POLYBROMINATED DIPHENYL ETHERS IN MENDOZA RIVER BASIN AND EL CARRIZAL RESERVOIR: LEVELS, DISTRIBUTION AND CORRELATION WITH PHYSICO-CHEMICAL VARIABLES

Jorgelina C. Altamirano [a,d,✉], Nerina B. Lana [a], José A. D`Angelo [b,d] and Néstor Ciocco [c,d]

[a] Grupo de Investigación y Desarrollo en Química Analítica (QUIANID), (LISAMEN, CCT CONICET – Mendoza), P.O. Box 131, 5500 Mendoza, Argentina.
[b] Departamento de Geología y Paleontología, IANIGLA-CCT CONICET-Mendoza, Mendoza.
[c] Instituto Argentino De Investigación de las Zonas Áridas (IADIZA), CCT CONICET-Mendoza, Argentina
[d] Departamento de Química, Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Mendoza, Argentina. ✉ *jaltamirano@mendoza-conicet.gov.ar*

1. INTRODUTION

Polybrominated diphenyl ethers (PBDEs) have become an issue of global contamination concern. PBDEs have been used extensively over the past two decades as additive brominated flame retardants (BFRs) in most types of polymers applied to electronic equipment, plastics, textiles, building materials, carpets, vehicles and aircrafts (Allchin et al., 1999). BFRs are used to prevent ignition of the polymer and to slow the initial phase of combustion. However, they are one of the most prominent and persistent environmental pollutants, which have adverse effects on human health and wild life.

Little information is found in the international literature on PBDEs in environmental systems of South America. It includes information about PBDEs presence in salmon and air samples from Chile (Pozo et al., 2004; Montory and Barra, 2006); and skipjack tuna and human breast adipose tissue from Brazil (Ueno et al., 2004; Kalantzi et al., 2009). Nevertheless there is not information about PBDEs in Argentina. The aim of the present work was to investigate PBDEs presence in Argentine environment. The first approach was across the study of the sediment of Mendoza River basin and El Carrizal reservoir. Additional physico-chemical analysis, including sample pH, electrical conductivity (C.E.), total organic matter (O.M) and characterization of the organic matter by infrared spectrometry were carried out. The information was analyzed using multivariate analysis in order to identify a possible correlation between those variables and presence of PBDEs for the analyzed samples.

The working hypothesis was: PBDEs levels and distribution in the basin are related to anthropogenic intervention.

2. MATERIAL AND METHODS

2.1 Reagents

The selected PBDEs for this work were those most commonly found in natural environmental samples: BDE-47, BDE-99, BDE-100 and BDE-153 (North, 2004; Oros et al., 2005). The standards of these PBDEs were purchased from Accustandard (New Haven, CT, USA). Isooctane, n-hexane, acetone, nitric acid and sodium sulfate were purchased from Merck (Darmstadt, Germany). Ultrapure water (18MΩ cm) was purchased from a Milli-Q water purification system (Millipore, Paris, France). The cupper granules 99,5 % was purchased from UCT (Bristol, PA, USA) and florisil cartridge 500 mg from Varian (Argentine). In the sample preparation for Infrared Spectrometry (IR) analysis, KBr of IR quality was use (Cole-Parmer, recorded in the region 400 cm^{-1} to 4000 cm^{-1} wavenumber). All reagents were of analytical grade or above.

2.2 Studied area and sampling

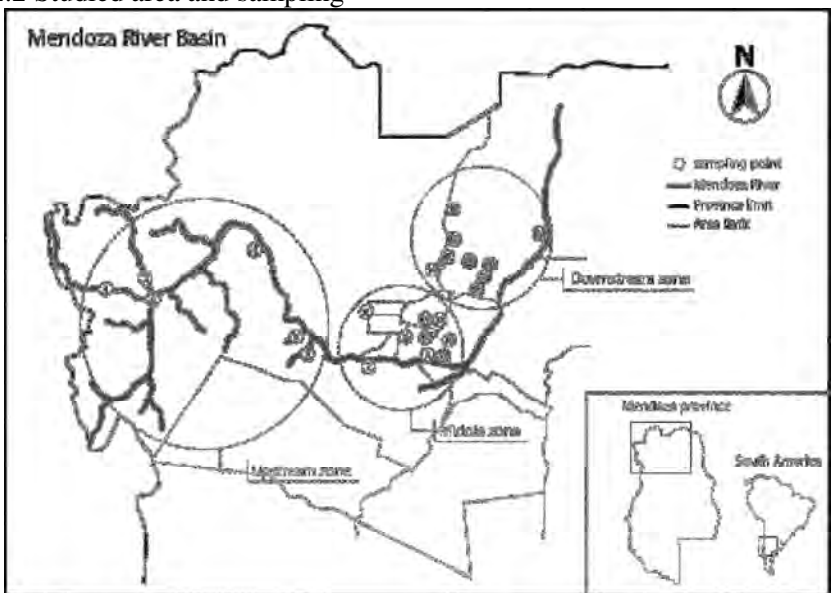

Fig. 1: North oasis of Mendoza province. Mendoza River and tributaries rivers are indicated in the map. Circles indicate monitored water sites.

