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Sediment physicochemical properties condition pollutant association: a multivariate study of polybrominated diphenyl ethers on the Mendoza River irrigation areas

Propiedades físico-químicas de sedimentos condicionan la asociación de contaminantes: un estudio multivariado de éteres bifenilos polibromados en áreas de irrigación del Río Mendoza

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ABSTRACT

This work is a multidisciplinary environmental study that provides new insights into the relationships between sediment-organic matter characteristics and polybrominated diphenyl ethers (PBDEs) concentration. The aim of the present multivariate study was to correlate factors influencing PBDEs accumulation in sediment by using principal component analysis (PCA). Organic matter studies by Fourier Transform-Infrared spectroscopy and physicochemical analyses (Total Organic Carbon, pH, electrical conductivity) of sediment samples were considered for PCA. Samples were collected from an artificial irrigation network on the Mendoza River irrigation areas. PCA provided a comprehensive analysis of the studied variables, identifying two components that explained 63% of the data variance. Those factors were mainly associated to organic matter degradation degree, which represent a new insight into the relationships between organic

RESUMEN

Este trabajo es un estudio ambiental multidisciplinario que proporciona nuevos conocimientos sobre las relaciones entre las características de la materia orgánica presente en sedimentos y la concentración de éteres difenilos polibromados (PBDEs). Se buscó correlacionar características físico-químicas de muestras de sedimento usando análisis de componentes principales (PCA). Las muestras fueron caracterizadas por su contenido de materia orgánica total, pH y conductividad eléctrica. Adicionalmente, la materia orgánica de dichas muestras fue analizada mediante Espectroscopía de Infrarrojos con Transformada de Fourier. Las muestras fueron colectadas en diferentes canales de irrigación de la red alimentada por el Río Mendoza. El PCA proporcionó un análisis exhaustivo de las variables estudiadas y su vinculación, resultando dos componentes que explicarían el 63% de la varianza de los datos. Ambas componentes se

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matter in sediments and PBDEs fate. In this sense it was possible to determine that not only the content but also the type of organic matter (chemical structure) could be relevant when evaluating PBDEs accumulation and transport in the environment. Typification of organic matter may be a useful tool to predict more feasible areas where PBDE, may accumulate, as well as sediment transportation capability.

asociaron al estado de degradación de la materia orgánica. En este sentido, fue posible determinar que tanto la cantidad de materia orgánica de los sedimentos como el tipo (estructura química) de materia orgánica estarían condicionando la acumulación y el transporte de PBDEs en el ambiente. A partir de los resultados es posible proponer a la tipificación de la materia orgánica de sedimento como herramienta útil y efectiva para predecir áreas donde es más factible que se acumule PBDE, así como la capacidad de transporte en los sedimentos.

Keywords

Sediment • organic matter • POPs • PBDEs

Palabras clave

sedimento • materia orgánica • POPs • PBDEs

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used in commercial flame retardants polymer additives. They constitute a family of 209 congeners with a different number and position of bromine atoms on a biphenyl ether structure, being *deca*-BDE the most brominated. PBDEs were used extensively over the past two decades in most types of polymers designed for electronic equipment, plastics, textiles, building materials, carpets, vehicles, aircrafts, etc. PBDEs can be easily released into the environment during the products lifetime, and after final disposal, since they are not covalently linked to the polymer structure. *Penta*- and *octa*-BDE commercial mixtures are listed in the Stockholm Convention (34). They have become an issue of global concern due to their environmental ubiquity and persistence (7, 30), as well as to their adverse effects on wildlife and human health (6). Due to their physicochemical properties and low decomposition rate, persistent organic pollutants (POPs) including PBDEs are transported over long distances and/or widely dispersed into the environment after released. This transport can be accomplished through atmospheric and/or water flows as a gas phase and/or associated to particulate matter (35). PBDEs present potential for bioaccumulation and biomagnification through food chains, resulting a threat to the environment and human health. These pollutants can reach the aquatic environment from primary or secondary sources by association, due to their a-polar character, with organic matter of sediments and/or lipids of organisms (22).

Soils and sediments are important to the global environmental cycle of PBDEs. This subject results of relevance since it could help to predict fate, distribution and/or accumulation, as well as bioavailability patterns in the aquatic environment, and consequently, could contribute to prevent or mitigate risks to environmental compartment (3). Literature reports that physicochemical properties of sediment might condition the accumulation of POPs, including PBDEs (4, 25, 33). However, there are discrepancies on the report results, which shows that some aspects in this regards still remain unclear. In this sense, Ramu *et al.* (2010) and Zhao *et al.* (2011) found positive correlations between

PBDE concentration and sediment total organic content (TOC) suggesting that organic matter plays an important role in the transport and trapping processes of these types of pollutants (29, 37). On the other hand, Chen *et al.* (2009) and Miglioranza *et al.* (2013) found low correlation between PBDE and TOC. As it is well known, humic substances are the main content of organic matter present in sediments (25) and are reported to play a significant role in POPs accumulation process since they condition their sorption. Moreover, several organic matter, including aromatic content, aliphatic content, polarity and molecular weight have also been reported to affect PBDEs sorption (27). These organic matter characteristics could be conditioned by physicochemical properties of the sediment, such as pH, and thus, affect PBDEs accumulation (1).

Urban settlements, industries and dams are recognized as potential sources of PBDEs to the environment. Mendoza Province is located in the Andean piedmont and characterized by arid climatic conditions, with a regime of summer rainfalls of 250 mm per year. It is cut across by three fluvial systems, which are constituted by one or two rivers with their headwaters located in the high Andes Cordillera: Mendoza River and Tunuyán River and on the other hand the Diamante and Atuel Rivers, respectively. River water discharges depend on the glacial melting and mainly winter precipitation of Pacific origin.

