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Determination of polybrominated diphenyl ethers in water samples from Mendoza River Basin by HS-SPME-GC-MS/MS

Determinación de éteres difenil-polibromados en aguas superficiales de la cuenca del Río Mendoza mediante HS-SPME-GC-MS/MS

Nerina Belén Lana¹
Ariel Ramón Fontana¹

Nestor Fernando Ciocco^{2,3}
Jorgelina Cecilia Altamirano^{1,2*}

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) are considered persistent organic pollutants because of their ubiquity, persistence and bioaccumulation. Its harmful effects on human health and the environment, has led to its inclusion of the Stockholm Convention. Little information is found about PBDEs in abiotic systems of the South America in open literature. This paper reports the presence and concentration level of four PBDEs congeners in Mendoza River, Argentina. The selected PBDEs were: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100) and 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153). The analytical methodology used was head space-solid phase micro extraction combined with gas chromatography-mass spectrometry (HS-SPME-GC-MS/MS). Several variables, including pH, salting out,

RESUMEN

Los éteres difenil-polibromados (PBDEs) son considerados contaminantes orgánicos persistentes debido a su ubicuidad, persistencia y capacidad de bioacumulación. Sus efectos nocivos sobre la salud humana y el ambiente, han motivado su inclusión en el Convenio de Estocolmo. Poca información se dispone en la bibliografía internacional sobre la presencia de PBDEs en los sistemas ambientales de Sudamérica. Este trabajo reporta la distribución y niveles de concentración de cuatro congéneres de PBDEs en la cuenca del Río Mendoza, Argentina. Los congéneres seleccionados fueron: 2,2',4,4'-tetrabromodifenil éter (BDE-47), 2,2',4,4',5-pentabromodifenil éter (BDE-99), 2,2',4,4',6-pentabromodifenil éter (BDE-100) y 2,2',4,4',5,5'-hexabromodifenil éter (BDE-153). La metodología analítica es la microextracción en fase sólida en espacio de cabeza seguida de cromatografía gaseosa con detección de masas (HS-SPME-GC-MS/MS). Variables

1 Grupo de Investigación y Desarrollo en Química Analítica (QUIANID), (Laboratorio de Investigaciones y Servicios Ambientales Mendoza -LISAMEN-, Centro Científico Tecnológico -CCT-, Consejo Nacional de Investigaciones Científicas y Técnicas - CONICET- Mendoza). Av. Ruiz Leal s/n. Parque General San Martín. (5500) Mendoza. Argentina.

2 Instituto de Ciencias Básicas (ICB). UNCuyo. Centro Universitario. Mendoza, Argentina. M5502JMA.

3 Instituto Argentino de Investigaciones de las Zonas Áridas (IADIZA). CCT CONICET-Mendoza, Argentina.

* Correspondencia del autor: Jorgelina C. Altamirano. Tel.: +54 261 524 4064; fax: +54 261 524 4001. E-mail: jaltamirano@mendoza-conicet.gov.ar

extraction technique type and extraction time were studied and optimized over the relative response the target analytes. The precision of HS-SPME-GC-MS/MS evaluated over five replicate, leading RSDs values <13%, detection limits (S/N=3) ranging from 0.03 pg ml⁻¹ to 0.12 pg ml⁻¹ and the calibration graph was linear with r²=0.9959. BDE-47 and BDE-100 were the predominant congeners found in the analyzed samples. Their concentrations ranged from not detected to 1.9 pg ml⁻¹ and to 0.5 pg ml⁻¹, respectively.

tales como pH, fuerza iónica, tipo, tiempo y temperatura de extracción fueron estudiadas y optimizadas. La precisión de HS-SPME-GC-MS/MS fue de RSD <13%, los límites de detección (S/N=3) se establecieron en el intervalo de 0,03 pg ml⁻¹ a 0,12 pg ml⁻¹ y la curva de calibración tuvo un r²=0,9959. BDE-47 y BDE-100 fueron los congéneres predominantes encontrados en las muestras de agua analizadas cuyas concentraciones máximas fueron 1,9 pg ml⁻¹ y 0,5 pg ml⁻¹, respectivamente.