Mendoza River basin (Fig.1): is in the Centre-West of the Argentina. Within its extents course is possible to find pristine zones faraway from township and anthropogenic activities as well as small townships and highly populated and industrialized cities.

The monitoring program was made up considering different zones with differential anthropogenic activities. Thirty stations were monitored and three samples were collected in each sampling point.

El Carrizal reservoir (Fig. 2): is a dike located in the average top course of the Tunuyán river, north center of the Province of Mendoza (33°18 ' 00"S - 68°43'15"W). It is a regulatory dike of the waters of the mentioned river which is in use for irrigating the productive region of Uco Valley (center oasis of Mendoza Province).

The monitoring program was made in September of 2009. In whole 17 points of sampling were established, and two samples were collected in each sampling point. Sediments samples were collected by a drag and stored in brown flasks. Samples were collected in brown flasks and immediately refrigerated at 4 ^{o}C and shipped to the laboratory where were stored at -14 °C until their analysis. Caution was taken to minimize contamination at all levels of sample collection and handling.

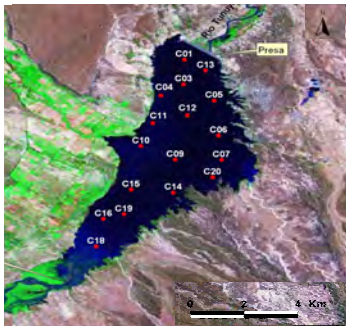

Fig. 2: El Carrizal reservoir. Circles indicate sampling sites.

2.3 Sediment sample analysis

Physicochemical analysis (pH, conductivity and organic matter): The analyses of organic matter were realized according to the norm IRAM-SAGPyA 29571-1. Conductivity and pH of soil were realized in the saturation extracts (Allison et al., 1954).

GC-MS/MS analyses: Prior to analysis, the sample was dried at 40 °C overnight and homogenized through a stainless steel 75 mesh (0.5 mm) sieve. The pretreatment and procedure was performed following the procedure described by Mai et al., 2005 with slight modification. GC-MS/MS analyses were performed 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 performed 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 °C, 50 °C and 280 °C, respectively. Samples were analyzed in MS/MS mode. The peak identification was based on the base peak and the isotopic pattern of the PBDEs congeners. Specific ions were selected for each PBDE congener and the base ion was selected as a quantitative ion, while two other ions were used as qualifiers. The quantification of PBDEs was accomplished by standards addition method. The detection limits calculated as three times the signal-to-noise ratio (S/N=3) were in the range of 3-7 pg g^{-1}.

Analysis by Fourier transforms Infrared Spectroscopy**:** Infrared spectra were collected on a Spectrum 100 FTIR (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. Spectral band assignments were made according to Colthup et al., 1990 and Shurvell, 2002 . Some area-integration methods (Sobkowiak and Painter, 1992.; D'Angelo, 2006) were applied in the following regions of FT-IR spectra to obtain semi-quantitative data: (a) 2825-3000 cm^{-1} (aliphatic C-H stretching), (b) 1600-1800 cm^{-1} and (c) 700-900 cm^{-1} (aromatic C-H out-of-plane bending). In the IR samples spectrums can be observed the presence of aliphatic and aromatic compounds. By means of IR spectrum processing program (OMNIC) methylene/methyl (CH_2/CH_3) and aliphatic/oxygen (Al/Ox) ratio was obtained. Both ratios were used for regression analysis.

Statistical analysis: Statistical analysis was performed using the programme STATISTICA® (StatSoft, 2001). The principal components analysis (PCA) was carried out including physico-chemical variables (pH, C.E. and O.M.), variables derived from FTIR's spectra (CH2/CH3 and Al/Ox) and concentrations of PBDEs in sediment samples. Statistical analysis included one-way analysis of variance (Ortega et al., 2005). This test was carried out to assess whether the different variables evaluated conducted to statistically different results.

