Environ Monit Assess (2009) 155:341–353
DOI 10.1007/s10661-008-0439-7

Butyltin compounds and their relation with organic matter in marine sediments from San Vicente Bay—Chile

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Received: 6 December 2007 / Accepted: 11 June 2008 / Published online: 24 July 2008

Abstract Tributyltin and its degradation products, mono-and dibutyltin have been determined in sediments collected in some representative sites in San Vicente Bay, Chile. The organic matter contents of sediments and water collected simultaneously from the same sampling sites were also determined. High levels of total organic carbon were found in sediments, especially in those from the northern part of the bay (1.80–8.87%). Good correlations were found between total organic carbon and the oxidizable and refractory carbon fractions. Among the butyltin species determined, TBT presented the highest levels, ranging from 14 to 1,560 ng Sn g^{-1} dry weight. Concentration ratios of TBT to DBT ranged between 1.33 and 3.10, showing a high degree of contamination in sediments of this Chilean bay. All data obtained were analysed by the chemometric method of principal components analysis. A strong correlation was found between TBT and DBT concentrations in sediments, the different organic matter contents in sediments and water. In marine organisms only TBT was detected, containing the filterer organism *Semele solida* higher level than *Perumytilus purpuratus* and *Pyura chilensis* (220, 150 and 120 ng Sn g^{-1} dry weight, respectively). For the alga *Rodoficea iridae* the TBT concentration was 60 ng Sn g^{-1} dw. Comparatively, these values are higher than those reported for the same kind of marine organisms worldwide. The different samples from San Vicente Bay were found to be contaminated by TBT. This contamination can be attributed to the different anthropogenic activities taking place in the bay.

Keywords Butyltin compounds · Organic matter · Marine sediments · Marine biota · San Vicente Bay, Chile

Introduction

Organotin compounds of Sn(IV) (OTCs), in particular tributyltin(IV) (TBT) and to a lesser extent triphenyltin(IV) (TPhT), are widely distributed through the marine environment due principally to the fact that these compounds were used for almost three decades in antifouling paints. Aquatic pollution by OTCs has been of great concern in many countries, because the antifouling agent TBT is extremely toxic, especially to marine mollusc. Several coastal areas throughout the world have been proven to be contaminated by OTCs. The eco-toxicological effects of TBT on aquatic systems is well documented, it has been

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shown that OTCs cause sex disturbance in some aquatic organisms, phenomena known as imposex (Alzieu 1996, 2000; Morcillo and Porte 1998). This effect has also been described in organisms on the coast of Chile (Gooding et al. 1999). Similarly, OTC compounds have caused severe effects in coastal population of oyster in Arcachon Bay in France in the early 1980s (Alzieu 2000). Due to these finding, many countries worldwide have regulated the use of TBT as an anti-fouling agent (Bosselmann 1996; Champ 2000). Moreover, the International Maritime Organization (IMO) proposed the global prohibition on the application of OTC compounds in antifouling systems on ships by January 2003 and a complete prohibition by January 2008 (IMO 1990). Chile, as member of IMO must adhere to this agreement and authorities have shown some worry concerning this theme (Berrios 2000). In marine ecosystems, the degradation products of TBT, dibutyltin (DBT) and monobutyltin (MBT) have also been detected. These species are less toxic than TBT. The presence of these OTCs in marine ecosystems has been reported in a number of papers and review papers (Hoch 2001; Diez et al. 2002; Mzoughi et al. 2005; Gómez-Ariza et al. 2006; Díaz et al. 2007; Chandrinou et al. 2007).

The destination, mobility and availability of TBT discharged into coastal marine ecosystems and also of its degradation products are strongly influenced by the organic matter contents. In natural water TBT has a short residence time. Adsorption of TBT onto suspended particular matter is through to be an important removal process. OTCs have a relatively high affinity in particulate matter; TBT is therefore expected to sorbs to organic matter of which most settle on the bottom sediments where it still may be available to the benthic organisms (Sigg et al. 2000a).

