

Seasonal changes in organotin compounds in sediments from the Bahía Blanca Estuary

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Abstract Twenty-four surface sediment samples were collected in the Bahía Blanca Estuary (Argentina) during 2013 in order to assess the occurrence of butyltin compounds. Then, six areas ranging from zones with intensive maritime traffic to other rural/recreational zones at the inner utmost point of the estuary were periodically sampled (3 months) along the whole year. After extraction/derivatization assisted by ultrasound, three target compounds—including monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT)—were analyzed by means of gas chromatography/mass spectrometry (GS/MS). Total butyltin (TBts) levels ranged from 73.5 to 395.2 ng Sn g⁻¹ dry wt. TBT was the minor contributor, accounting for 12.6 % of the TBts. On the other hand, MBT, for which no baseline precedents were available, accounted for the 51.4 % of TBts. Sampling sites could be classified, in terms of environmental health regarding the organotin compounds (OTs) relationship, each from lightly (3–20 ng Sn g⁻¹ dry wt) to moderately polluted (20–100 ng Sn g⁻¹ dry wt). In the light of TBts levels, distributions and covariation with

environmental parameters such as granulometry and sediment organic carbon the occurrence of DBT and MBT could not be uniquely attributed to the degradation pathway of the TBT; in fact, results outlined the possible contribution of some punctual and diffuse sources at the area such as refineries, PVC industry inputs and the city hall main sewage.

Keywords Organotin compounds · Ultrasound · Sediments · Bahía Blanca Estuary

Introduction

Organotin compounds began to be widely used after the 1940s when the plastic industry, particularly the production of polyvinyl chloride (PVC) was expanded (Blunden et al. 1984). Dibutyltin (DBT) and monobutyltin (MBT) were used as stabilizing additives against the effects of light and heat on PVC (Ebdon et al. 1998; Hoch 2001; Olushola Sunday et al. 2012). In the 1960s, tributyltin (TBT) also began to be used as an antifouling agent in paints for the hulls of ships and boats, and surfaces of stationary structures in prolonged contact with seawater. TBT controls the growth and attachment of barnacles, mussels, tubeworms, algae and other marine fouling organisms and its application has resulted in enormous savings to the shipping industry. However, the widespread use of these compounds resulted in a serious problem for the marine ecosystems. TBT has been defined as the most toxic substance ever introduced into the marine environment (Goldberg 1986; Sonak et al. 2009), even at very low concentrations (Szpunara et al. 1996; Hoch 2001).

Consequently, the global environmental impacts of TBT have led to its regulation. Then, the use of TBT in small

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boats has been forbidden in many countries since the mid-1980s. Further, in 2001 the European Commission Parliament included the TBts as priority hazardous substances subjected to cessation of emissions, discharges and losses into water (Amending water policy directive 2000/60/EC). Finally, in Argentina, the institution that regulates maritime transportation (Prefectura Naval Argentina) banned the use of TBT-based antifouling paints in all types of vessels back in 1998 (Resolution 04/98) (Ohji et al. 2007).

Despite this fact, TBT and its degradation products DBT and MBT are still of concern in the aquatic environment, due to its persistence, potential and high toxicological effects and bioaccumulation on non-target aquatic life (Komoike and Matsuoka 2013). Once released from an antifouling coating, due to their hydrophobic properties, TBT is rapidly absorbed by organisms such as bacteria and algae, adsorbed onto the surface of particles suspended in the water and thus it accumulates in sediments (Burton et al. 2004; Luan et al. 2006). Subsequently, TBts are readily incorporated into the tissues of filter-feeding zooplankton, grazing invertebrates and, eventually, into higher organisms such as fish, water birds, and mammals (Borghi and Porte 2002; Berge et al. 2004; Ohji et al. 2007).

In situ degradation of TBT could be caused through various processes such as ultraviolet irradiation (photolysis) and chemical and biological cleavage and also depends on the environmental conditions, i.e., at ambient temperature degradation depends on seasonal variation and geographic conditions on the sites (Sakultantimetha et al. 2011). The TBT degradation is considered to be a fast process in the water column, with a half-life about of days (Clark et al. 1988). However, the half-life of organotin compounds (OTs) can be very long (in the order of years) in sediments (Alzieu 1998).

Considering all the above-mentioned and that the unique precedents for the area of the study date from 10 years ago (Delucchi et al. 2007), the main objectives of this study were: (i) to assess the present occurrence of TBT and its degradation products, DBT and MBT in surface sediment samples from the Bahía Blanca Estuary; (ii) to elucidate their seasonal and spatial distribution; (iii) to perform a source apportionment.

Study area

The study area is a mesotidal coastal plain estuary, with an approximate total area of 2300 km², located between 38°45'S and 39°40'S and 61°45'W and 62°20'W on the southeastern area of Buenos Aires Province, Argentina (Fig. 1). The Bahía Blanca Estuary has an elongated form, northwestern–southeastern directed, about 80 km long within the Main Channel, and has numerous streams which

separate islands and tidal flats (Perillo and Piccolo 1991; Marcovecchio and Ferrer 2005).

Water interchange within the bay is influenced by a semidiurnal tidal regime. The mean tidal amplitude varies between 3.5 and 2.2 m at the head and mouth of the estuary, respectively. The water surface at low tide is 400 km², while at high tide this area rises to nearly 1300 km² (Fernández Severini et al. 2009).

Most of the freshwater inflow is contributed by the Sauce Chico River and the Naposta Grande Creek. Both, the occurrence of north-westerly winds as well as the oscillation of the semidiurnal tidal wave lead to a vertical mixing and homogeneous distribution of the main oceanographic parameters (Hempel et al. 2008), except in the inner zone during rainfall periods which could eventually function as a partially stratified system.

The hydrography of the estuary is strongly influenced by climatic conditions (Freije et al. 1981). Perillo and Piccolo (1991) have recorded very high sediment transportation rates for the area which is added to the periodical remobilization of sediments by dredging. Various ports, towns (with a population exceeding 300,000 inhabitants) and industries, as oil refineries and terminals, petrochemical industries, meat factories, leather plants, fish factories, textile plants, wool washing plants, silos and cereal mills are located at the northern boundaries of the estuary. As a result, this estuary is extensively used by oil tankers, cargo vessels and fishing boats and, due to frequent shipping of cargo and transport vessels, the Main Channel requires regular dredging (Botté et al. 2010). Thus, this coastal marine system receives contaminant inputs from municipal wastewaters, direct industrial discharges, harbor-related operations, runoff water which carries materials from land development areas and aerial fallout from atmospheric pollutants (Marcovecchio and Ferrer 2005).