Keywords

brominated flame retardants • head space-solid phase micro extraction • polybrominated diphenyl ethers • water monitoring

Palabras clave

retardantes de llama bromados • micro-extracción en fase sólida en espacio de cabeza • éteres difenil-polibromados • monitoreo de aguas

INTRODUCTION

Brominated flame retardants (BFRs) are chemical compounds used in most types of polymers applied to electronic equipment, plastics, textiles, building materials, carpets, vehicles and aircrafts (3). They are used to prevent ignition of the polymer and to slow the initial phase of combustion. BFRs constitute 5-30 wt % of the total mass of the polymer product (30). Organohalogenated flame retardant are the most commonly used in the polymer industry due to their remarkable efficiency to capture free radicals, which are essential for the flames spread (2). Their production and use scale have increased notoriously. In 1990 global production of BFR was 145 000 tones, while in 2000 grew to over 310 000 tones, which represents a growth over 100% with regard to the 90's decade (2). However, due to its harmful effects on human health and environment, they were incorporated into the list of persistent organic pollutant (POPs) in the Stockholm Convention (36).

PBDEs have been used extensively over the past two decades as additive BFRs. Due to their additive role in the polymeric mass, they are easily released to the atmosphere during the manufacturing process and later, during their use and after been discards as waste. Thus, their emission is diffuse and difficult to control (3). The similarity in molecular structure with polychlorinated biphenyl (PCBs), and their resistance to environmental degradative process (27), gives rise to concern that they may lead to similar environmental contamination problems (39, 40, 41). These evidences have motivated many countries to prohibit their use, sale and importation of tetra-, penta- and hexa-diphenylether congeners as well as mixtures, polymers and resins containing these substances (1, 7).

Due to their physicochemical properties, PBDEs have affinity to particulate matter; therefore they can potentially be transported in the atmosphere and water across long

distance (11). Although the presence PBDEs is associated with highly industrialized and urbanized areas, it has been detected in organisms of the Antarctic and Arctic regions, confirming their transport and distribution worldwide (10). PBDEs presence has been detected in environmental samples as water samples, sediments, sludge and effluent (23, 27, 29, 35). Also, they have been determined in breast milk samples, human adipose tissue and serum (31, 42), where they can easily be accumulated due to its non-polar character.

Additionally, concern for this persistent pollutant is enhanced by their toxicological effects. Among the effects on human health is to act as endocrine disruptor, specifically on the thyroid system (16). It is also suspected of acting as a carcinogenic agent, through non-mutagenic mechanisms (17). Other effects include significant changes in the homeostasis of the thyroid gland (16, 25, 47), effects on the endocrine system (8, 9) and similar effects on the estrogen receptors to those produced by the dioxins (5).

The available information about PBDEs concentration in environmental systems of South America is very scarce and includes PBDEs presence in salmon and air samples from Chile (26, 33) and skipjack tuna and human breast adipose tissue from Brazil (20, 44). Nevertheless there is not information about PBDEs in Argentinean environment.

Sample preparation plays an important role in the determination of PBDEs in environmental samples because of the matrixes complexity and the low concentration of these analytes. Highly selective and sensitive analytical techniques are required for their unequivocal identification and determination. In this way, head space-solid phase extraction (SPME) combined to capillary gas chromatography with electron-capture (ECD) or mass spectrometry (MS) detection are the chosen techniques for this type of analysis (32). In order to optimize the extraction technique, some variables were studied including extraction temperature and time, extraction pH and sample salting out. These studies lead to an adjustment of the SPME technique for extraction of PBDEs in natural water samples.

Therefore, the aim of the present work was to develop sensitive and selective analytical techniques for the determination of PBDEs in environmental samples as well as investigate its presence and distribution in the ecosystems of Mendoza province. In this sense, surface water samples of the north oases of Mendoza province, which is irrigated by Mendoza River, tributaries and irrigation waterways were analyzed. North oases concentrated 64.5% of the provincial population (45) and its water is used mainly for farming and urban consumption (12), so their quality is very important because it may impact on the population and the environment.

