shimadzu, Japan), fitted with a fused silica capillary column: 25 m, 0.2 mm i.d. and 0.25 µm film HP-5 (Agilent-HP, CA, USA). The mass spectrometer Class 5000 was operated in the electron impact ionisation mode (EI 70 eV). Identification of individual compounds was based on comparison of retention times and mass spectra using pure compound and the assistance of mass spectral database (NIST 107).

The GC temperature programme was as follows: initial 80ºC during 3 min, heating at 10ºC min^{-1} until 120ºC, further increase at 30ºC min^{-1} until 280ºC, held for 3 min. The total run time was 15.3 min. The injector and detector-interface temperatures were set at 250ºC and 280ºC, respectively. The carrier gas was helium (≥99.999% purity) at a flow rate of 1.9 mL min^{-1}. Samples were injected manually by splitless mode using a special fibre-holder obtained from Supelco, USA.

To increase sensitivity and specificity, the MS detector was operated in the Single Ion Monitoring (SIM) mode, selecting ions at m/z 146, 148 and 151 for all DCBs, while 3-chloro-1-bromobenzene was monitored at m/z 190, 192 and 194.

2.3 Headspace SPME procedure

Before starting, the fibre was conditioned in the hot injection port of the gas chromatograph at 250ºC during 2 h. Control runs were performed using conditioned fibre to confirm the absence of interferences. Control runs were repeated frequently during assays to confirm the absence of carry over.

2.4 Optimisation of water samples analysis

DCBs analyses were performed by applying the SPME fibre in the headspace of water samples (60 mL), contained in 100 mL sealed vials, which were previously spiked with each DCB isomer dissolved in methanol until reach a concentration of 5 µg L^{-1}. Each vial was also supplemented with NaCl amounts ranging 0–360 g L^{-1} and with 30 µL of a solution of 3-chloro-1-bromobenzene in methanol as internal standard (10 µg L^{-1}). After spiking, vials were sealed using PTFE-coated silicone rubber. Sealed vials were equilibrated at 30°C during 10 min. After the SPME fibre was plunged into the headspace and it was continuously stirred to decrease the time required to reach the equilibrium between liquid and vapour phases. The temperature was varied between 20ºC and 50ºC as well as the exposition time 0–30 min to verify the optimal absorption condition. Thermal desorption of analytes was achieved by introducing SPME fibre into the GC injection port at 250°C for 4 min (Potter and Pawliszyn, 1994).

2.5 Optimisation of sediment samples analyses

A procedure similar to that employed for water samples was used to evaluate the performance of SPME for analysis of sediment. Thus, 30 g of wet clean sludge Natural Organic Matter (NOM), Dry Weight (DW), sludge from Los Hornillos (moisture = 20.94 %; NOM = 2.0 g % DW) were mixed with 50 mL ultrapure water, contained in

100 mL sealed vials, spiked with each DCB isomer dissolved in methanol until reach a concentration of 3 µg kg^{-1} DW, NaCl (0–360 g L^{-1}) and the corresponding internal standard. The sludge used during these assays was obtained from an unpolluted site, and verified as clean by HS-SPME-GC-MS analyses of unspiked samples.

Results from HS-SPME/GC-MS (optimised) spiked with DCBs (ranging 1–30 µg L^{-1}) in water and (ranging 1–15 µg kg^{-1} DW) in sediment were used to construct calibration plots by linear regression, which were applied to evaluate levels of DCBs in the Suquía River basin. Linear behaviour was not observed when the concentration of DCBs exceeds 30 µg L^{-1} in water, or 15 µg kg^{-1} DW in sediments. Thus, samples presenting DCBs close or above these concentrations were diluted to fit the linear range.

2.6 Suquía River monitoring

Monitoring stations were selected on the basis of previous reports (Pesce and Wunderlin, 2000; Wunderlin et al., 2001; Amé et al., 2003; Nimptsch et al., 2005) pointing out the presence of *quasi* pristine areas located upstream from Córdoba city, as well as an important pollution gradient caused by human activities. Figure 1 shows six monitoring stations: four corresponding to less polluted sites (Los Hornillos: 31° 09′ 10.67′′ S–64° 21′ 06.12′′ W, Colanchanga: 31° 08′ 41.59′′ S–64° 21′ 14.89′′ W, Río Ceballos: 31° 08′ 51.21′′ S–64° 20′ 11.89′′ W, El Diquecito: 31° 21′ 12.07′′ S–64° 23′ 47.63′′ W), one with moderate pollution (Isla de los Patos: 31° 24′ 03.65′′ S–64° 12′ 14.63′′ W), and one highly polluted (Bajo Grande: 31° 24′ 59.01′′ S–64° 04′ 18.00′′ W) downstream from the Córdoba city sewage exit (Pesce and Wunderlin, 2000; Wunderlin et al., 2001; Amé et al., 2003; Nimptsch et al., 2005).