Materials and methods

Sampling and sample treatment

Oceanographic surveys were carried out along the Main Channel. Surface sediment samples were obtained using a stainless steel sediment sampler. Sampling was performed every 3 months along the year 2013 in six sampling zones with different anthropogenic impact (Table 1).

Sampling site S1 is located at Rosales Harbor, which includes oil tankers and port service vessels. This site is in the proximity of the Belgrano Harbor, the most important military harbor of Argentina, where the hulls of many commercial and military ships are continuously repaired and painted. S2 is located in the proximity of the “Luis Piedra Buena” Thermoelectric facilities, which supplies

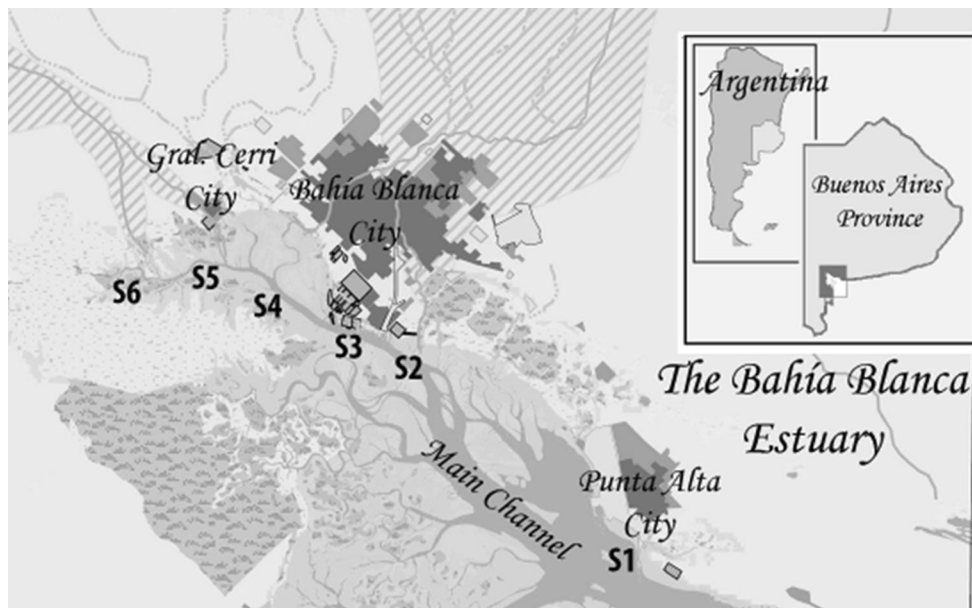


Fig. 1 Sampling sites at the Bahía Blanca Estuary, Argentina. S1 Rosales Harbor; S2 “Luis Piedra Buena” Thermoelectric; S3 abandoned dock; S4 loading buoy; S5 Cuatrerros Harbor and S6 Villarino Viejo

Table 1 Location of samples sites in the Bahía Blanca Estuary, Argentina

Sites	Name	Latitude (S) ^a	Longitude (W) ^a	Classification
S1	Rosales Harbor	38°55'43.69"	62° 4'14.50"	Harbor
S2	“Luis Piedra Buena” Thermoelectric	38°47'54.50"	62°15'23.07"	Thermoelectric facility
S3	Abandoned dock	38°46'46.43"	62°18'28.73"	Harbor/industry
S4	Loading buoy	38°46'58.82"	62°18'29.99"	Harbor/industry
S5	Cuatrerros Harbor	38°45'0.78"	62°23'21.95"	Fishing and recreational port
S6	Villarino Viejo	38°45'54.20"	62°25'35.50"	Rural zone

^a Coordinates determined by global positioning system (GPS)

electric power to the area in a petroleum gas and fuel oil combustion basis. S3 and S4 are located within the Galvan Harbor, the heavily industrialized core of the estuary. While S3 is situated in an abandoned dock, S4 is located in the proximity of a petroleum and oil derivatives loading buoy. S5 is located at Cuatrerros Harbor, a small fishing and recreational dock located in the inner part of the estuary. Finally, S6 is located at Villarino Viejo, the most inner zone close to the head of the estuary, in the vicinity of rural lands.

Surface oxic sediment samples were taken from the superficial layer (1–5 cm) using a stainless steel grab sampler. Immediately after collection, the samples were refrigerated, stored on solvent-cleaned amber glass containers avoiding exposure to light, and then rapidly transported to the laboratory, where they were stored at –20 °C. Sediments samples were lyophilized, powdered, sieved (250 mesh) and stored at 4 °C until analysis. The lower particle size fraction (<63 μm) was used for organotin compound extraction. Sample variance is substantially

reduced by analyzing this fine-grained fraction of sediment to minimize the confounding effects of variable grain size (Buggy and Tobin 2006).

Standards and reagents

Butyltin trichloride (MBT, 97 %), dibutyltin dichloride (DBT, 97 %), tributyltin chloride (TBT, 96 %) and tetrabutyltin (TeBT, 93 %) used as internal standard, were obtained from Sigma-Aldrich; tripropyltin chloride (TPrT, >99 %) used as recovery control standard was purchased from LGC Promochem.

Standard stock solutions of MBT, DBT, TBT, TPrT and TeBT were prepared in chromatographic-grade methanol (U.V.E.) (Merck) to obtain solutions containing 1 mg mL⁻¹ of Sn for each compound. Stock solutions were freshly prepared by appropriate dilutions in methanol.

All standard solutions were stored in amber flasks and vials at 0 °C in the darkness (UNEP/IOC/IAEA 1994).

Sodium borohydride ($\text{NaBH}_4 > 96\%$) was purchased from Fluka Chemika. Sodium hydroxide methanolic solution was prepared by dissolving 1.0 g of sodium hydroxide (98 %) in 1 L of chromatographic-grade methanol (U.V.E.) to get a 0.1 % solution (UNEP/IOC/IAEA 1994). Chromatographic-grade hexane (U.V.E.) (Merck) was used.

PACS-2 marine sediment reference material (National Research Council of Canada, Ottawa, Canada) was used to assess the method accuracy.