MATERIAL AND METHODS

Reagents

The selected PBDEs for this work were the most commonly found in natural water samples: BDE-47, BDE-99, BDE-100 and BDE-153 (27, 29). The standards of these polybrominated diphenyl ethers were purchased from Accustandard (New Haven, CT,

USA) in isooctane. The PBDEs standards were stored tightly closed in the dark at -14°C . Stock solutions of PBDEs were prepared in methanol at concentration levels of $1\ \mu\text{g mL}^{-1}$. Further dilutions were prepared weekly in methanol and stored in brown bottles. Methanol, sodium chloride and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Sodium hydroxide was obtained from Sigma–Aldrich (Steinheim, Germany). Ultrapure water ($18\text{M}\Omega\ \text{cm}$) was purchased from a Milli-Q water purification system (Millipore, Paris, France). All reagents were of analytical grade or above.

The SPME manual holder and $30\ \mu\text{m}$ film thickness polydimethylsiloxane (PDMS) fibers were obtained from Supelco (Bellefonte, PA, USA). The fibers were conditioned in the GC injection port as recommended by the manufacturer.

Studied area

Mendoza province is located at the center west of Argentina ($32^{\circ}\text{--}38^{\circ}\ \text{S}$, $66^{\circ}\ 30'\text{--}70^{\circ}\ 30'\ \text{W}$) and it has a total area of $150\ 839\ \text{km}^2$. The territory is structured following a pattern that distinguishes between two subregions: irrigated oases and non-irrigated lands. The productive and commercial activity is located at the oases of the province: north, center and south. The north oases (Mendoza City, Guaymallén, Godoy Cruz, Las Heras, Maipú and Lujan de Cuyo areas) is the most densely populated with a total of 986 341 inhabitants (19). This area is irrigated by the Mendoza River, tributary rivers and irrigation waterways (figure 1).

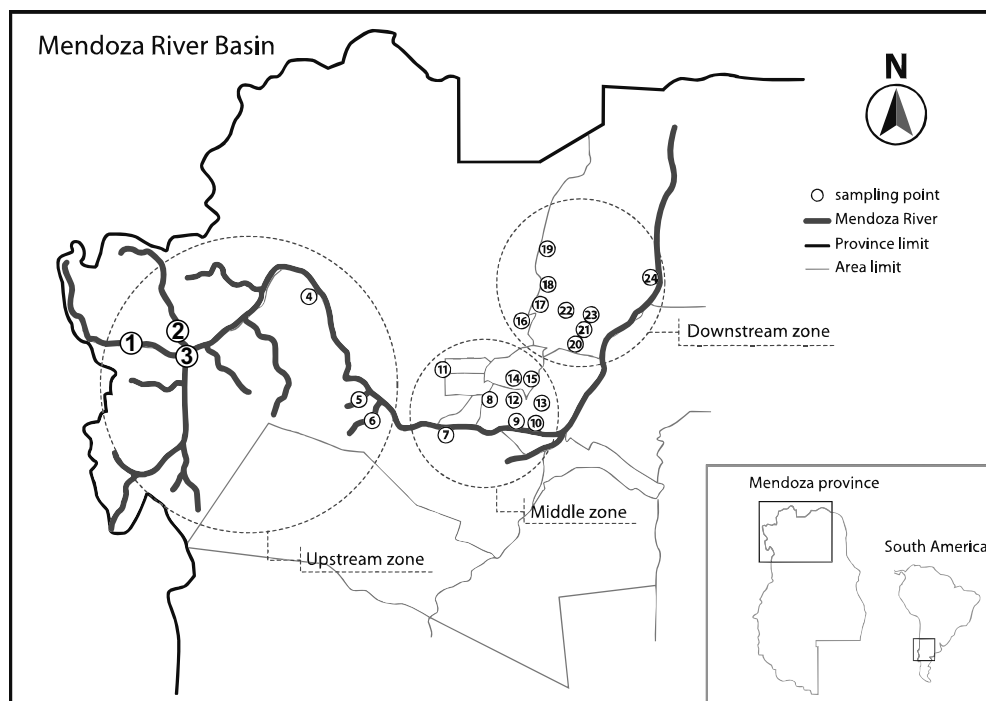


Figure 1. North oases of Mendoza Province. Mendoza River and tributaries rivers are indicated in the map. Circles indicate monitored water sites.