Water and sediment samples were collected at each monitoring station, water sampled at 20–50 cm below river surface and superficial sediment 0–20 cm. Samples were conditioned in glass bottles/jars, filled without headspace, ice-refrigerated, and transported to the laboratory within 4 h, to be stored at –20°C until analysis.

Determinations of moisture were carried out using 20 g of sediment sample and dried at 105°C in an oven until constant weight. Then, 5 g were combusted at 500–525°C during 2 h to determine NOM (APHA, 1998).

3 Results and discussion

3.1 Optimization of headspace SPME

SIM mode was used for DCBs analysis in order to increase the selectivity and to avoid matrix and chromatographic interferences, which results in high noise in baseline and consequently in high Limit of Detection (LOD) and Limit of Quantification (LOQ). SPME procedure was optimised by appropriate time, temperature of the absorption process and the amount of added NaCl.

The SPME absorption time was optimised by monitoring changes in GC-MS peak area as a function of the absorption time, keeping water/sediments at 30ºC without addition of NaCl. Figure 2A shows the results obtained by measuring DCBs by

HS-SPME. Thus, the optimal absorption was established at 15 min for all the studied compounds. In the following, the SPME fibre was exposed for 15 min considering a compromise between adequate absorption and the time required for the analysis.

The effect of temperature on the amount of DCBs absorbed was studied by exposing the fibre for 15 min for a temperature range from 20ºC to 50ºC without addition of NaCl. The results are shown in Figure 2B. It was observed that increasing the absorption temperature enhances the diffusion of analytes from the liquid phase to the headspace (Potter and Pawliszyn, 1994). However, a decrease in the amount of DCBs extracted was observed when the temperature was over 40ºC that might be due to the exothermic process (Zhang and Pawliszyn, 1993). Thus, 30°C was selected as the optimal absorption temperature.

NaCl is added to the sample to increase the ionic strength and enhance the amount of analyte extracted (Ai, 1997; Beltran et al., 1998; Peñalver et al., 1999). The optimal concentration of NaCl was determined by adding variable amounts of NaCl, ranging from 0 g L^{-1} to 360 g L^{-1}, keeping the absorption time (15 min) and temperature (30°C) constant. Results are shown in Figure 2C, demonstrating that the highest peak area was obtained at a saturation concentration of 360 g L^{-1} NaCl for all DCBs and therefore is considered as the optimal NaCl concentration.

Optimal SPME conditions obtained for sediment samples were very similar to those obtained for water samples. Thus, the same conditions (temperature, time and NaCl amount) were used for water and sediments.

These results are in good agreement with the optimised parameters obtained by He et al. (2000), where they found that rapid absorption occurred during the first 10 min for DCBs and 26°C was the optimum temperature for analysing them in water. In contrast, they found that the optimum adsorption on the fibre was observed at 20% NaCl concentration, while our present results indicate that using saturated NaCl solutions gave better results.

Additionally, the present results for sediment are in good agreement with those reported by Santos (1997). They found that 15 min and 30°C were the optimum extraction time and temperature respectively, required to reach an optimal equilibrium between the stationary phase and the sediment. Both results considered that DCBs are volatile compounds and having high vapour pressure.

3.2 Quantitative analysis

Once the SPME parameters had been optimised, the internal calibration curves by linear regression using several DCBs concentrations at either water or sediment samples were constructed. Good linearity ($R^2 > 0.9826$) was observed for the three isomers over the range 1–30 μg L^{-1} in water, and 1–15 μg kg^{-1} DW in sediment, (Table 1). The observed linearity is in good agreement with He et al. (2000) findings, who found $R^2 > 0.988$ when analysing water samples containing 0.02–20 μg L^{-1} DCBs (He et al., 2000).