The sorption processes of OTC on particle matter depend in great extent on the complexation of tri-substituted Sn(IV) cations by carboxylate and phenolic ligands present in the structure of humic acids (Arnold et al. 1998; Bueno et al. 2001). Relative to this subject, it has been postulated that can also occur hydrophobic interactions between the butyl chain of the OTC and the aromatic structure of the humic acids. In the literature contradictory results have been reported relative to the relation between the OTCs levels and the organic matter content present in the media. Some authors have demonstrated that significant correlations exist; however, others have found little or no correlation between these parameters (Randall and Weber 1986; Shim et al. 1999).

In this work, for the first time a detailed study on the presence of butyltin species in Chilean marine ecosystems are reported. The concentration of TBT, DBT and MBT were determined in surface sediments collected from different sites in San Vicente bay and also in biota of human consumption from the only site where this kind of sample was found. The concentration of organic carbon in sediment and water samples was also determined. To demonstrate if the OTCs concentrations are related to organic matter contents a chemometric method by principal components analysis was applied to all dataset, using the computer software package Unscrambler 7.0.

San Vicente Bay is located in the south-central region of Chile (36°45′S, 73°10′W). The bay is an area of multiple uses and important maritime activity, in which different industries may be found, among which may be highlighted a steel factory, a petroleum discharge terminal and a fishing port. Some studies have demonstrated that the sediments in this bay show high organic matter contamination (Mudge and Seguel 1999) which influences the dissolved oxygen levels in waters (Rudolph et al. 2002) and the macrofaunal community structure of the bay (Siemens et al. 2001).

Materials and methods

Study area

In this study, sediment and water samples were collected from seven representative sites in San Vicente bay, indicated as S1 to S7 (see Fig. 1) and biota samples were collected in the proximity of site S7, indicated as B. The bay is located in the temperate south-central region of Chile (36°45′S, 73°10′W). In the northern of this bay is located Talcahuano city and along the bay are placed several industries, including a steel factory and others major industries and commercial fishing activities. Some industrial wastes and Talcahuano municipal wastewaters were discharged, and to day at lesser

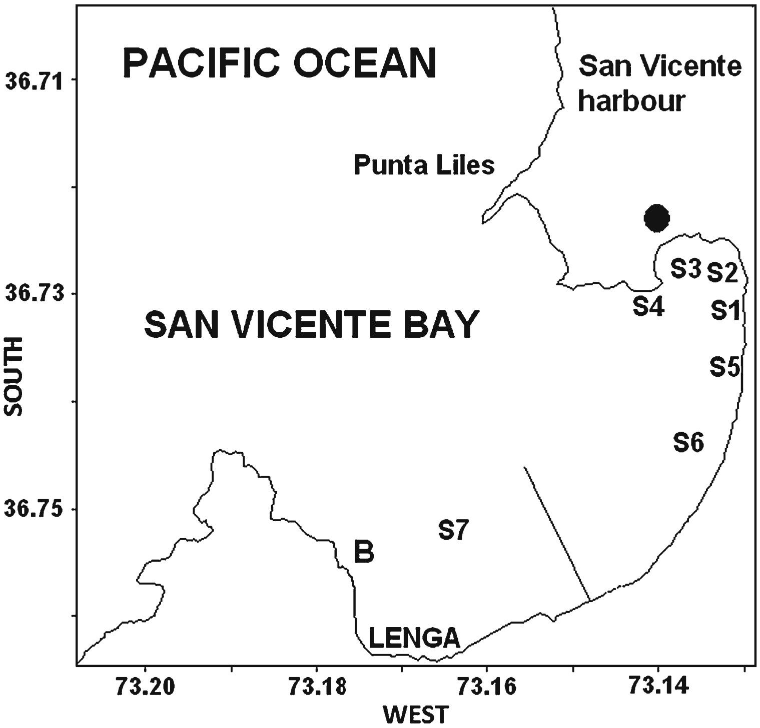


Fig. 1 Map of San Vicente Bay showing the locations of the sampling stations. Water and sediments were collected from S1 to S7 stations, biota samples from site B