Mendoza River is 300 km long and runs from the Andean Mountains (about 6962 m a.s.l.) to the Eastern flat plains of Mendoza Province (about 600 m a.s.l.). Its headwater is situated between the Aconcagua Mountain and the Tupungato volcano (Northwestern Mendoza Province). It ends in the Guanacache wetland (630 m a.s.l.) on the North-East side of Mendoza Province. Mendoza River has an average flow rate of $50.03 \text{ m}^3 \text{ s}^{-1}$ (38) (figure 2) and it is originated by the confluence of Las Cuevas, Tupungato and Vacas rivers.

Sampling was conducted in the period 2007-2008 and included two consecutive seasons at beginning of the thaw period (figure 2), and when the province registers the maximum productive activity. The monitoring program includes different zones with differential anthropogenic activities. The zones considered were the following one: upstream zone: rural and sub urban areas, middle zone: great Mendoza and the downstream zone: rural area (figure 1, page 88). Twenty four sampling stations were monitored and three samples were collected in each sampling point. The water samples were collected in 1 L brown bottles at a depth of 20 cm against the flow current of the river. Samples were immediately refrigerated at 4°C and analyzed within the week. Caution was taken to minimize contamination at all levels of sample collection and handling.

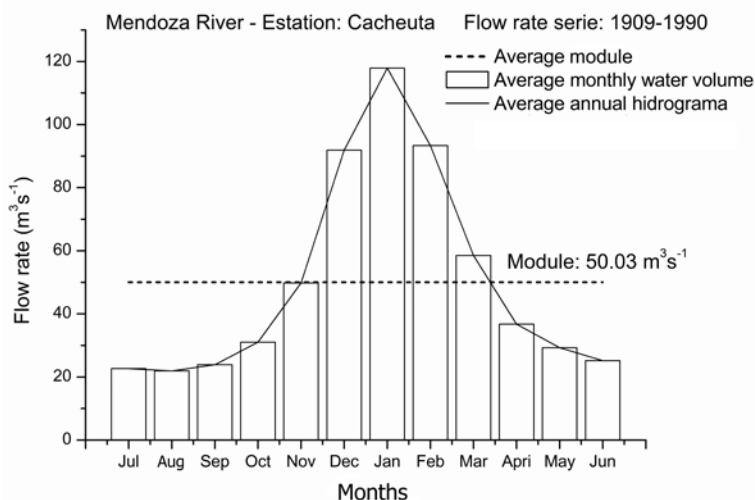


Figure 2. Hidrogram of Mendoza River.

Sample preparation and analysis

Water samples were accomplished by standards addition method. Ten milliliters of water sample were filtered ($0.45 \mu\text{m}$ pore size) and placed into a 20 mL headspace vials. One milliliter 6.15 mol L^{-1} sodium chloride and $50 \mu\text{L}$ methanol were added and mixed up and the pH was adjusted to ca. 7. The vial was finally sealed with a headspace cap isolated by a teflon-faced septum. The vial was thermostated at 90°C during 5 min prior exposing the PDMS fiber while it was magnetically stirred at 1000 rpm. The fiber was exposed into the head space of the sampling vial during 20 min. Fiber desorption was carried out into GC injector port before chromatographic analysis.