Figure 2 Efficiency of absorption to 100 µm PDMS fibre from the headspace of DCBs in water (5 µg L^{-1}): (A) according to extraction time (min) at 30ºC without addition of NaCl; (B) according to extraction temperature using 15 min absorption time without addition of NaCl; (C) according to added NaCl (g L^{-1}), using 15 min absorption time at 30ºC

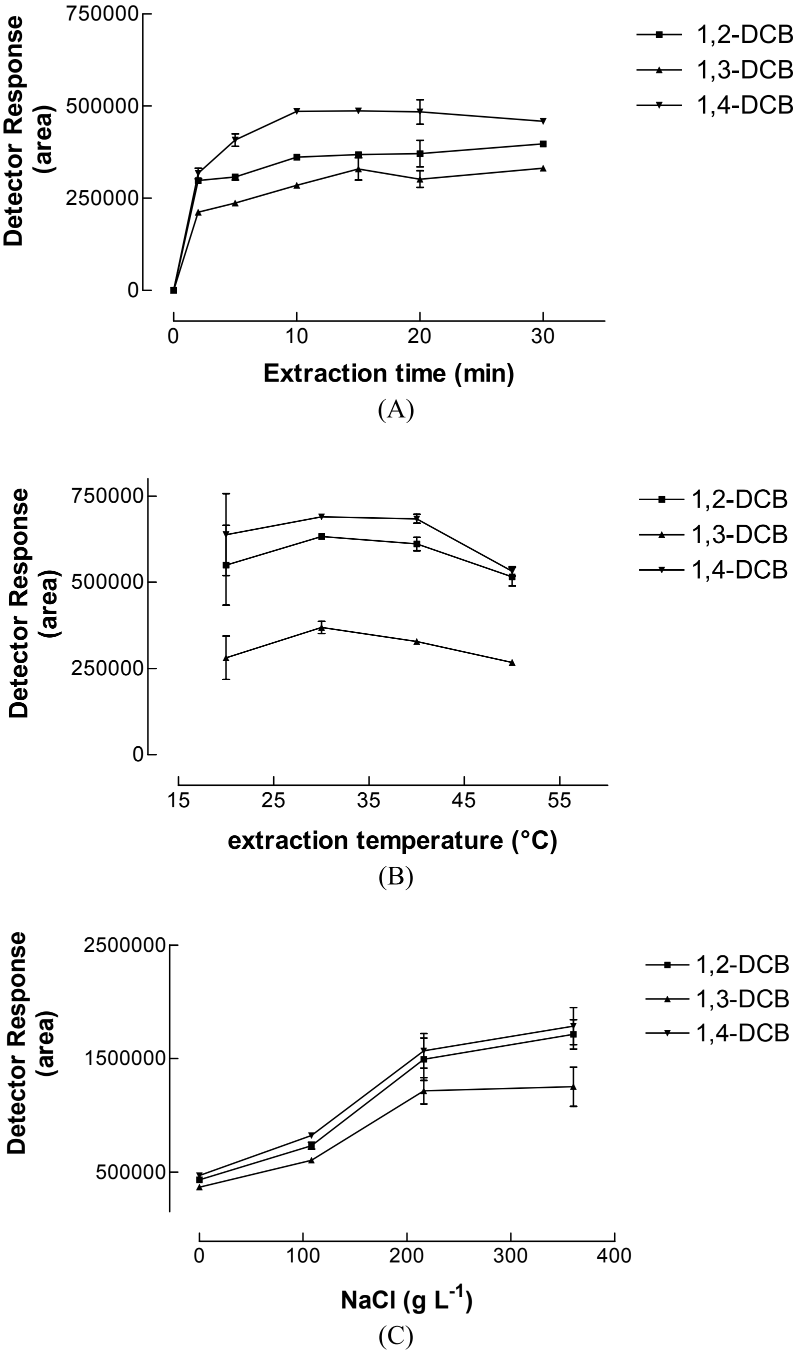


Table 1 Quantitative analysis of DCBs in aqueous samples using HS-SPME-GC-MS. Correlation coefficients (R^2). LOD (limit of detection), LOQ (limit of quantification)

	Calibration curve					
	Water sample			*Sediment sample*		
	1,2-DCB	*1,3-DCB*	*1,4-DCB*	*1,2-DCB*	*1,3-DCB*	*1,4-DCB*
Slope	2.6945	3.6443	3.0286	0.5757	0.7322	0.5166
Intercept	–0.0131	0.0606	0.0004	0.0807	0.1209	0.0909
R^2	0.9860	0.9826	0.9886	0.9985	0.9985	0.9970
LOD	0.008[a]	0.014[a]	0.015[a]	0.014[b]	0.023[b]	0.026[b]
LOQ	0.027[a]	0.047[a]	0.051[a]	0.046[b]	0.079[b]	0.088[b]

Notes: [a] $\mu g\ L^{-1}$; [b] $\mu g\ kg^{-1}$ (dry weight).