Procedures

Extraction and derivatization of organotin compounds

A schematic of the procedure is shown in Fig. 2. Typically, 2 g of freeze-dried sediments were humidified with at least 2 mL of milliQ water in 50-mL polypropylene centrifuge tubes. Then, 100 μL of tripropyltin were added to the samples as surrogate recovery standard, and sediments were allowed to stand for 30 min at 0 °C. Next, an appropriate volume of 0.1 % sodium hydroxide in methanol was added to obtain 4:1 methanol: water (v:v) ratio. After that, the tubes were capped and sonicated (at 0 °C) for 8 min. Then, 2 mL of hexane and approximately 100 mg of sodium borohydride were added. Finally, the tubes were sonicated for 1 min and left 1 h at 0 °C. The samples were then treated with sodium sulphate anhydrous and finally centrifuged at 4000 rpm for 20 min at 4 °C to prevent evaporation losses. After the sonication, the hexane layer containing the derivatized compounds was collected into an amber glass vial. After that, the volume was blown down to approximately 1.5 mL by a gentle stream of pure N_2 and finally 7 μL of TeBT standard solution is added as internal standard and immediately injected in the gas chromatograph.

GC-MS operational conditions

Separation and quantifying of organotin compounds were performed by a capillary gas chromatography (Agilent 7890B) coupled with a mass spectrometer (Agilent 5977A). The GC column was an HP-5MS fused silica column (30 m; 0.25 mm i.d.; 0.25 μm film thickness). One microliter of sample—or standard mixture, or blank—was injected on split-less mode at 220 °C. Helium was used as the carrier gas at a constant flow of 1 mL min^{-1} . The temperature program was 55 °C for 1 min, then 20 °C/min to 200 °C, which was held for 5 min.

The organotin hydrides were determined in the selected ion monitoring (SIM) mode. The selected ions were 121, 177, 179 m/z for DBT, the same ions plus 119 m/z for MBT and for TBT the selected ions were 119, 121, 177, 179, 233 and 235 m/z . For TeBT the ions were the same

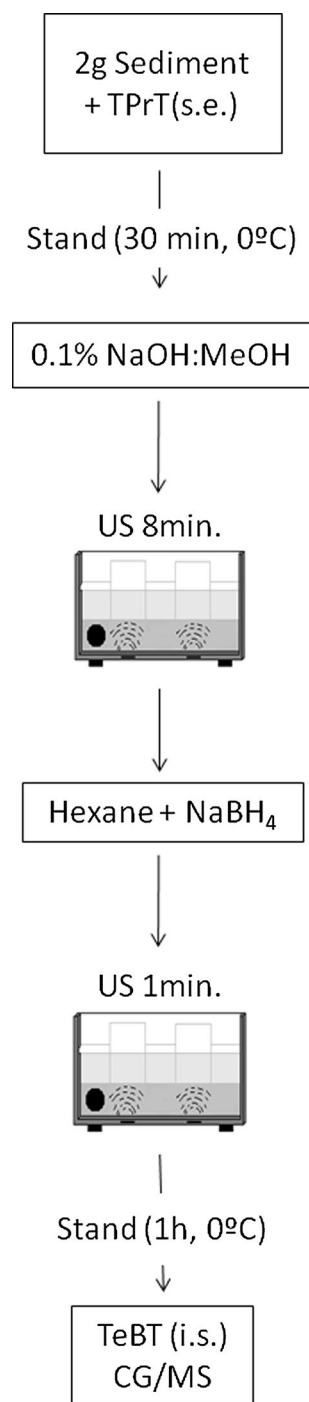


Fig. 2 Schematic representation of the ultrasound-assisted method

that for TBT plus 289 and 291 m/z . The TPrT was detected using the ions 119, 121, 163, 165, 205 and 207 m/z .

Physico-chemical parameters

Granulometric analysis The sediment granulometry was analyzed by a laser diffractometer (Malvern Mastersizer 2000). Prior to analysis, samples were treated with

hydrogen peroxide to eliminate organic matter, and the result was expressed as the total percentage of sediment particles below 63 mm in diameter.

Determination of organic-matter (%) and organic carbon (%) Organic matter (%) was determined by ignition loss. A subsample of 10–20 g of dry sediment (105 °C until constant weight) was heated in a muffle furnace at 500 °C for 3 h (Commendatore and Esteves 2004).

Organic carbon (%) was expressed from the organic matter content by using a correction factor (Pribyl 2010). The equation for the estimation of the organic carbon (%) according to this factor is $OM (\%) = 1.9 \times TOC (\%)$.

pH, salinity and temperature Temperature, pH and conductivity were measured at each sampling point. Salinity was calculated by conductivity and expressed as practical salinity units. The measurements were recorded with a multisensory HORIBA U-10.

Statistical analysis

The results were statistically analyzed using INFOSTAT software version 2008. The normal distribution of the characteristics in each group was tested with the modified Shapiro–Wilk test ($p > 0.05$), the correlation analysis ($p < 0.05$ was regarded as significant) and principal component analysis (PCA), the latter was carried using Matlab 7.0 (The Math Works), in order to evaluate the relationships between the organotin concentration in the sediment and other parameters.

Results and discussion

Physico-chemical parameters

As stated by Pinochet et al. (2009), the organic matter contents plays a significant role for the destination, mobility and availability of TBts into coastal marine ecosystems; in fact, the organic matter has been pointed out as the main sorbent matrix from where TBts will become more or less available to the benthic organisms through the settled sediments.

Table 2 shows the seasonal information about TBT, DBT and MBT concentrations together with the physico-chemical parameters collected for each sample point. The concentration of organic matter (OM, expressed in %) varies from 3.2 % (S5 in spring) to 11.0 % (S1 in autumn). No significant correlations ($p < 0.05$) were found with TBT, DBT and MBT concentrations.

In the diverse literature, contradictory results have been reported between organic matter content and organotin

level correlations. For instance, Pinochet et al. (2009) showed good relationships among organic matter content, TBT, and DBT concentrations in marine sediments from San Vicente bay in Chile. On the other hand, Abidli et al. (2013) demonstrated little or no correlations for these parameters in surface sediments from the Tunisian coast. This hardly predictable behavior can be attributed to the inherent physicochemical sediment complexity, such as the different composition of organic matter, relative adsorbability on inorganic particles and the existence of biological activity (bioturbation) in the upper sediment layers (Town and Filella 2002; Braga Castro et al. 2012). Further, the occurrence of multi-sources contributing to the same ecosystem could possibly pose a “masking effect”, biasing a possible correlation.