The mentioned rivers give origin to three Oases: Northern, Valle de Uco and Southern, respectively. They are defined by an artificial network of irrigation channels and ditches. Mendoza River is an endorheic basin that drains into Guanacache lagoon after traveling about 330 kilometers from the source. It is one of the most important rivers of the Cuyo region (ca. 150,839 km², ca. 50 m³ s⁻¹), and it is used as the main water source for human consumption of the fourth largest city of the country (over 1,050,000 people with 2426.3 habitants km⁻²), hydroelectric power generation as well as for agriculture and industrial activities of Mendoza (32°53'00" S 68°49'00" W). Besides the desert character of the region, the metropolis is known for grove streets and avenues which are irrigated by a specific set of open artificial ditches.

As mentioned before, the water provision and distribution for these activities is accomplished by an artificial network of irrigation channels and ditches. Since the network extension has been designed according the natural altitudinal gradient, surplus flows can re-enter the system after leaving the city and be used for agricultural purposes.

The remaining flow plays an important role in preserving water level of Guanacache lagoons. Provincial economy is characterized by the production and processing of agricultural products. Its capital, Mendoza, was internationally acknowledged, together with other nine renowned regions, as a Great Wine Capital due to the outstanding role of the wine in the economy and cultural asset.

The aim of the present multivariate study was to correlate factors influencing PBDE accumulation in sediment by using principal component analysis (PCA). For this purpose several analysis of the sediment, including organic matter studies by Fourier Transform-Infrared (FT-IR) spectroscopy and physicochemical analyses (TOC, pH, electrical conductivity), were carried out.

Semi-quantitative determinations of functional groups by FT-IR spectrometry, traditionally used in geochemical studies of sedimentary organic materials *e.g.*, coals, kerogen and coalified fossil compressions (9, 26), is a useful tool for assessing the maturation (degradation) degree of the organic matter (20). Samples were collected from an artificial irrigation network of the fourth most populated city of Argentina, Mendoza. Mendoza River basin was previously studied for the fate and concentration of PBDEs (12, 16, 17) reporting maximum values of 0.32 ng g⁻¹ dry weight (d.w.) in sediments. These studies were considered for selecting the sampling points.

MATERIALS AND METHODS

Studied area and sample collection

The studied area, the Northern Oasis irrigated by Mendoza River (figure 1, page 61), was previously explored for PBDEs fate and concentration (12, 16, 17). Based on these reports fifteen locations from the artificial network of irrigation channels and ditches following an altitudinal gradient (881 - 583 meters above sea level) were sampled. Additionally, it is worth to mention that the elevation difference between sampling points considered in this work diminish as the network progresses.

Urban settlements (U), industrial (I) and farming (F) activities, as well as their combination, were considered for sampling point selection (table 1, page 62). Three bottom sediment (0-10 cm deep) sub-samples (200 cm³ each) were collected from the edge of channels and/or ditches at 15 sites using a non-commercial sediment sampler (stainless steel ladle). They were per site integrated in a 600 cm³ brown flask and transported at 4°C to the laboratory where they were stored at -14°C until analysis. Prior to analysis the samples were defrosted, dried at 40°C and homogenized through a 75 mesh stainless steel sieve.

Reagents and materials

Isooctane, n-hexane, dichloromethane, acetone and sodium sulfate were purchased from Merck (Darmstadt, Germany). Ultrapure water (18 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Paris, France). Copper granules (30 mesh) were purchased from UCT (Bristol, PA, USA) and florasil cartridge 500 mg from Varian (Lake Forest, CA, USA).

The PBDE standards (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) 50 µg mL⁻¹ in isooctane were purchased from Accustandard (New Haven, CT, USA).