Instrumental analysis

GC-MS/MS analyses were carried on a Varian 3900 gas chromatograph equipped with Varian Saturn 2000 ion trap mass detector (Varian, Walnut Creek, CA, USA). The system was operated by Saturn GC-MS WorkStation v6.4.1 software. The GC column used was VF-5ms (30m×0.25 mm, 0.25µm film thickness; Varian, Lake Forest, CA, USA). The temperature program was: 150°C, held 1 min; rating 15°C min⁻¹ to 250°C; rating 10°C min⁻¹ to a final temperature of 300°C and held for 7 min. Helium (purity 99.999%) was used as a carrier gas at flow rate of 1.0 mL min⁻¹. The injector temperature was set at 250°C and the injections were carried out in splitless mode. Three minutes assured a complete desorption of the analytes and no carry over effect was observed in the following injections. The mass spectrometer was operated in electron impact ionization mode at 70 eV. The trap, manifold and transfer line temperatures were set at 220°C, 50°C and 280°C, respectively. Samples were analyzed in MS/MS mode. The peak identification was based on the base ion and the isotopic pattern of each PBDEs congener in the MS/MS spectra. Base ion was selected as a quantitative ion, while the other ions were used as qualifiers (table 1).

Table 1. GC-MS-SIR parameters for PBDE determination.

Analytes	t_R' (min)	Target ion (m/z)	Confirmation ions (m/z)	logK _{ow} (6)
BDE-47	9.9	486	324,326,328	6.81
BDE-100	11.2	564	402,404,406	7.24
BDE-99	11.6	564	402,404,406	7.32
BDE-153	13.3	644	482,484,486	7.90

t_R' : Times retention

logK_{ow}: octanol/water partition coefficient

RESULTS

Analytical performance

The limits of detection (LODs) of the analytes for 10 mL sample volume were calculated based on background noise as three times the standard deviation of the blank. The LODs ranged from 0.04 pg mL⁻¹, 0.03 pg mL⁻¹, 0.04 pg mL⁻¹ and 0.12 pg mL⁻¹ for BDE-47, BDE-100, BDE-99 and BDE-153, respectively. The precision of HS-SPME-GC-MS/MS evaluated over five replicate, leading RSDs values <13%. The calibration graph was linear with a correlation coefficient of 0.9959 at levels near the quantification limits and up to at least 5 pg mL⁻¹ for each congener. There is no certified references material commercially available for PBDE in natural water samples. Therefore, the method robustness was evaluated through a recovery study at two concentration levels (5 and 25 pg mL⁻¹). This study led to a satisfactory robustness achieving recoveries ≥ 95 %.

Study and optimization of HS-SPME variables

Ten milliliters aqueous solution containing 1 µg L⁻¹ of each PBDE was used to carry out the study of the analytical variables of the extraction technique. The assays were done by duplicate. The HS-SPME procedure was the one described above. From this study it was found necessary to adjust the salt concentration of the samples and to set up an optimum extraction time. The salting out study was carried out by adding

different volumes (0.1 - 1.5 mL) of 6.15 mol L⁻¹ sodium chloride to the sample prior HS-SPME. From figure 3a it is possible to observe that the best relative response for all studied PBDEs was achieved when 1 mL 6.15 mol L⁻¹ sodium chloride was added to the sample. SPME operational procedure was defined by comparing two different approaches. The maximum relative response values for all PBDEs were achieved when the extraction was carried out at 90°C for 18 min, remaining invariant at higher extraction temperatures and longer extraction time. Therefore, 90°C extraction temperature and 20 min extraction time were chosen as working conditions (figure 3b). The effect of the sample pH was investigated since it can affect the affinity of PBDEs for the matrix concomitants and thus, the extraction efficiency of SPME. Therefore, it was found interesting to study the pH effect on the extraction efficiency of the SPME technique. The studied pH range was 3-10 and it was adjusted by adding hydrochloric acid or sodium hydroxide solutions. From the results it was possible to observe that the relative responses of the studied PBDEs reported higher values within the pH 6-8 (figure 3c). Therefore, in order to get higher relatives responses and lower matrix effects, sample pH was adjusting within this range for further studies.