The grain size (clay, silt and sand) distribution in sediment samples is shown in Table 3. With regard to the grain size fractions, the totality of the sampling stations were classified as silty/clay sediments. Despite the fact that TBts would preferentially partition into the $<63 \mu\text{m}$ fraction, no significant correlation was found between TBT, DBT or MBT and the finest fraction ($p > 0.05$). This absence of correlation could be attributed to the great variability in deposition dynamics observed for the area of study. In addition, in the same table seasonal temperature variations are shown. The values of temperature ranged from a mean value of 8.7 °C in winter to 21.2 °C in summer.

The sorption/desorption activity of organotin compounds in relation to sediments can be strongly influenced by changes in the pH and salinity (Table 2). Regarding the pH variations, the values are almost constant for all the sampling sites within each season. A significant increase of pH is recorded in summer, while the other seasons have similar pH values (showing the lower values in autumn).

This can be explained by considering the contrasting sorptive behavior of the neutral and ionic species at a given pH and variable salinity conditions (Arnold et al. 1997, 1998; Meador 2000; Hoch et al. 2003; Burton et al. 2004). Taking this into account, the pH values measured at the area of study varied from 7.8 (autumn) in Rosales Port to 9.6 (summer) in Villarino Viejo, while salinity ranged between 27.8 (spring) and 35.8 (summer) both in Villarino Viejo. In general, salinity showed a general decreasing pattern outward (SW), as a main consequence of a dilution effect caused by the brackish tributaries of the drainage basin. There is an increase in summer, particularly in the sampling points situated in the inner zone of the estuary, due to the evaporation.

Organotin compounds determination

The seasonal concentrations of TBT, DBT and MBT are shown in Table 2. In this study, TBT levels ranged

Table 2 Concentration of organotin compounds in sediment samples from the Bahía Blanca Estuary (ng Sn g⁻¹ dry wt) and physicochemical variables

Sampling legs	Sites	TBT	DBT	MBT	TBts	BDI	OM (%)	% TOC	pH	Salinity	Temp. °C
Summer	S1	11.58 ± 0.85	66.79 ± 3.21	33.69 ± 1.15	112.06 ± 3.51	0.12	8.75	4.61	9.3	36.37	19.30
	S2	16.42 ± 0.99	77.68 ± 2.94	67.58 ± 1.15	161.68 ± 3.31	0.11	6.88	3.62	9.45	35.47	22.10
	S3	13.26 ± 0.38	74.35 ± 4.84	49.26 ± 3.06	136.87 ± 5.74	0.11	4.60	2.42	9.42	35.79	21.20
	S4	24.40 ± 1.15	66.86 ± 1.33	58.39 ± 3.08	149.65 ± 3.55	0.19	4.57	2.41	9.46	36.43	20.10
	S5	7.68 ± 0.15	76.81 ± 7.87	54.24 ± 2.68	138.73 ± 8.32	0.06	3.85	2.03	9.49	37.64	21.40
	S6	8.57 ± 0.52	65.06 ± 1.67	32.38 ± 0.07	106.01 ± 1.75	0.09	4.54	2.39	9.58	38.54	22.90
Autumn	S1	28.53 ± 0.54	67.64 ± 6.84	116.17 ± 7.83	212.34 ± 10.41	0.16	11.0	5.80	7.82	34.26	14.90
	S2	21.14 ± 1.06	84.90 ± 9.91	181.94 ± 6.07	287.98 ± 11.67	0.08	5.99	3.15	7.9	33.97	14.90
	S3	20.78 ± 1.40	74.36 ± 3.67	57.84 ± 5.12	152.98 ± 6.45	0.16	5.30	2.79	7.88	33.39	14.50
	S4	19.97 ± 1.73	61.48 ± 5.64	47.80 ± 4.24	129.25 ± 7.26	0.18	4.11	2.16	7.56	32.85	14.60
	S5	17.62 ± 0.11	52.76 ± 1.00	52.83 ± 5.64	123.21 ± 5.73	0.17	3.75	1.97	8.09	30.76	14.40
	S6	25.56 ± 1.27	77.08 ± 6.61	292.62 ± 8.44	395.26 ± 10.80	0.07	3.43	1.81	8.21	28.33	14.20
Winter	S1	19.69 ± 2.84	55.09 ± 5.24	216.86 ± 14.52	291.64 ± 15.70	0.07	4.95	2.61	8.31	35.60	9.50
	S2	12.53 ± 0.50	35.51 ± 1.54	213.64 ± 13.66	261.68 ± 13.76	0.05	7.62	4.01	8.29	34.83	8.70
	S3	8.45 ± 1.05	26.67 ± 2.80	41.34 ± 1.99	76.46 ± 3.59	0.12	5.49	2.89	8.45	34.52	8.20
	S4	7.71 ± 0.57	34.97 ± 3.78	52.86 ± 6.86	95.54 ± 7.85	0.09	4.48	2.36	8.46	34.52	8.10
	S5	15.41 ± 0.51	27.09 ± 2.89	31.05 ± 2.47	73.55 ± 3.84	0.27	5.30	2.79	8.51	32.09	8.00
	S6	10.28 ± 0.96	156.09 ± 12.20	35.43 ± 2.74	201.8 ± 12.54	0.05	4.13	2.17	8.74	30.69	9.70
Spring	S1	31.98 ± 3.78	16.59 ± 1.51	63.98 ± 7.14	112.55 ± 8.22	0.37	5.00	2.63	8.3	34.83	17.40
	S2	23.37 ± 2.88	16.51 ± 0.82	234.90 ± 5.60	274.78 ± 6.35	0.09	5.44	2.86	8.23	33.30	17.20
	S3	36.75 ± 3.39	26.59 ± 2.76	75.01 ± 4.24	138.35 ± 6.09	0.36	4.89	2.57	8.44	32.54	15.80
	S4	20.84 ± 2.04	14.32 ± 0.77	152.83 ± 18.48	187.99 ± 18.61	0.12	3.47	1.83	8.46	32.60	17.60
	S5	28.86 ± 4.64	20.40 ± 1.99	116.74 ± 19.86	166.00 ± 20.49	0.19	3.22	1.69	8.4	29.60	15.60
	S6	20.82 ± 0.36	36.78 ± 3.36	31.73 ± 0.71	89.33 ± 3.45	0.30	3.63	1.91	8.25	27.75	17.70

Values reported are the mean of three replicates together with the corresponding standard deviation

TBts TBT + DBT + MBT, BDI butyltin degradation index, OM organic matter, TOC organic carbon

Table 3 Average grain size of sediments at each sampling site. Results are expressed in percentages