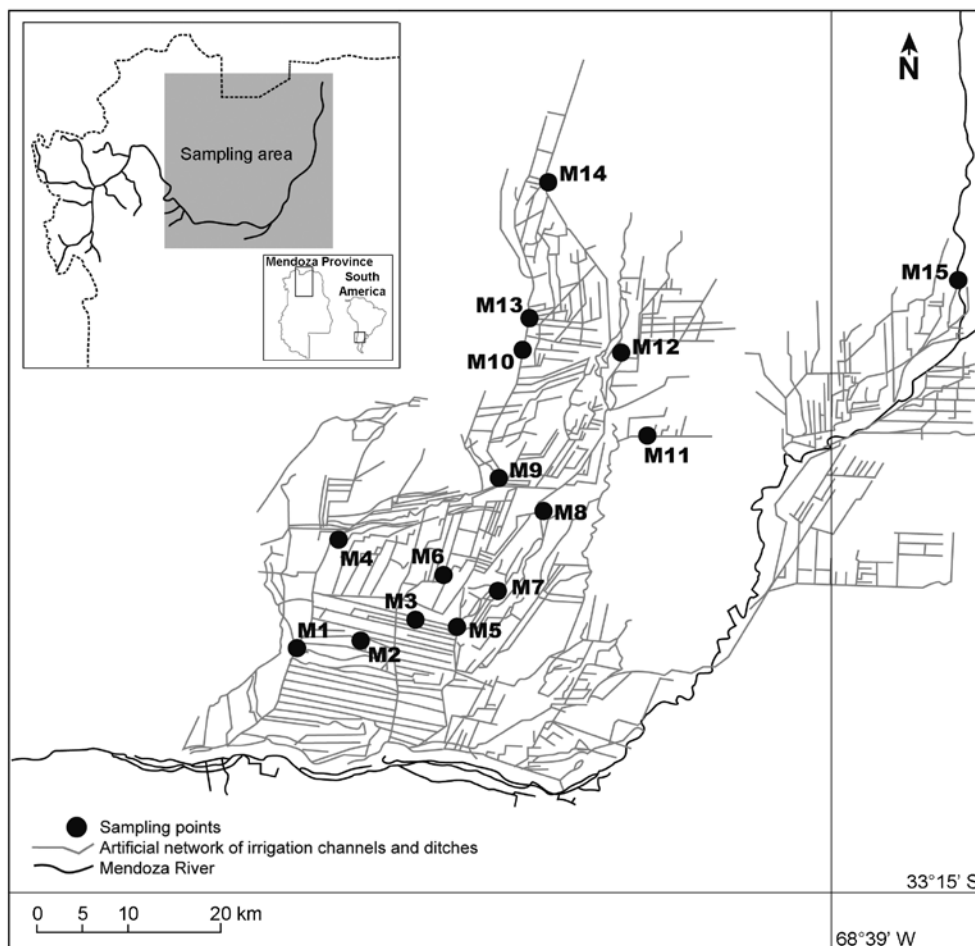


Figure 1. Location map: Northern Oasis of Mendoza: Mendoza River and artificial irrigation ditches and channels. Mendoza River water flows from West to North-East. Sampling points follow an altitudinal detriment gradient from M1 at 881 m a. s. l. to M15 at 583 m a. s. l.

Figura 1. Mapa: Oasis Norte de Mendoza: Río Mendoza y red artificial de canales y acequias. El sentido de flujo del Río Mendoza es de Oeste a Noreste. Los puntos de muestreo siguen un gradiente altitudinal decreciente desde M1 a 881 m s. n. m. hasta M15 a 583 m s. n. m.

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 at -14°C . Hexane rinsed capacity 600 cm^3 brown flask were used for sample collection, and 75 mesh stainless steel sieve was used for sample preparation. For FT-IR analysis, IR quality potassium bromide (Cole-Parmer, III, USA) was used. All reagents were of analytical grade or above.

62 Table 1. Physicochemical data, PBDE concentration levels and semi-quantitative IR-derived area ratios relating to studied samples.

Tabla 1. Datos físicos-químicos, niveles de concentración de PBDEs y conciente de área derivados de análisis semicuantitativos de IR relativos a las muestras estudiadas.

Sample	TOC (g/Kg)	pH	EC ($\mu\text{s}/\text{cm}$)	PBDEs (pg g^{-1} d.w.) *				CH_2/CH_3	A/Ox
				BDE-47	BDE-99	BDE-100	BDE-153		
M1	11.36	5.5	1023	<3.4	<3.0	<5.6	<7.3	1	1.51
M2	26.58	5	2280	<3.4	<3.0	<5.6	<7.3	2.4	0.6
M3	25.60	5	3030	<3.4	<3.0	<5.6	<7.3	2.6	0.74
M4	11.95	5	1569	<3.4	<3.0	<5.6	<7.3	2.2	0.73
M5	59.57	5.5	3710	<3.4	<3.0	<5.6	<7.3	2.3	0.31
M6	45.16	6	4160	59	10	19	24	1.8	0.48
M7	14.88	7.5	1796	178	144	67	69	1.2	0.69
M8	23.13	7.3	1826	11	47	54	<7.3	1.8	0.31
M9	5.78	7.3	1926	<3.4	<3.0	<5.6	<7.3	2.3	0.2
M10	10.40	7.8	2480	<3.4	<3.0	<5.6	<7.3	1.6	0.43
M11	14.95	5	5430	<3.4	<3.0	<5.6	<7.3	1.7	0.1
M12	18.55	4.5	3780	12	10	19	24	1.6	0.29
M13	11.31	5.5	5580	15	10	19	24	0.9	0.25
M14	10.30	5	1145	97	115	40	63	1.1	0.54
M15	14.32	7.3	2730	<3.4	<3.0	<5.6	<7.3	3	0.07

* LODs: 3.4 pg g^{-1} , 3.0 pg g^{-1} , 5.6 pg g^{-1} and 7.3 pg g^{-1} for BDE-47, BDE-100, BDE-99 and BDE-153, respectively.

* LODs: 3.4 pg g^{-1} , 3.0 pg g^{-1} , 5.6 pg g^{-1} y 7.3 pg g^{-1} para BDE-47, BDE-100, BDE-99 y BDE-153, respectivamente.

Sample analysis

PBDEs determination by GC-MS/MS

The quantification of PBDEs by GC-MS/MS was accomplished by standards addition method. The detection limits (LODs) estimated as three times the standard deviation of the background signal (3σ), ranged between 3.0 - 7.3 pg g^{-1} . The precision of Soxhlet-GC-MS/MS was evaluated over five replicates, leading RSDs values $<13\%$.

The calibration graph was linear with a correlation coefficient of 0.9957 at levels near the detection limits and up to five times 10^3 pg g^{-1} .