Additionally, detection and quantification limits for 1,2-, 1,3- and 1,4-DCB were determined. The LOD was taken at a signal-to-noise ratio (S/N) of 3.33, while the LOQ at a S/N ratio of 10. When determined LOD and LOQ, both fibre and solution blanks were carried out after each GC run to ensure absence of sample carryover from either the fibre or the aqueous matrix. Significant carryover was not observed when using optimised absorption desorption time and temperature.

Additionally, good recoveries (>93%) were obtained over the studied concentrations range (1–30 $\mu g\ L^{-1}$), with a reasonable day-to-day precision (RSD ≤10%) in comparison with purge-and-trap methods (RSD ≤15%) (Monferrán et al., 2005). Similar results were obtained with sediments spiked with different concentrations of DCBs (recoveries >93%, RSD ≤10%).

3.3 Monitoring of Suquía River basin for DCBs

The presence of DCBs in the Suquía River basin was evaluated over one year. Table 2 and Table 3 show concentrations observed in water and sediments respectively, arising from different monitoring stations (Figure 1). Values reported as <LOQ correspond to traces of the corresponding compound. Values reported as <LOD correspond to absence of DCBs, though in some cases it is possible to see a small peak, which S/N ratio is lower than the assigned as LOD.

DCBs were not detected in water as well as in sediments samples collected from stations Los Hornillos or Colanchanga (Table 2 and Table 3). These stations were chosen as *quasi* pristine areas because they are located upstream from Córdoba city, and correspond to a protected reserve with less human activities. However, these two brooks form a small reservoir (La Quebrada dam), where Ceballos River begins (Figure 1). It is interesting to note that samples of Ceballos River in July evidence the presence of 1,2-DCB and 1,3-DCB in both water or sediment, while 1,4-DCB was present only in sediment samples. 1,4-DCB has low aqueous solubility and high K_{oc}, so lower concentration can be expected in water than in sediment as observed.

Table 2 Concentration of DCBs in water samples from Suquía River basin (μg L^{-1}) (<LOD = below detection limit; <LOQ = below quantification limit)

		Stream Los Hornillos (LH)	*Stream Colanchanga (COL)*	*La Quebrada (Ceballos River) (CR)*	*Suquía River Diquecito (DIQ)*	*Suquía River Isla de los Patos (IDP)*	*Suquía River Bajo Grande (BG)*
Sample mar-05	1,2-DCB	<LOD	<LOD	<LOD	17.72	3.36	24.10
	1,3-DCB	<LOD	<LOD	<LOD	<LOD	<LOD	0.22
	1,4-DCB	<LOD	<LOD	<LOD	3.42	0.21	4.62
Sample may-05	1,2-DCB	<LOD	<LOD	<LOD	5.30	9.00	1.97
	1,3-DCB	<LOD	<LOD	<LOD	0.42	0.82	<LOD
	1,4-DCB	<LOD	<LOD	<LOD	1.10	2.14	0.37
Sample jul-05	1,2-DCB	<LOD	<LOD	2.36	1.67	1.32	1.44
	1,3-DCB	<LOD	<LOD	0.60	0.41	<LOD	0.38
	1,4-DCB	<LOD	<LOD	<LOD	0.11	0.20	0.08
Sample sep-05	1,2-DCB	<LOD	<LOD	<LOD	1.82	<LOD	2.50
	1,3-DCB	<LOD	<LOD	<LOD	<LOD	<LOD	7.75
	1,4-DCB	<LOD	<LOD	<LOD	1.34	<LOD	6.34
Sample nov-05	1,2-DCB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	1,3-DCB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	1,4-DCB	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ