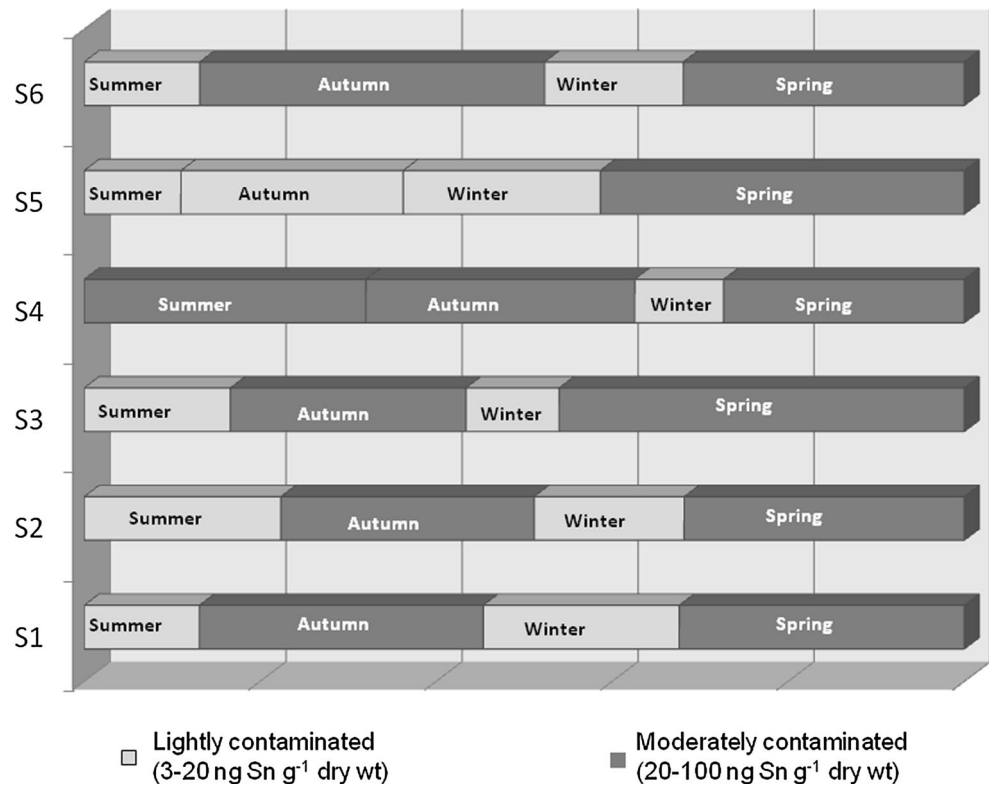
Fractions (<63 μm)	Sites					
	S1	S2	S3	S4	S5	S6
Clay	55.25	51.16	49.36	34.76	43.76	34.08
Silt	42.5	41.48	48.06	47.25	48.60	54.67
Ratio S/C	0.77	0.81	0.97	1.36	1.11	1.60
Sand	0.95	5.64	2.38	16.83	6.14	10.20
Classification	Silty-loam	Silty-loam	Silty clay	Silty-loam	Silty clay	Clay-loam

between 7.68 and 36.75 ng Sn g⁻¹ dry wt. Figure 3 shows a bar chart based on the classification proposed by Dowson et al. (1993). In accordance, samples for the first sampling leg (summer 2013) were found to be lightly contaminated by TBT (3–20 ng Sn g⁻¹ dry wt) with the exception of site S4 (loading buoy) which could be classified as moderately contaminated (20–100 ng Sn g⁻¹ dry wt). On the contrary, during the second sampling leg (autumn) all sites could be classified as moderately contaminated by TBT with the

exception of S5 (Cuatros Harbor, lightly contaminated). While all samples belonging to the winter period could be classified as lightly contaminated, the following period (spring) showed all sediments in the range of 20 to 100 ppb of TBT (moderately contaminated).

Thus, the TBT concentration is higher in autumn and spring. This seasonal variation could be attributed to several reasons. First, the dredging of the navigation route (Main Channel) remobilizes bottom sediments. Discharges

Fig. 3 The contamination pattern based on TBT concentration, according to Dowson et al. (1993), in sediments from Bahía Blanca Estuary



of dredged material can be expected to have high levels of TBT (Santos et al. 2004). In anaerobic conditions (bottom sediments), the half-life of TBT appears to be in the order of tens of years (Dowson et al. 1993). Anoxic sediments can act as reservoirs of TBT which can be remobilized to the water column by desorptive processes (Unger et al. 1988). Also in autumn, there is a noticeable increase of maritime traffic due to the grain export activities during the period between April and June.

The concentration of TBT in sediments during winter diminishes, probably due to an accelerated degradation process caused by diatoms (Seligman et al. 1996). In the temperate and eutrophic Bahia Blanca estuary, the phytoplankton annual cycle is characterized by a winter diatom bloom (June–September) (Guinder et al. 2015). In spring there is an increase of TBT concentration in sediments. An explanation of this fact could be that the organotin compounds can be adsorbed onto the surface of fine-grained sediment fractions, such as detritus and organic material coating mineral particles and colloids (Buggy and Tobin 2006). After the diatom bloom, sedimentation of phytodetritus contributes with a significant part of the total annual sedimentary input. Thus, the TBT adsorbed to the organic matter is settled down in the sediment.

Finally, in summer, the TBT concentration in sediments decreases. One reason for this behavior could be attributed to a desorption process. The optimum pH for the adsorption

of TBT on the surface of organic matter is around 6 (Buggy and Tobin 2006). In summer, the measured pH reaches values as high as 9.5. At this pH value the TBT adsorption is less favored (Hoch et al. 2002; Hoch and Schwesig 2004). Another explanation could be a dilution phenomenon caused by a peak of sedimentation recorded in summer (Cuadrado et al. 2011). The sediments in the column water are exposed to an accelerated degradation and, therefore, there are lower amounts of TBT associated with them (Clark et al. 1988).

The data have an intrinsic three-way structure, i.e., there are three modes [sampling sites ($I = 6$), variables ($J = 7$) and seasons ($k = 4$)] that constitute the data matrix X (Fig. 4). Unfold principal component analysis (UPCA) is an extension of PCA that was developed to handle multi-dimensional data sets (Villez et al. 2009), such as those arising from this study. As PCA cannot handle three-way datasets directly, unfolding is a straightforward approach to overcome this problem. In this work, so-called column-wise unfolding is applied (Fig. 4).