Sample preparation procedure for preparing the samples was described by Mai *et al.*, 2005. Briefly, an aliquot of 10 g of dried and sieved sediment sample of each sample point was mixed with 5 g anhydrous sodium sulfate and copper granules (2 g) before extracting it with 150 mL of acetone: hexane (1:1, v/v) in a Soxhlet extractor for 8 h (8). The supernatant was rota-evaporated to 2-3 mL and cleaned using preconditioned SPE florisil cartridges (36). Finally, the analytes were eluted with 3 mL of n-hexane by gravity. The extract was evaporated to near dryness under a gentle N_2 stream and reconstituted with 100 μL of isooctane. Gas chromatography coupled to mass detector (GC-MS/MS) analyses were carried out on a Varian 3900 gas chromatograph equipped with Varian Saturn 2000 ion trap mass detector (40 to 670 Da; 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 (25m \times 0.25 mm, 0.25 μm film thickness; Varian, Lake Forest, CA, USA). The temperature program was: 150 $^\circ\text{C}$, held 1 min; rate 15 $^\circ\text{C min}^{-1}$ to 250 $^\circ\text{C}$; rate 10 $^\circ\text{C min}^{-1}$ to a final temperature of 300 $^\circ\text{C}$ and held for 7 min. Helium (purity 99.999%) was used as a carrier gas at a flow rate of 1.0 mL min^{-1} . The injector temperature was set at 250 $^\circ\text{C}$ and injections were carried out in the splitless mode. The mass spectrometer was operated in electron impact ionization mode at 70 eV. The trap, manifold and transfer line temperatures were set at 220 $^\circ\text{C}$, 120 $^\circ\text{C}$ and 280 $^\circ\text{C}$, respectively. Samples were analyzed in MS/MS mode. Specific MS/MS conditions were described previously (12). The peak identification was based on the base peak and the isotopic pattern of the PBDEs congeners. The selected PBDEs were those most commonly found in the literature in environmental samples: BDE-47, -99, -100 and -153 (13). Decabromodiphenyl ether (BDE-209) could not be determinate due to mass range limitation of the spectrometer.

Organic matter characterization by FT-IR

FT-IR analysis technique provided a qualitative means to identify functional groups contained in the organic matter. Semi-quantitative data were obtained after processing digitized spectra using area ratios of IR absorbance peaks (18, 19). Quantitative determinations of the studied functional groups were not possible because there are not commercially available certified reference materials for the complex and relatively variable mixtures of organic compounds constituting the organic matter of sediments.

The samples specimens were prepared using the potassium bromide pellet technique. Two milligrams of each sieved sample together with 200 mg potassium bromide were homogenized in an agate mortar and finally pressed under vacuum to produce 13 mm

diameter pellets. Infrared spectra were collected using a Spectrum 100 (PerkinElmer) spectrometer, equipped with a DTGS-CsI detector and a DynaScan source. The acquisition conditions were 4 cm⁻¹ resolution and 64 interferograms were co-added before Fourier transformation. Area-integration methods (32) were applied to the following regions of FT-IR spectra to obtain semi-quantitative data peaks centered at 3050 cm⁻¹ are assigned to aromatic C-H stretching vibrations. Absorption peaks ascribed to aliphatic C-H stretching vibrations are recorded in the region 2800- 3000 cm⁻¹. These bands are assigned to asymmetric methylene (CH₂) stretch (2916-2936 cm⁻¹ region) and symmetric CH₂ stretch (2843-2863 cm⁻¹ region). A broad, intense and unspecific band with maximum absorption at 1635-1640 cm⁻¹ is produced by the contribution (overlapping bands) of several groups. They include aromatic, oxygen- and nitrogen-containing structures, including conjugated carboxyl and amide groups (the presence of mineral matrix peaks cannot be ruled out). This band is designated as an aromatic carbon plus oxygen-containing band. Some low intensity bands occur in the region 700-900 cm⁻¹, which are assigned to aromatic C-H out-of-plane bending vibrations. By means of IR spectrum processing CH₂/CH₃ (methylene/methyl groups) and Al/Ox (aliphatic/oxygen containing compounds) (table 2) ratios were obtained. Those ratios, CH₂/CH₃ and Al/Ox, are used as indicative of degradation state of organic matter. In this sense, the lower CH₂/CH₃ and Al/Ox values the more degraded state of the organic matter is.

Table 2. Definition of IR-derived semi-quantitative CH₂/CH₃ and Al/Ox ratios.

Tabla 2. Definición de los cocientes semi-cuantitativos CH₂/CH₃ y Al/Ox derivados de IR.

Ratio	Band region (cm ⁻¹)	Interpretation of the ratios
	Band-region ratios	
CH ₂ /CH ₃	2800 - 3000	This ratio relates to the aliphatic chain length and the degree of branching of aliphatic side groups (side chains attached to macromolecular structure). Interpretation: A larger ratio implies comparatively longer and straight chains, a smaller ratio shorter and more branched chains (18, 19).
Al/Ox	(2800 - 3000) / (1600 - 1800)	Relative contribution of aliphatic stretching bands (Al) to the combined contribution of oxygen-containing groups and aromatic carbon (Ox). Interpretation: From larger ratios decreasing oxygen-containing groups can be inferred, and vice versa (the lower the Al/Ox ratio, the higher the Ox term).

Physicochemical analysis of sediments

TOC determinations were carried out by gravimetric method (23). Briefly 10 g sieved sediment aliquot was dried at 105°C until constant weight. Dried samples were ignited at 430°C for 24 h. TOC was determined as weight difference of these two steps (10).

Electrical conductivity (EC) and pH were determined on 500 g aliquot of dried and sieved sediment sample. After saturating with deionized water and achieving a uniform paste it was left standing for 2 hours. EC and pH were determined on the aqueous extract after filtration using a digital electrical conductivity and pH meter, respectively (2).