Table 3 Moisture, NOM and DCBs contents in sediments from Suquía River basin

		Stream Los Hornillos (LH)	*Stream Colanchanga (COL)*	*La Quebrada (Río Ceballos) (CR)*	*Suquía river Diquecito (DIQ)*	*Suquía river Isla de los Patos (IDP)*	*Suquía river Bajo Grande (BG)*
Moisture		20.94 ± 0.25	19.80 ± 0.83	21.00 ± 1.41	26.62 ± 3.85	16.70 ± 2.40	19.05 ± 0.78
NOM		0.88 ± 0.25	1.05 ± 0.14	1.18 ± 0.09	3.49 ± 0.46	3.80 ± 1.84	3.57 ± 0.09
Sample mar-05	1,2-DCB	<LOD	<LOD	<LOD	49.00	14.90	62.10
	1,3-DCB	<LOD	<LOD	<LOD	14.00	11.40	<LOD
	1,4-DCB	<LOD	<LOD	<LOD	20.20	<LOD	10.70
Sample may-05	1,2-DCB	<LOD	<LOD	<LOD	245.20	27.25	13.50
	1,3-DCB	<LOD	<LOD	<LOD	27.30	2.60	1.35
	1,4-DCB	<LOD	<LOD	<LOD	19.40	1.60	3.10
Sample jul-05	1,2-DCB	<LOD	<LOD	95.00	46.30	6.70	2.70
	1,3-DCB	<LOD	<LOD	12.00	2.20	1.20	<LOD
	1,4-DCB	<LOD	<LOD	6.30	3.27	2.45	1.85
Sample sep-05	1,2-DCB	<LOD	<LOD	<LOD	7.22	18.25	3.70
	1,3-DCB	<LOD	<LOD	<LOD	19.00	7.45	0.80
	1,4-DCB	<LOD	<LOD	<LOD	10.35	764.70	6.50
Sample nov-05	1,2-DCB	<LOD	<LOD	<LOD	84.70	81.30	<LOD
	1,3-DCB	<LOD	<LOD	<LOD	73.60	55.00	15.40
	1,4-DCB	<LOD	<LOD	<LOD	44.70	57.00	13.20

Notes: Moisture is expressed as g 100 g^{-1} sediment (wet weight). NOM are informed as g 100 g^{-1} sediment (dry weight). DCBs are reported in µg kg^{-1} sediment (dry weight). (<LOD = below detection limit). Values are averaged over at least three replicates.

Moreover, samples of July correspond to the dry season, with almost no rain and the consequent low river flow, which causes temporal concentration of some compounds (Pesce and Wunderlin, 2000; Wunderlin et al., 2001), as demonstrated by Pesce and Wunderlin (2000) using Water Quality Index (WQI). Water quality of Suquía River shows statistical significant temporal changes from wet to dry season, mainly in those monitoring stations located downstream from sewage input (Bajo Grande: wet season: WQI = 56 ± 6, dry season: WQI = 47 ± 6). The presence of DCBs in Ceballos River during the dry season could imply some degree of pollution, even at this station located close downstream to a natural reserve. It should be mentioned that the reservoir formed by streams Colanchanga and Los Hornillos (La Quebrada dam) could be acting as a concentrator of DCBs arising from a small village located upstream, on the side of Colanchanga stream.

An even worse situation was found when analysing water and sediment from El Diquecito, which is located on the main course of Suquía River upstream from Córdoba city (Figure 1). El Diquecito was previously reported with less pollution level (Pesce and Wunderlin, 2000; Wunderlin et al., 2001), but it exhibits variable amounts of DCBs in both water and sediment throughout the studied period, showing the highest DCBs concentrations in the sediment (Table 2 and Table 3). From Figure 1, it can be seen that this station is also located downstream to San Roque dam, receiving the water from San Antonio River and Cosquín River, which are surrounded by many cities.

If it is considered that there are no important human activities between San Roque dam and El Diquecito, the presence of DCBs in this station should be attributed to pollution arising from San Roque reservoir, which receives the product of human activities from upstream. This is a similar situation to those here discussed for Ceballos River station, where a reservoir could be concentrating pollutants produced either upstream or along its coasts. Furthermore, if it is considered that the sediment of El Diquecito is mainly constituted by sand, coated with a thin layer of NOM (ca. 3%, Table 3), it seems evident that this organic layer could be responsible for transporting DCBs downstream from their discharge or concentration point, thus spreading the pollution throughout the basin.

Additionally, it has been reported that native bacteria of the Suquía River are able to perform biodegradation of DCBs after acclimation period (Monferrán et al., 2005). Biodegradation of DCBs by native bacteria could explain why accumulation of these xenobiotics is not observed within the basin, although DCBs are being transported by the river, probably associated to NOM.