Three components were necessary to collect a 99.6 % of the total variance. Figure 5a–c shows the graphs for the loadings obtained after U-PCA analysis. The first component or factor has a great contribution of the MBT concentration, whereas the second principal component reflects the contribution of the DBT concentration. The third factor shows a major influence from the TBT

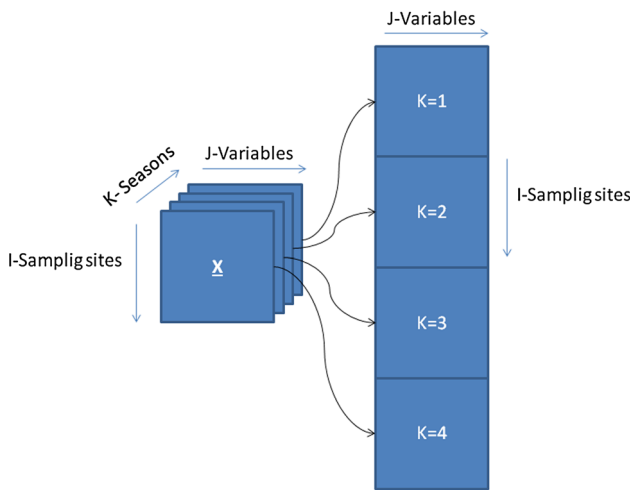


Fig. 4 Column-wise unfolding of the three-way matrix \underline{X} into a two-dimensional matrix

concentration, whereas temperature contributes in a lesser extent. The other variables (salinity, pH and organic matter content) do not show such a variability that may influence in the model.

From the scores plot (Fig. 5d–f) it can be seen that the sites S1, S3 and S5 in spring, S1 in autumn and S4 in summer seem to be the sites with a greater content of TBT. These sites seem to have lower degradation rates since there are no important contributions of DBT and MBT. On the other hand, sampling site S6 in winter is the most contaminated with DBT. In this site the contribution of TBT and MBT are non-significant. The amounts of DBT found in this site does not match with the corresponding values for DBT, so this could indicate that a fresh input of DBT in winter enters in the estuary, probably from the PVC industry. The amount of DBT slows down in the following spring and summer. Sites S2 and S6 in autumn show high concentrations of DBT; however, these sites also show important contents of MBT.

Regarding MBT, the sites S2 and S6 in autumn, S2 and S4 in spring and S1 and S2 in winter have the higher concentrations of the mono derivative, indicating either an important degradation process or fresh inputs from the PVC industries. Sites S2 and S4 in spring and S1 and S2 in winter do not have important contribution of both TBT and DBT.

In a general way, sites S3, S4 and S5 in winter are the less contaminated ones (they are always in the fourth quadrant). In summer, the sites have the lower contents of TBT (except for S4) and MBT. All of these sites have moderate to low concentrations of DBT.

Both, DBT and MBT—the degradation products of TBT—were detected in all the sampling stations. The concentration of DBT ranged from 14.32 ± 0.77 ng Sn g⁻¹

dry wt (S4: loading buoy, spring) to 156.09 ± 12.20 ng Sn g⁻¹ dry wt (S6: Villarino Viejo, winter). On the other hand, MBT concentrations ranged from 31.05 ± 2.47 ng Sn g⁻¹ dry wt (S5: Cuatros Harbor in winter) to 292.62 ± 8.44 ng Sn g⁻¹ dry wt (S6: Villarino Viejo in autumn). The unique precedent for DBT levels registered by Delucchi et al. (2007) ranged from 0.0 to 75.2 ng Sn g⁻¹ dry wt (Table 4). Then, the newly recorded concentrations have suggested possible additional sources contributing to the area. Looking at the area, there is an industrial hub in the vicinity of the sampling points, which includes the presence of a PVC plastic factory (poly-vinyl chloride and derivatives) close to the sampling stations (in particular S3 and S4). As DBT (and MBT) are commonly used as heat and light stabilizers in the chemical plastic industries (Ebdon et al. 1998; Olushola Sunday et al. 2012), the registered DBT inputs might be attributed to this source as industrial effluents are known to be released to the estuary between S3 and S4 sites. Further, domestic wastewaters and sewage sludge are daily released into the area of study which poses an additional possible diffuse source of organotin compounds.

Although Table 4 shows the butyltin concentrations reported in sediments from different regions of the world, it is difficult to draw a comparison with other areas as the field data of each location is influenced by factors such as geographical location, hydrographic conditions, water temperature, biotic and abiotic factors, intensity of maritime activity (Garg et al. 2011). In general, TBT levels in the sediment samples in this study were less than those reported in other locations, such as the Zuari estuary in India (Jadhav et al. 2009), Gdynia Port in Poland (Radke et al. 2012) and Santos-São Vicente Estuarine, Itajaí-Navegantes Harbor and Imbituba Harbor in Brazil (Buru-aem et al. 2013). Furthermore, the TBts levels in Bahía Blanca estuary here are similar to those in some other locations such as Kaohsiung Harbor in Taiwan (Dong et al. 2015), Shenzhen Bay in China (Deng et al. 2015) and San Jorge gulf in Patagonia, Argentina (Commendatore et al. 2015).

Spatial distribution

Figure 6 shows the distribution patterns of TBT, DBT and MBT in the studied sediments. S1 presented the highest TBT proportion (around 30 %) in spring. A possible rationale for this behavior can be found in the area of influence since this site is located in the proximity of Belgrano Harbor which includes military facilities and two commercial dry docks where ships (national and international service) are repaired and painted. The highest proportion of DBT is presented in winter for S6 (around 77 %). S2 showed the highest MBT proportion with a