Multivariate analysis

PCA is a nonparametric, statistical pattern-recognizing method that can be used at its most basic to visualize multivariate data in a simplified way. This is accomplished through data reduction where the number of components is less than the number of variables, in line with preference for a parsimonious scientific explanation and through groupings using component scores (15). It was decided to retain the first two principal components. Inherent assumptions include orthogonal (uncorrelated) components, no error variance and data structure. Statistical analysis was carried out using the computer program STATISTICA® on raw data consisting of 15 samples with 9 variables each. The included variables were: pH, EC, TOC, CH₂/CH₃, Al/Ox and the 4 BDE congeners concentration levels (BDE-47, -99, -100, and -153).

RESULTS AND DISCUSSION

PBDEs Level

The research was focused on tetra- to hexa-BDEs, components of *penta*- and *octa*- commercial mixtures, which are among the most toxic BDEs congeners associated to aquatic environments and represent a threat for aquatic biota.

PBDEs levels found were comparable to those reported by Miglioranza *et al.* (2013) for the Rio Negro basin, Argentina. Although those values are associated to low polluted areas (11), they represent an environmental risk. Sampling points levels recorded showed a non-homogeneous PBDEs distribution; however it was not possible to identify primary emission source of PBDEs. This is expected for the studied region due to the type of industrial activity developed in the region. These results support the suggestion that there is no relation between the arbitrary assigned areas of influence (U, I and F) and PBDEs fate. Therefore, influence areas were not further included in the PCA analysis. The sampling points where PBDEs were found (M6, M7, M8, M12, M13 and M14) were associated with areas influenced by I, U and F, that generally reports the highest contamination levels (MAyOP/97, Gobierno de Mendoza) of the studied oasis.

The total concentrations of PBDEs ranged from <LOD to 178 pg g⁻¹ d.w. (table 1, page 62). The average PBDE profile in sediments from areas influenced by I and U showed BDE-47 and BDE-99 congeners as the predominant, while BDE-153 and BDE-100 were the most abundant for those samples influenced by F. These differences could be attributed to recent use of the *penta*-BDE commercial mixture in I and U influenced areas. The PBDEs levels found in F areas could be due to the impact of environmental processes (transport, accumulation and degradation) on higher brominated mixtures, such as commercial *deca*-BDE (14, 28). The BDE-153 and BDE-100 is characterized by a high persistence while BDE-47 is the most ubiquitous BDE as a result of atmospheric transport.

Sediment physicochemical characterization

Although physicochemical properties of PBDEs are independent of the media pH and/or EC, these variables may influence the physicochemical characteristics of

sediment. Thus, pH and/or EC could condition pollutant affinity for sediments, as well as sediment solubility in the surrounding aqueous media (37). This could affect the PBDEs partition equilibrium between environmental compartments; influencing thus, on their accumulation and/or distribution in aquatic environment.

Table 1 (page 62) summarizes physicochemical data (TOC, EC and pH), PBDE levels and semi-quantitative IR-derived area ratios for the studied samples. Although physicochemical data were within the established limits (Res. 778/96 Dep. General de Irrigación, Gobierno de Mendoza), a significant difference among them was observed; which could be attributed to the anthropogenic activities related to each sample point.

Sediment of Mendoza River basin is slightly alkaline mainly because of its glacial origin and volcanic history of the region (24). Only five samples showed this feature, while the remaining showed pH values slightly lower (<6). EC values followed the same variation pattern as pH did. TOC ranged between 6 g kg⁻¹ and 60 g kg⁻¹ being the highest values related with I rather than F or U. Due to the type of industry that develops in the region (winery and olive-oil industry), it is expect to find high TOC values associated to its discharge to the ditches network.

FT-IR spectra of the studied samples reveal the presence of aliphatic and aromatic compounds. Table 1 (page 62) shows the values for CH₂/CH₃ and Al/Ox ratios observed in the analyzed samples. From this table it is possible to observe a generalized tendency of higher CH₂/CH₃ and Al/Ox ratios in sampling points influenced mainly by I and U; while those influenced by U showed the lowest. The data suggest that the organic matter from sampling point influenced by I and U was less degraded than that from those surrounding by F, which are dominant at the end of the network (figure 1, page 61). This gradient could be attributed to gradual degradation of the organic material that entered the network near sampling points influenced by I and U, while being transported along the network.

From the analysis of individual physicochemical variables of the sediment it was not possible to establish a correlation among them and PBDE accumulation.

Principal Component Analysis

In order to correlate physicochemical factors influencing PBDE affinity for sediment, a principal components analysis was performed using fifteen samples and nine variables: TOC, pH, EC, CH₂/CH₃ and Al/Ox ratio, BDE-47, BDE-100, BDE-99 and BDE-153 concentration levels (table 1, page 62).

Cumulatively, two components account for 63% of the data variance of table 1 (page 62); the loading plots and scores are shown in figure 2 and figure 3 (page 67), respectively. The first component (PC1: x axis; figure 2) accounted for 46% of data variance, resulting positive for PBDEs and negative for CH₂/CH₃. This implies an inverse relationship between PBDEs and CH₂/CH₃ ratio. Although pH also scored positively its contribution to the variance was low. Even though pH might not be directly influencing PBDEs-sediment affinity, it could be conditioning the studied environmental compartment by determining bacterial diversity that will indeed degrade organic matter (5).