3. RESULTS AND DISCUSSION

This is the first study that reports the presence of PBDEs in Argentinean environment, and in particular in Mendoza province.

The most abundant PBDEs congeners found in sediments of Mendoza River and waterways were BDE-47, BDE-100 and BDE-99 with a total of concentrations of 1499.9; 1644.1 and 1273.6 pg g^{-1} respectively. The geographical sites where PBDEs have been found were associated with urban and industrialized area. The most abundant PBDEs congeners found in sediments of El Carrizal reservoir were BDE-47, BDE-99 and BDE-153 with total concentrations of 179.1, 15.3 and 9.8 pg g^{-1} respectively. The highest values were found on the south-east coast of the reservoir in the proximities of camping and nautical clubs.

From the analysis of correlation matrix it is possible to observe low correlations between PBDEs concentrations and pH, C.E. and O.M variables. The correlation never exceeded $r_{=}0.37$ which shows a low dependence between studied variables. Nevertheless, the negative correlations turn out significant ($r>-0,46$) between PBDEs concentrations and CH_2/CH_3 ratio of the aliphatic components present in organic matter. The CH_2/CH_3 ratio related to the aliphatic chain length and the degree of ramification of aliphatic groups. A minor CH_2/CH_3 relation would indicate shorter lateral hydrocarbonade chain and/or more branched out chains (Lin and Ritz, 1993a; 1993b). A decrement in the CH_2/CH_3 ratio might be associated with the break of lateral chains aliphatic (Guo and Bustin, 1998) presents in the organic matter of sediments. This agrees with affinity between PBDEs and organic matter expressed by Oros et al., 2005 . Additionally our study suggests that transport and accumulation of PBDEs in environmental samples are favored by major degradation level of the organic matter (low CH_2/CH_3 ratio).

The determination of these pollutants in Argentine constitutes an important advance in environmental matter since it allows knowing the current condition of our ecosystems. The PBDEs concentration

found in the analyzed sediments samples from Mendoza river basin and El Carrizal reservoir were within the range of concentration reported in open literature.

REFERENCES

Allchin C. R., R. J. Law and S. Morris, 1999. Environmental Pollution, 105, 197-207.

Allison L. E., J. W. Brown, H. E. Hayward and L. A. Richards, 1954. Diagnóstico y Rehabilitación de Suelos Salinos y Sódicos 172,
Colthup N. B., L. H. Daly and S. E. Wiberley, 1990. Academic Press New York, 547 pp.

D'Angelo J. A., 2006. Ameghiniana, 43 (4), 669–685.

Guo Y. and R. M. Bustin, 1998. International Journal of Coal Geology, 36 (3-4), 259-275.

Kalantzi O. I., F. R. Brown, M. Caleffi, R. Goth-Goldstein and M. Petreas, 2009. Environment International, 35, 113-117.

Lin R. and G. P. Ritz, 1993a. Applied Spectroscopy, 47, 265- 271.

Lin R. and G. P. Ritz, 1993b. Organic Geochemistry, 20, 695-706.

Mai B., S. Chen, X. Luo, L. Chen, Q. Yang, G. Sheng, P. Peng, J. Fu and E. Y. Zeng, 2005. Environ. Sci. Technol., 39, 3521-3527.

Montory M. and R. Barra, 2006. Chemosphere, 63, 1252-1260.

North K. D., 2004. Environ. Sci. Technol., 38, 4484-4488.

Oros D. R., D. Hoover, F. Rodigari, D. Crane and J. Sericano, 2005. Environ. Sci. Technol., 39, 33-41.

Ortega J. A., J. Ferrís, A. Cánovas, L. Claudio-Morales, O. Berbel and P. Lupíñez, 2005. Neurotóxicos medioambientales (III), 63, 429-436.

Pozo K., T. Harner, M. Shoeib, R. Urrutia, R. Barra, O. Parra and S. Focardi, 2004. Environ. Sci. Technol., 38, 6529-6537.

Shurvell H. F., 2002. J. Chalmers and P. Griffiths (Eds.). Handbook of Vibrational Spectroscopy, Vol 3. Sample Characterization and Spectral Data Processing. John Wiley & Sons Ltd, Chichester, UK 611 pp.

Sobkowiak M. and P. Painter, 1992. Fuel 71, 1105-1125.

Ueno D., N. Kajiwara, H. Tanaka, A. Subramanian, G. Fillmann, P. K. S. Lam, G. J. Zheng, M. Muchitar, H. Razak, M. Prudente, K. H. Chung and S. Tanabe, 2004. Environ. Sci. Technol., 38, 2312-2316.