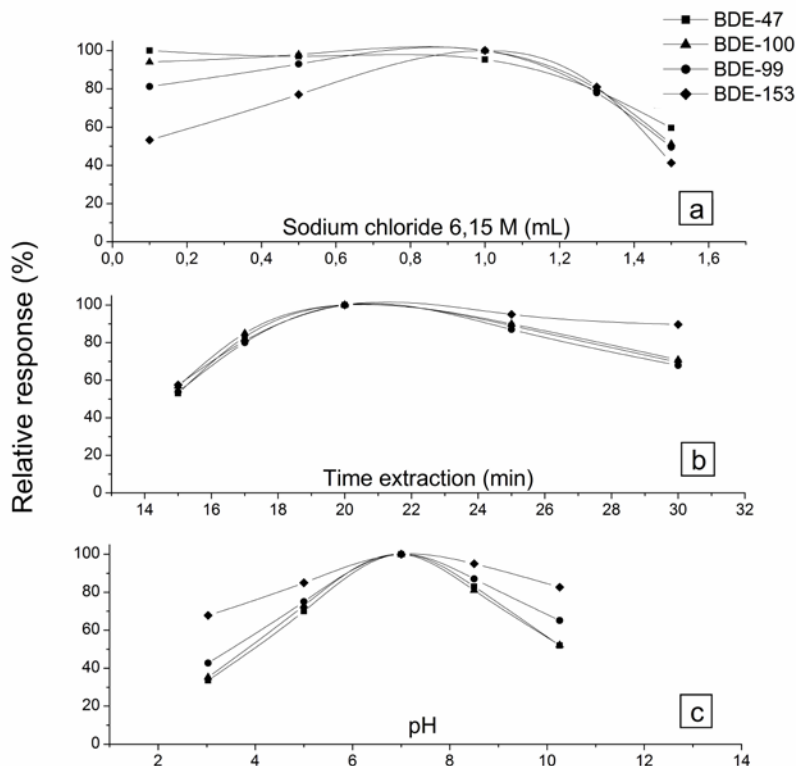


Figure 3. Optimization of HS-SPME technique for determining PBDE by HS-SPME-GC-MS/MS. a) 6.15 mol L⁻¹ sodium chloride volume, b) Extraction time and c) Sample pH effect on the analytical response of the studied PBDEs. Extraction conditions: sample volume, 10 ml; 50 μ l methanol; 1 ml of 6.15 mol L⁻¹ NaCl (except for a), extraction time: 20 min (except for b) and pH ca. 7 (except for c). Extraction temperature: 90°C.

PBDEs in environmental water samples**Table 2.** Concentration of PBDEs in water samples of Mendoza River, tributary rivers and irrigation waterways (pg mL⁻¹).

Ref.	Location	Description	December-2007				March-2008				Total
			BDE-47	BDE-100	BDE-99	BDE-153	BDE-47	BDE-100	BDE-99	BDE-153	
1	S32.81318 W70.04649	Cuevas River	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
2	S32.84700 W69.76283	Vacas River	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
3	S32.82725 W69.70364	Mendoza River	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
4	S32.67007 W69.36458	Uspallata stream	0.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.4
5	S32.95431 W69.30006	El Salto	0.3	n.d	n.d	<0.4	n.d	n.d	n.d	n.d	0.3
6	S32.99198 W69.25247	Blanco River	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
7	S33.05087 W68.93795	Chipoletti Dike	0.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.4
8	S32.95359 W68.82264	Hijuela Pereyra	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
9	S32.58997 W69.35101	Naciente waterway	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
10	S33.03933 W68.77790	Chachingo waterway	0.4	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.4
11	S32.89279 W68.87789	Civit waterway	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
12	S32.93857 W68.77093	Pescara y R. Peña upstream	0.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.2
13	S32.90786 W68.74272	Negro stream	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
14	S32.94951 W68.72665	Pescara	n.d	n.d	n.d	n.d	n.d	0.2	n.d	n.d	0.2
15	S32.91567 W68.68746	Pescara waterway	0.5	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.5
16	S32.73433 W68.68926	Fernández stream	0.9	n.d	n.d	0.6	n.d	n.d	n.d	n.d	1.5
17	S32.71521 W68.66514	Moyano wastewater	1.9	0.5	n.d	n.d	n.d	n.d	n.d	n.d	2.4
18	S32.69030 W68.66073	Jocolí waterway	1.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.2
19	S32.58981 W68.64213	Jocolí-Collector final	<0.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
20	S32.86953 W68.64094	Aux. Tulumaya I	0.2	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.2
21	S32.72242 W68.60489	Aux. Tulumaya II	0.1	n.d	<0.1	n.d	n.d	n.d	n.d	n.d	0.1
22	S32.83047 W68.68259	Aux. Tulumaya III	1.1	n.d	n.d	n.d	n.d	n.d	n.d	n.d	1.1
23	S32.72562 W68.56927	Santos Lugares	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	--
24	S32.64935 W68.32083	Col final C. Araujo	0.3	0.1	0.3	n.d	n.d	n.d	n.d	n.d	0.7