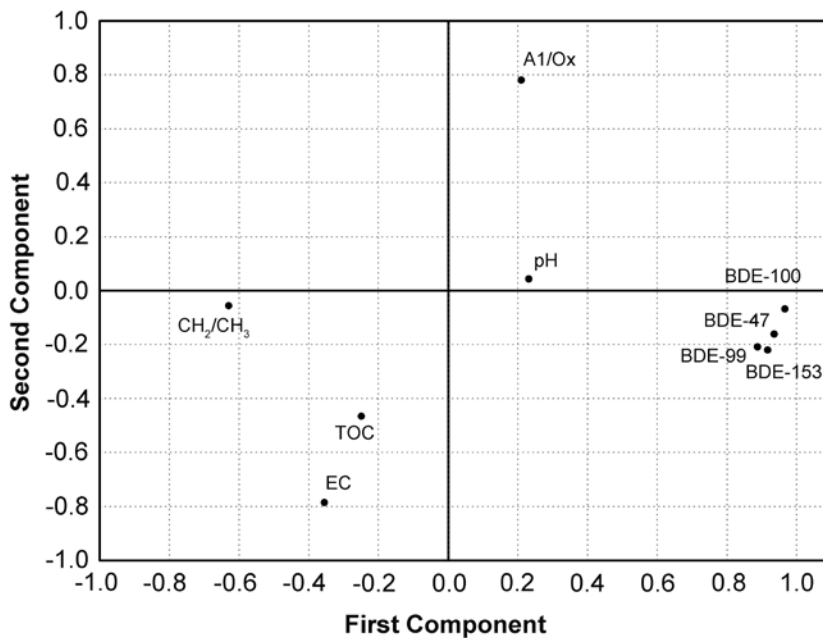


Figure 2. Plot of component loadings.

Figure 2. Representación de variables en el plano definido por las componentes 1 y 2.

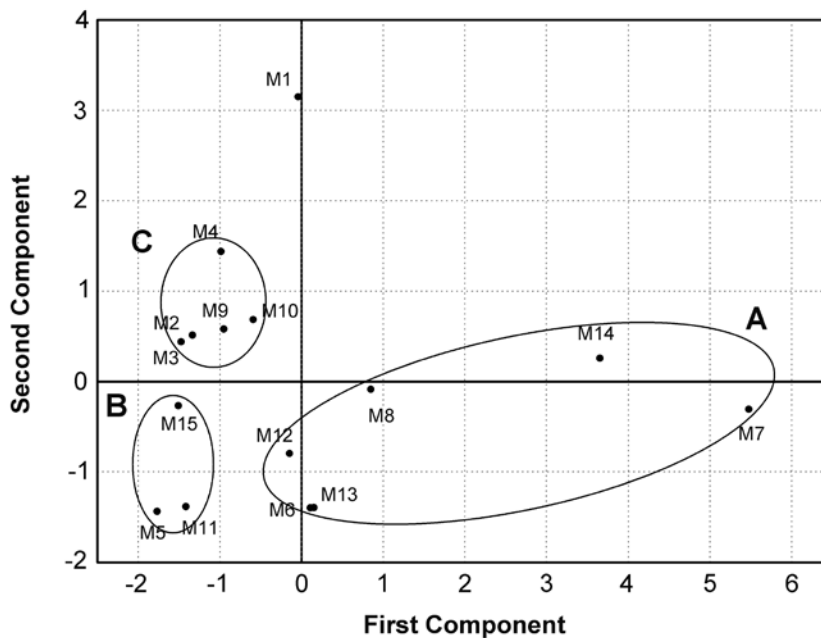


Figure 3. Plot of component scores

Figure 3. Representación de las muestras en el plano definido por las componentes 1 y 2.

PBDE-containing samples (M6, M7, M8, M12, M13 and M14) exhibit, in general, the most positive scores (figure 3, page 67; x axis) showing low CH_2/CH_3 , which is related to high organic matter degradation degree. The higher the breaking of carbon-carbon bonds of the organic matter, the aliphatic chains of the macromolecules will be shorter and branched. This gives a greater nonpolar character, which apparently favors the affinity towards PBDEs. It should be mentioned that M12 showed a negative score against PC1. Although it presented low CH_2/CH_3 values, this sample had low PBDEs levels and high EC values that have a positive and negative influence over PC1, respectively. Considering the distribution of PBDE containing samples, it is expected to find a gradient in the degradation degree of the organic matter along the network, as described in: "Sediment physicochemical characterization".

The second component (PC2: y axis, figure 2, page 67) accounted for 17% of data variance, resulting it predominantly negative, except for the high loading on the Al/Ox ratio, which makes it relevant. The inverse relationship between Al/Ox ratio and TOC is an expected result. As the organic content in sediment degrades the Ox decreases faster than Al values in Al/Ox ratio, therefore the ratio increases (31).

The score plotting (figure 3, page 67) is particularly useful in showing the different distribution pattern of samples as a function of sediment physicochemical data, PBDEs levels and organic matter-chemical structure (functional groups). Delimited ellipses around the groups in figure 3 (page 67) are for illustrative purpose only and do not have any statistical significance. Three groups of samples can be identified (A, B and C groups; figure 3, page 67); only one of them containing PBDE congeners (group A). These groupings suggest a correlation between the presences of PBDEs and oxidized organic matter content. Sample M1 (no PBDEs detected) is particularly different, showing the most positive score against this component (PC2, figure 3, page 67), as a result of its Al/Ox and EC values being the highest and lowest, respectively in the entire data set (table 1, page 62).

No PBDE congeners were detected in groups neither B (M5, M11 and M15) nor C (M2, M3, M4, M9 and M10). Even though group B showed high TOC and CH_2/CH_3 ratios, the Al/Ox ratios (table 1, page 62) were low. Therefore a likely explanation could be that the organic matter did not show an advanced degradation degree. On the other hand, samples of group C were characterized by low TOC and high Al/Ox ratios, and medium to high CH_2/CH_3 values, showed no PBDE.