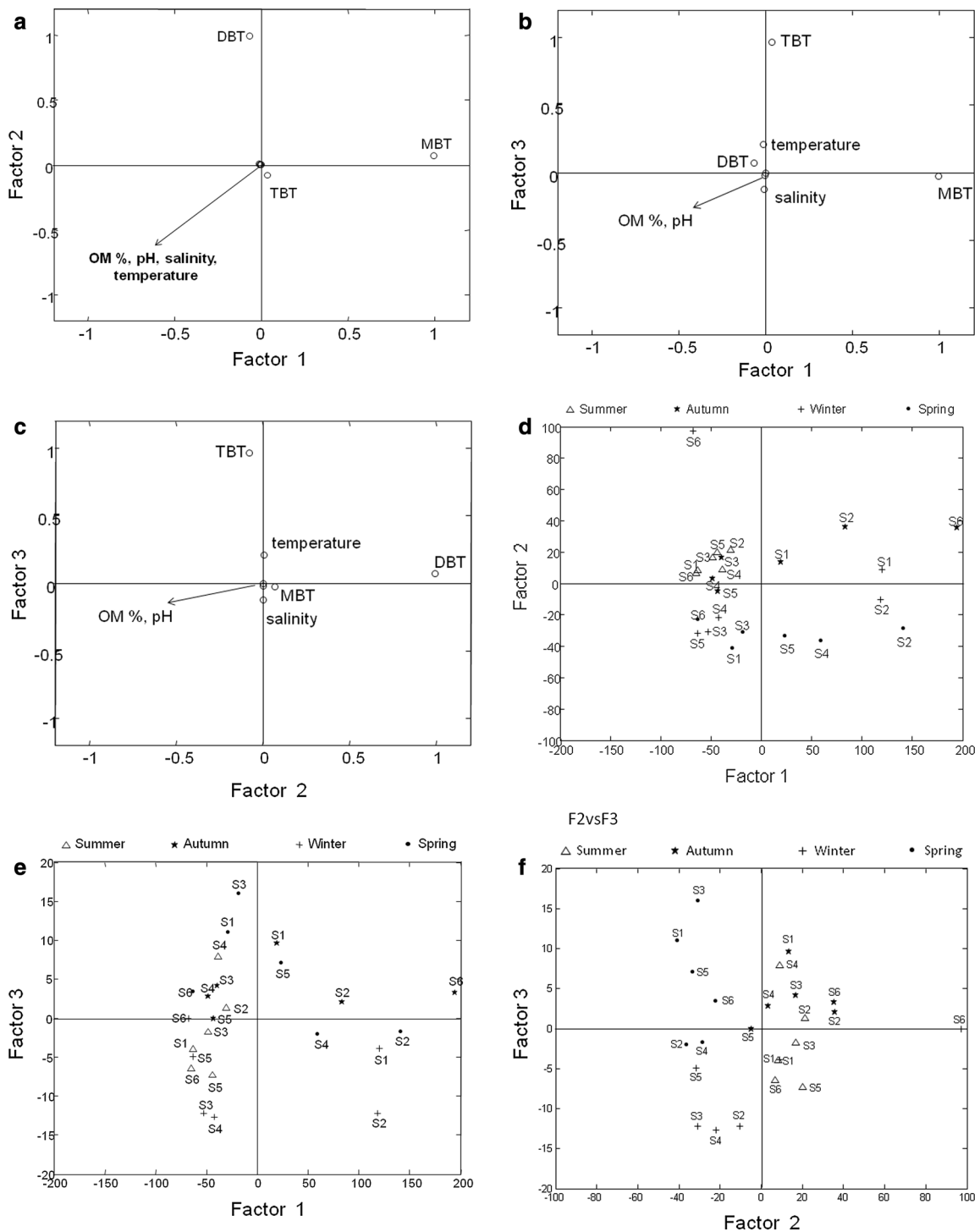


Fig. 5 a–c Loadings plots, d–f scores plots

seasonal increasing tendency reaching about 85 % of the TBTs in spring.

Some literature suggest that TBT can degrade directly to form MBT (Marcic et al. 2006), while others conclude that MBT is found mainly in estuaries because of its strong adsorption on sediment particles by ionic/polar interaction

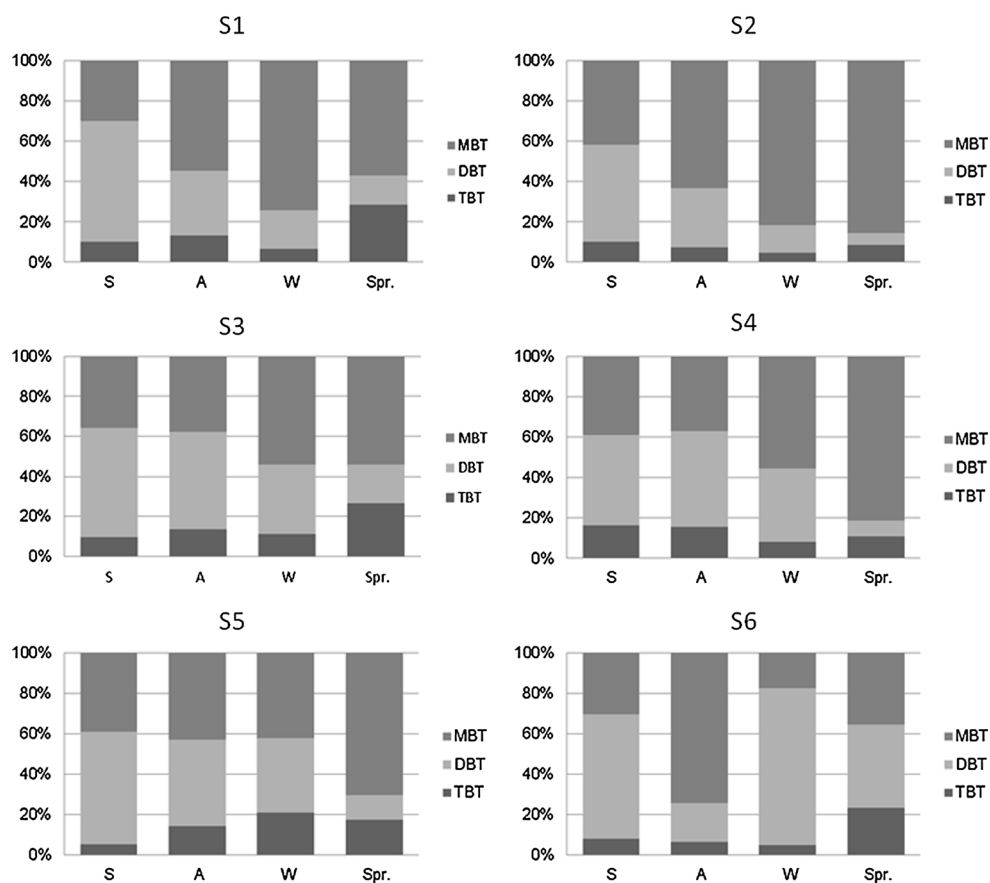
(Hoch 2001). In support of the first hypothesis, S2 is located in the proximity of “Luis Piedra Buena” Thermoelectric facilities, where high-temperature water is discharged to the estuary waters. Firstly, as is well known, higher temperatures contribute to faster degradation of the labile TBT (Almeida et al. 2004). This may explain the