LOD = Limit of detections: 0.04 pg mL⁻¹; 0.03 pg mL⁻¹; 0.04 pg mL⁻¹; 0.1 pg mL⁻¹
for BDE-47, BDE-100, BDE-99 and BDE-153
n.d = not detected

Total PBDEs were detected in water samples at concentrations levels ranging from “not detected” to 1.9 pg mL⁻¹. Table 2 (page 92) shows individual PBDE average concentrations in studied natural water samples. The most abundant PBDE congeners were BDE-47 and BDE-100.

The major concentrations for the monitoring program were associated with the middle zone (Ref 15; table 2 and figure 1, page 88) and the downstream zone (Ref 16, 17, 18 and 22; table 2 and figure 1). The highest result for upstream zone was Uspallata stream (Ref 4, table 2 and figure 1), where BDE-47 was found in a concentration level of 0.4 pg mL⁻¹.

DISCUSSIONS

HS-SPME working condition

The extraction efficiency of HS-SPME technique can be affected by several variables, including pH, salting out, extraction technique type and extraction time. Due to the PBDEs nature, it is to be expected that the sample pH would not affect the extraction efficiency of the PBDEs. However, in this study, it was found important to adjust the sample pH in order to achieve the maximum analytical response of the extraction technique. This phenomenon was observed in several different natural water samples assayed. It could be possible that at neutral and alkaline sample pH, the effect of other naturally present concomitant are suppressed enhancing the analytical response of PBDEs. Similar results were reported by Tian and Feng (43) and Labadie *et al.* (21), who informed that the extraction efficiency did not increase at low or high pH but increased suddenly at neutral pH.

By increasing the salt concentration the extraction efficiency of the SPME technique is affected by upsetting the affinity of the analyte for the sample (13). Additionally, as the salt concentration of the medium increases, the viscosity increase; diminishing thus, the efficiency of the mass-transfer process and consequently, the extraction efficiency of the technique (32, 34). The literature reports discrepancies about the salting out effect on the extraction efficiency of PBDEs from aqueous samples (4, 13, 21). In the ion concentration study carried out in this work, it was observed that it was necessary to increase the sodium chloride concentration in order to achieve the best relative response of the studied PBDEs. However, excessively high salt concentration led to a decrement of the PBDEs analytical signal.

In addition to adjusting pH and rising ionic strength of the sample, 50 µl of MeOH were added in order to reproduce the experimental conditions of the calibration curve.

The SPME operational procedure study was carried out by comparing two different approaches. The first one was carried out at room temperature and the mass-transfer process was assisted by using an ultrasound bath. The analytical response was studied within 20-30 min time frame. The best relative response values for all PBDEs were observed at 30 min extraction time. The second approach was carried out in the conventional way. The extraction temperature was set and kept at 90°C (13) and the sample was

magnetically stirring (1000 rpm) to favor the mass-transfer process from the aqueous bulk to the gas phase. The analytical response was studied within 15-30 min time frame. By comparing the best results obtained with each approach, the highest relative response values for all studied PBDE were those obtained by using an extraction temperature of 90°C and 20 min extraction time (fiber exposition time) (figure 3b, page 91).