Finally, stations located at Isla de Los Patos (close to Córdoba downtown) and Bajo Grande (downstream from city effluent) presented high DCBs levels in both water and sediments (Figure 1, Table 2 and Table 3), confirming that these stations present high pollution within the studied basin area (Pesce and Wunderlin, 2000; Wunderlin et al., 2001; Amé et al., 2003; Nimptsch et al., 2005). Diquecito, Isla de Los Patos and Bajo Grande had samples with DCBs levels that did not exceed limits reported by other authors as having negative effects on the aquatic biota (19,900 µg kg^{-1} DW) (Table 2 and Table 3) (Malcolm, et al., 2004). Additionally, DCBs levels were higher in sediment than in water for most of the samples from these stations (Table 2 and Table 3). This is due to the fact that DCBs have low water solubility and high K_{oc} values. Furthermore, NOM values are in the range of 3% for these sediments, slightly greater than 1% measured in the tributaries upstream (Table 3), which show higher levels of pollution downstream. These last aspects evidence once more that DCBs are being absorbed in river sediment, probably associated with its NOM, which is consistent with the hydrophobic characteristic of these compounds (Wang and Lee, 1998) as well as their sorption to colloid particles in surface waters, or to the organic matrix of sediments (Rapp and Timmis, 1999). Volatile Suspended Solids (VSS) in water have been reported for the studied basin area, with values close to 0.006% (Diquecito = 60 ± 21 mg L^{-1}; Isla de los Patos = 41 ± 15 mg L^{-1}; Bajo Grande = 57 ± 32 mg L^{-1}) (Wunderlin et al., 2001). VSS are representative of organic matter suspended in water, evidencing that its amount in the studied basin area is far below the concentration on NOM in sediments (close to 3% in polluted areas). Thus, it is reasonable to find more DCBs in sediments that in water.

Further work is necessary to fully elucidate how different amounts and types of NOM could affect the absorption of DCBs to sediments.

Mean concentration of DCBs in water of Suquía River basin (1.84 µg L^{-1} 1,4-DCB and 6.33 µg L^{-1} 1,2-DCB) are comparable to values reported for river in heavily populated and/or industrialised areas. For instance, 0.6 µg L^{-1} 1,4-DCB and 5.0 µg L^{-1} 1,2-DCB have been reported in Besos River (Gomez Belichon et al., 1991). Similarly, 1,4-DCB has been reported in concentrations ranging from not detected to >10 µg L^{-1} in Ohio River basin (USA) (US EPA, 1985).

1,4-DCB has a range of domestic uses, namely as a moth repellent but more importantly, as a toilet block deodorant. It has also several industrial uses as an intermediate in dye and pesticide manufacture, also used in heat transfer media. Other DCBs have primarily industrial uses, though 1,2-DCB is used as a sewer and septic tank cleaner (Meharg et al., 2000). It is likely that the contribution of 1,4-DCB to the basin, with a peak during the dry season (Table 3), reflects the input of DCBs from domestic origin, which is consistent with previous reports pointing out 1,4-DCB as having the highest concentration in contemporary sewage sludge. However, the input of 1,2-DCB and 1,3-DCB is not understandable because there are not intensive industries located in the studied area. Thus, the presence of these two isomers could be due to reduction of highly chlorinated compounds, occurring in the sewage of cities located upstream on the basin (Fathepure et al., 1988), or directly in reservoirs (like San Roque and La Quebrada). The production of DCBs isomers from highly chlorinated compounds cannot be discarded because they are formed during the aerobic or anaerobic biodegradation of Pentachlorobenzenes (PCB), Hexachlorobenzenes (HCB) and Lindane in water and sediments. For instance Fathepure et al. (1988) reported that HCB could be reduced to Tetrachlorobenzenes (TCBs) and DCBs in anaerobic sewage sludge, arguing that HCB could be dechlorinated into TCBs and DCBs in sediments. Moreover, Beurskens et al. (1994) found that lower chlorinated benzenes, produced from HCB, appeared to accumulate in anaerobic sediments.

The other possible source for DCBs is atmospheric deposition, since they have been detected in the air in USA, Japan, The Netherlands, Canada and Italy (Wang et al., 1995). Atmospheric depositions may therefore provide an additional input of DCBs to the Suquía River basin. Further studies on the presence of DCBs in the atmosphere of the studied region are necessary to confirm this last possibility.

4 Conclusion

The optimised HS-SPME/GC-MS method provided us with a fast, precise, less expensive and solvent-free method, which can be applied to both water and sediment, allowing us to monitor the water quality of Suquía River basin, and denoting the presence of DCBs in some stations previously assumed as *quasi* pristine.

Most of DCBs found in Suquía River basin could be attributed to domestic origin; however, atmospheric deposition, and reduction from highly chlorinated compounds in either sewage or reservoirs could not be discarded. Once introduced to the stream, DCBs seem to associate to NOM present in water and sediment, enabling their concentration in reservoirs as well as their transport downstream from the source.

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