Table 4 Butyltin compounds in sediments (ng Sn g⁻¹ dry wt) from different from worldwide locations and from this study

Locations	MBT	DBT	TBT	Reference
Zuari estuary, India	2.0–2238	1.8–1030	6.5–4353	Jadhav et al. (2009)
São Francisco do Sul Harbor, Brazil	<33–312.2	<16–394.4	<7–125.0	de Oliveira et al. (2010)
Itajaí-Navegantes Harbor, Brazil	<33–126.3	<16–115.2	<7–1136.6	
Imbituba Harbor, Brazil	<33–181.1	<16–125.2	<7–428.9	
Gdynia Port, Poland	274–1310	549–3810	1717–6743	Radke et al. (2012)
Elbe estuary, Germany	<1–31	<1–20	<1–100	Wetzel et al. (2013)
Santos-São Vicente Estuarine, Brazil	9.98–22.48	14.26–15.66	13.72–159.2	Buruam et al. (2013)
Kaohsiung Harbor, Taiwan	0.7–5.4	0.5–26.1	2.3–27.6	Dong et al. (2015)
Shenzhen Bay, China	na	2.30–24.20	nd–3.27	Deng et al. (2015)
San Jorge gulf (Patagonia), Argentina	<0.9–131.9	<0.7	<0.2–34.7	Commendatore et al. (2015)
Mar del Plata Port, Argentina	<3–258.8	<3–11.8	<2–150.4	Laitano et al. (2015)
Bahía Blanca Estuary, Argentina	na	0.0–75.2	0.0–170.3	Delucchi et al. (2007)
Bahía Blanca Estuary, Argentina	31.05–292.62	14.32–156.9	7.68–36.75	This study

na not available, nd not detected

Fig. 6 Distribution pattern of organotin compounds (TBT, DBT and MBT) in sediment from Bahía Blanca Estuary associated to each sampling site and season (S Summer, A Autumn, W Winter, Spr Spring)



augmented MBT levels recorded in the area throughout the sampling period. Moreover, S2 is located nearby the main city hall sewage outlet, which drains domestic (black waters) without any treatment. This area has been

particularly classified in bacteriological hazard due to the extreme microbial counts (Baldini et al. 1999). Studies have shown that microalgae and bacteria can play an important role in the biodegradation of TBT in aquatic

systems (Hoch 2001) then, the biological generation of MBT from TBT can be present at the area and would explain the high MBT yields recorded.

In terms of organotin distribution, S3 and S4 presents a similar behavior to S5, following the general pattern by which MBT increase during the spring season, possibly attributable to vessel repairing duties. All these sites present an intense shipping traffic and hold an artisanal fishing fleet of more than 40 boats.

Finally, despite S6 being surrounded by agriculture/rural lands and presents scarce to null fishing activities, presented the highest average concentration of DBT for the area of study. This site accounts for several special characteristics such as shallow water, low tidal energy and thinner layer of oxic sediments. The DBT accumulates in this site and the degradation process is less effective than in other sites of the estuary. As noted by Almeida et al. (2004), tidal currents are effective in conveying particulate matter carrying TBT and its degradation products from the main source areas to these remote zones, where settling of particles is favored by hydrodynamics. Then, results for this site outline the importance of transport and depositional behavior of particles at the Bahía Blanca Estuary.

Organotin degradation index

To assess whether organotin contamination derives from relatively fresh sources or not, it is useful to calculate butyltin degradation index (BDI), defined as the ratios between parent compound and its breakdown products (TBT/MBT + DBT) (Díez et al. 2002).

Many factors are responsible for the degradation of these compounds in the marine environment and it is not easy to assess how recent the input is. Taking into account that the samples were collected at the same time, in a relatively small area and under similar environmental conditions, the use of BDI seems to be appropriate.

Ratios >1 would suggest that the contamination is due to recent inputs of parent compounds; on the contrary, ratios <1 would mean that the parent compounds have degraded and thus the contamination should be considered “old” (Díez et al. 2002). Table 2 shows degradation index. According to BDI the obtained values indicate that the contribution of TBts at Bahía Blanca Estuary is old and under a general degradation process. As general TBts levels are much higher than the closer precedents (Delucchi et al. 2007)—indicating certain fresh inputs—these results should be interpreted settling the hypothesis by which local conditions such as temperature, microbial communities and the hydrodynamics pose an accelerated TBT degradation process which may explain the obtained values.

The values for BDI, in general, are higher in spring due mainly to a transport effect. The amounts of TBT

Table 5 Organotin compounds expressed as ng Sn g⁻¹ dry wt in the reference material

	Values		
	Determined	% recovery	Certified
TBT	863 (1.5)	97.0	890 ± 105
DBT	998 (1.9)	95.3	1047 ± 64
MBT	495 (1.1)	82.5	600 ^a

^a For information only

RSD% are included bracketed

originating from the vessels maintenance were incorporated to the estuary in winter. The remobilization of the sediments taking place in winter and spring is responsible for this behavior in BDI.

Validation requirements of the method

Accuracy of the method was assessed in terms of precision and trueness, using PACS-2 marine sediment reference material (National Research Council of Canada, Ottawa, Canada).

Precision was evaluated under repeatability conditions and was estimated as percent relative standard deviation, RSD (%), $n = 3$. Trueness was assessed in terms of recovery of extraction/derivatization reaction. The recoveries varied between 82.5 and 96.7 % and the associated RSD (%) were <15 % (Table 5). The results were in good agreement with the certified values and were in accordance with analytical validation recommendations (Eurachem 1998; IUPAC-International Union of Pure and Applied Chemistry 2002), i.e., recovery of 70–120 % and RSD (%) below 20 %.

Detection limits were calculated as three times the baseline noise of chromatograms taking into account the recoveries of analytes, using a sample mass of 2 g and a final extract volume of 1.5 mL approximately. Obtaining for TBT: 0.78; DBT: 1.08 and MBT 3.5 (ng Sn g⁻¹ dry wt).

Conclusions

Organotin compounds were detected at all the sampled sediments from February to November of 2013 along the Bahía Blanca Estuary. The different levels of TBT allowed the classification of the sampling sites from lightly to moderately contaminated and a higher income of these pollutants was registered during spring season, matching with the main ship/boats tuning season. According to the spatial distribution it was possible to associate different point and diffuse sources such as navigation traffic, ship-

repairing, proximity to plastic industries, industrial effluents, sewage outlets and domestic wastewaters. Finally, general organotin levels were higher than previously reported and the calculated degradation index classified the inputs under a degradation process.

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