PBDEs in Mendoza environment

This is the first study that reports the presence of PBDEs in Argentinean Rivers, and in particular in Mendoza River basin. BDE-47 is generally reported as the most abundant congener in environmental water samples according with worldwide bibliography (15, 18). This fact can be explained taking into account the polarity of the compounds. Lower bromination degree turns PBDEs into more polar compound compared to higher brominated one (6, 46) (table 1, page 90). Thus, their abundance in environmental water samples is higher as it diminishes the number of present bromines in the molecular structure. The main geographical sites where PBDEs have been found are associated with downstream of the industrialized and urbanized areas (figure 1-page 88- and table 2-page 92-). Nevertheless PBDEs presence has been detected in upstream zone like Uspallata stream (Ref. 4; table 2). Uspallata stream crosses Uspallata village, which is located in a high mountain area and has a permanent population of 3437 inhabitants (19). The village is a touristic and non industrialized city. Therefore, the presences of detectable levels of PBDEs in Uspallata stream could be due the contribution of landfills sites. Additionally, due to PBDEs physicochemical properties; they would undergo long-range atmospheric transport to even remote regions of the world. In this sense, some authors say that atmospheric transport would be one of the main sources of PBDEs input to the ecosystem (14, 37).

In the middle zone (Ref 7-15) PBDEs presence was associated with areas close to industrial parks. An example of this is Chipoletti Dike (Ref. 7) which is a dam that regulates the Mendoza River's flow. It is located at 2 km downstream from Lujan's industrial park, and collects the industrial effluent of this area. Pescara waterway (Ref. 12 and 14; table 2) is an artificial channel destined for the superficial outlet for industrial collector and irrigation water. Approximately 60 industrial establishments of the industrial park unload their wastewater to the collector (28). The channel is 15 km long and starts in Maipu area. It goes all the way down to Guaymallén area, where it connects to Aux Tulumaya (Ref. 20, 21 and 22) and both end in Lavalle area.

The downstream zone receives the rain, surface, industrial wastewater and agricultural discharges of the whole metropolitan area, and thus reports higher contamination level (24). Moyano wastewater and Jocoli waterway (Ref. 16 and 17 respectively) are the collector channels that receive sewage water of treatment plants. According to Law *et al.* (22) sewage sludge is considered to be one of the main matrixes that accumulate PBDEs. Even do, the values found in this work are far below those mentioned in the international bibliography (27) probably due to the minor levels of industrialization. The Jocolí and Cuádruple Comparto waterway (Ref. 17 and 18, table 2, respectively) present the major levels of PBDEs concentration. This area of Mendoza River constitutes waterway irrigation of the downstream areas basin and receives urban, industrialized and rural wastewater streams.

CONCLUSIONS

The extraction technique, HS-SPME constitutes a simple and efficient analytical technique for PBDEs analysis at trace levels in environmental water samples. Although some works used this technique for the PBDEs analysis, there is scarce information about the specific-variables behavior in those scientific works. Therefore, this work is a contribution for analytical aspects related to the analysis PBDEs in real water samples. This methodology requires minimum sample manipulation, organic solvents consumption and increases sample throughput of the analysis. The method performs well achieving good linearity, precision and low detection limits.

Despite the comprehensive international environmental legislation frame work on POPs, there is scarce information about BFRs in Argentinean environment. PBDEs were suspected to be found in Argentinean ecosystems since many polymeric materials are used domestically and industrially in our country. Additionally, it is well known that they can be easily transported by the particulate matter of water and air streams reaching distant region from their emission source.

This study contributes the report of the water quality of the main river of the metropolitan Mendoza area. It is the first time that it was studied and reported the presence of these persistent pollutants in the Argentina. Thus, it is an important contribution in environmental matter. Based on the reported results, detailed studies including seasonal variations and dynamic pollution mechanisms are recommended to carry out in this region.

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