CONCLUSIONS

Even though it is well known that physicochemical variables could influence PBDEs-sediment affinity, their individual analysis is not enough to reliably identify which are the conditioning ones. In this sense the PCA statistical approach provided a more comprehensive analysis of the studied variables, allowing to identify two components that explained 63% of the data variance. The factors identified were associated to organic matter degradation, which represent a new insight into the relationships between organic matter in sediments and PBDEs fate. Therefore, not only the content but the type of

organic matter (chemical structure) is a variable to be taken under consideration when evaluating accumulation and transport of PBDEs in the environment.

Additionally, the typification of sediments organic matter (functional groups determination) may be a useful tool (faster, cheaper, effective environmental friendly and reliable) to identify areas where PBDE may accumulate, as well as sediment transportation capability in hydrobiological studies. These results are particularly important since they are a significant contribution in setting baseline study report and condition water quality in a region where water is a scarce and valuable resource. Additionally, this perspective would settle the bases for further monitoring studies that will contribute to improve environmental policies, disposal treatments along with regulation protocols. Due to the physicochemical similitude, this approach could be applied to other POPs.

REFERENCES

- Adema, C. M.; Hanington, P. C.; Lun, C.-M.; Rosenberg, G. H.; Aragon, A. D.; Stout, B. A.; Lennard Richard, M. L.; Gross, P. S., Loker, E. S. 2010. Differential transcriptomic responses of *Biomphalaria glabrata* (Gastropoda, Mollusca) to bacteria and metazoan parasites. *Schistosoma mansoni* and *Echinostoma paraensei* (Digenea, Platyhelminthes). *Molecular Immunology*. 47: 849-860.
- Allison, L. E.; Brown, J. W.; Hayward, H. E., Richards, L. A. 1954. Diagnosis and improvement of saline and alkali soils: L.A. Richards. 172.
- Besteiro, S. I., Gaspari, F. J. 2012. Modelization of the sediments emission in a watershed with forestations of Northeast Pampean. *Revista de la Facultad de Ciencias Agrarias de la Universidad Nacional de Cuyo*. 44: 111-127.
- Chen, L.; Huang, Y.; Peng, X.; Xu, Z.; Zhang, S.; Ren, M.; Ye, Z., Wang, X. 2009. PBDEs in sediments of the Beijiang River, China: Levels, distribution, and influence of total organic carbon. *Chemosphere*. 76: 226-231.4.
- Chen, C.-Y.; Tien, C.-J.; Sun, Y.-M.; Hsieh, C.-Y., Lee, C.-C. 2013. Influence of water quality parameters on occurrence of polybrominated diphenyl ether in sediment and sediment to biota accumulation. *Chemosphere*. 90: 2420-2427.
- Costa, L. G.; Giordano, G.; Tagliaferri, S.; Caglieri, A., Mutti, A. 2008. Polybrominated diphenyl ether (PBDE) flame retardants: Environmental contamination, human body burden and potential adverse health effects. *Acta Biomedica de l'Ateneo Parmense*. 79: 172-183.
- Covaci, A.; Gheorghe, A.; Voorspoels, S.; Maervoet, J.; Steen Redeker, E.; Blust, R., Schepens, P. 2005. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): Analytical aspects and depth profiles. *Environment International*. 31: 367-375.
- Covaci, A.; Gheorghe, A.; Hulea, O., Schepens, P. 2006. Levels and distribution of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in sediments and biota from the Danube Delta. Romania. *Environmental pollution*. 140: 136-149.
- D'Angelo, J. A., Zodrow, E. L. 2011. Chemometric study of functional groups in different layers of *Trigonocarpus grandis* ovules (Pennsylvanian seed fern, Canada). *Organic Geochemistry*. 42: 1039-1054.
- Davies, B. E. 1974. Loss-on-ignition as an estimate of soil organic matter. *Soil Science Society of America Journal*. 38: 150-151.
- Dosis, I.; Kamarianos, A.; Athanasiadou, M.; Athanassiadis, I., Karamanlis, X. 2011. Polybrominated diphenyl ethers (PBDES) in marine sediment of Thermaikos Gulf, Greece. *International journal of environmental analytical chemistry*. 91: 1151-1165.
- Fontana, A. R.; Lana, N. B.; Martinez, L. D., Altamirano, J. C. 2010. Ultrasound-assisted leaching-dispersive solid-phase extraction followed by liquid-liquid microextraction for the determination of polybrominated diphenyl ethers in sediment samples by gas chromatography-tandem mass spectrometry. *Talanta*. 82: 359-366.
- Hale, R. C.; La Guardia, M. J.; Harvey, E.; Gaylor, M. O., Mainor, T. M. 2006. Brominated flame retardant concentrations and trends in abiotic media. *Chemosphere*. 64: 181-186.

14. Hassanin, A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Thomas, G. O., Jones, K. C. 2004. PBDEs in European Background Soils: Levels and Factors Controlling Their Distribution. *Environmental Science and Technology*. 38: 738-745.
15. Johnson, R. A., Wichern, D. W. 2008. *Applied Multivariate Statistical Analysis*. Wisconsin, 761.
16. Lana, N. B.; Fontana, A. R.; Ciocco, N. F., Altamirano, J. C. 2010. Determination of polybrominated diphenyl ethers in water samples from Mendoza River basin by HS-SPME-GC-MS/MS. *Revista de la Facultad de Ciencias Agrarias de la Universidad Nacional de Cuyo*. 42: 85-98.
17. Lana, N. B.; Berton, P.; Covaci, A.; Atencio, A. G.; Ciocco, N. F., Altamirano, J. C. 2013. Ultrasound leaching-dispersive liquid-liquid microextraction based on solidification of floating organic droplet for determination of polybrominated diphenyl ethers in sediment samples by gas chromatography-tandem mass spectrometry. *Journal of Chromatography A*. 1285: 15-21.
18. Lin, R., Ritz, G. P. 1993a. Reflectance FT-IR microspectroscopy of fossil algae contained in organic-rich shale. *Applied Spectroscopy*. 47: 265- 271.
19. Lin, R., Ritz, G. P. 1993b. Studying individual macerals using I.R. microspectroscopy, and implications on oil versus gas/condensate proneness and "low-rank" generation. *Organic Geochemistry*. 20: 695-706.
20. Lis, G. P.; Mastalerz, M.; Schimmelmann, A.; Lewan, M. D., Stankiewicz, B. A. 2005. FTIR absorption indices for thermal maturity in comparison with vitrinite reflectance R_0 in type-II kerogens from Devonian black shales. *Organic Geochemistry*. 36: 1533-1552.
21. Mai, B.; Chen, S.; Luo, X.; Chen, L.; Yang, Q.; Sheng, G.; Peng, P.; Fu, J., Zeng, E. Y. 2005. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environmental Science and Technology*. 39: 3521-3527.
22. Miglioranza, K. S. B.; Gonzalez, M.; Ondarza, P. M.; Shimabukuro, V. M.; Isla, F. I.; Fillmann, G.; Aizpún, J. E., Moreno, V. J. 2013. Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin. *Science of The Total Environment*. 452-453: 275-285.
23. Miyazawa, M.; Pavan, M. A.; Oliveira, E. L.; Ionashiro, M., Silva, A. K. 2000. Gravimetric determination of soil organic matter. *Brazilian Archives of Biology and Technology*. 4: 475-478.
24. Morábito, J.; Salatino, S.; Medina, R.; Zimmermann, M.; Filippini, M. F.; Bermejillo, A.; Campos, S.; Nacif, N.; Dediol, C.; Genovese, D.; Pizzuolo, P.; Mastrantonio, L., Valdés, A. 2007. Irrigation water quality in the Mendoza river basin: temperature, pH, soluble and solid ions. *Revista de la Facultad de Ciencias Agrarias. Universidad Nacional de Cuyo. Mendoza. Argentina*. 39(1): 9-20.
25. Nam, J. J.; Gustafsson, O.; Kurt-Karakus, P.; Breivik, K.; Steinnes, E., Jones, K. C. 2008. Relationships between organic matter, black carbon and persistent organic pollutants in European background soils: Implications for sources and environmental fate. *Environmental pollution*. 156: 809-817.
26. Painter, P. C.; Snyder, R. W.; Starsinic, M.; Coleman, M. M.; Kuehn, D. W., Davis, A. 1981. Concerning the Application of FT-IR to the Study of Coal: a critical assessment of band assignments and the application of spectral analysis programs. *Applied Spectroscopy*. 35: 475-485.
27. Pan, B.; Ning, P., Xing, B. 2008. Part IV - Sorption of hydrophobic organic contaminants. *Environmental Science and Pollution Research*. 15: 554-564.
28. Parolini, M.; Binelli, A.; Marin, M.; Matozzo, V.; Masiero, L., Provini, A. 2012. New evidences in the complexity of contamination of the lagoon of Venice: polybrominated diphenyl ethers (PBDEs) pollution. *Environmental Monitoring and Assessment*. 184: 2001-2015.
29. Ramu, K.; Isobe, T.; Takahashi, S.; Kim, E. Y.; Min, B. Y.; We, S. U., Tanabe, S. 2010. Spatial distribution of polybrominated diphenyl ethers and hexabromocyclododecanes in sediments from coastal waters of Korea. *Chemosphere*. 79: 713-719.
30. Schechter, A.; Pavuk, M.; Pöpke, O.; Ryan, J. J.; Birnbaum, L., Rosen, R. 2003. Polybrominated diphenyl ethers (PBDEs) in U.S. mothers' milk. *Environmental Health Perspectives*. 111: 1723-1729.
31. Schlesinger, W. H., Bernhardt, E. S. 2013. *Biogeochemistry: an analysis of global change*. USA: Academic press.
32. Sobkowiak, M., Painter, P. 1992. Determination of the aliphatic and aromatic CH contents of coals by FT-I.R.: studies of coals extracts. *Fuel*. 71: 1105-1125.
33. Sun, K.; Zhao, Y.; Gao, B.; Liu, X.; Zhang, Z., Xing, B. 2009. Organochlorine pesticides and polybrominated diphenyl ethers in irrigated soils of Beijing, China: Levels, inventory and fate. *Chemosphere*. 77: 1199-1205.
34. UNEP. 2009. Stockholm Convention on persistent organic pollutants Available in: <http://chm.pops.int> (Accessed 30/5/2013).

35. Wania, F., Mackay, D. 1996. Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology*. 30: 390-396.
36. Watanabe, I.; Kashimoto, T., Tatsukawa, R. 1987. Polybrominated biphenyl ethers in marine fish, shellfish and river and marine sediments in Japan. *Chemosphere*. 16: 2389-2396.
37. Zhao, X.; Zhang, H.; Ni, Y.; Lu, X.; Zhang, X.; Su, F.; Fan, J.; Guan, D., Chen, J. 2011. Polybrominated diphenyl ethers in sediments of the Daliao River Estuary, China: Levels, distribution and their influencing factors. *Chemosphere*. 82: 1262-1267.

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