extent, into the northern of the bay. Different studies have demonstrated that, as a consequence of these activities, the northern of the bay contains high organic carbon contamination, resulting in a reduction of dissolved oxygen levels in the water column, high organic carbon content in sediment and the absence of benthic organisms. In contrast, the southern sector is relatively undeveloped and an area of recreational use is located there. It is in this sector of the bay where some benthic and others organisms may be found (Furet et al. 1993; Mudge and Seguel 1999; Siemens et al. 2001; Rudolph et al. 2002).

Sampling and sample treatment

Sediment and water samples were collected simultaneously by a diver in January 2006. Water samples were taken with 2 l Niskin bottles, at 1 m from the sea bed. Water samples were filtered through a 0.45-μm pore size membrane, acidified at pH 2 and stored deep frozen at −20°C in glass bottles until analysis was carried out.

Surface sediments (10 cm depth) were taken with a Birge–Ekman dredge (15 × 15 × 15 cm). Approximately 3 kg of sediment was collected from each site (composite samples from different sites) and were placed in plastic flasks. They were then frozen at −20°C and lyophilized at 15°C, 0.1 mbar pressure, for 72 h. The dried samples were sieved to 1 mm. The <1 mm fractions were stored in desiccators at room temperature until analysis.

Perumytilus purpuratus (mussel) and *Pyura chilensis* (tunicate) samples were collected from rocks while the clam *Semele solida* was taken from surface sediments at 800 m near the Lenga stream mouth. Approximately 4 kg of each species were thoroughly washed with water from the same sampling site and were immediately stored in plastic containers. They were frozen and transported the same day in containers with ice packs and stored at −20°C until their treatment. They were defrosted, and opened with a titanium knife. The whole soft tissue was carefully removed from the shells and then crushed and homogenized in a plastic food processor with a homemade titanium blade. The homogenized samples were transferred to plastic flasks, frozen at −20°C and then lyophilized for 48 h at 15°C and 0.1 mbar pressure. The dried samples were re-homogenized and stored in desiccators until the analyses were carried out. A similar treatment was applied to the alga *Rodoficea iridaea* sample, taken at an inter-tidal zone.

Experimental

Determination of organic matter in water and sediment samples

Dissolved organic carbon (DOC) in the water samples was determined by the dichromate reflux method (Greenberg et al. 1992). The excess of dichromate was titrated by potentiometry. Chloride interference was avoided by precipitation with 0.15 M $AgNO_3$. Results for DOC are expressed in mg O_2 l^{-1}.

Total organic carbon (TOC) in sediment samples was determined by the flash combustion method. Level of CO_2 was determined by gas chromatography with a thermal conductivity detector (GC-TCD; AOAC Method 972.43 1997).

Oxidizable organic carbon (COx) in sediment samples was determined by oxidation of organic carbon with dichromate and subsequent potentiometric titration of the dichromate excess. The % COx was calculated on the base of organic matter containing 58% carbon (Nelson and Sommers 1982). It is important to remark that before TOC and COx determination, the sediment samples were pre-treated with 1 M HCl for inorganic carbon elimination. Refractory Organic Carbon (% ROC) was determined as the difference between %TOC and %COx.

Determination of butyltin(IV) species in marine sediment and biota

The butyltin species in sediment extracts were determined by gas chromatography with pulsed flame photometric detector (GC-PFPD). The analytical method used for extraction, derivatization and quantification of butyltin(IV) species by GC-PFPD in sediments has been described in detail elsewhere (Bravo et al. 2005). In brief, 1.0 g (±0.1 mg) of freeze-dried sample, spiked with tri-n-propyltin (TPrT) as the internal standard was extracted with 20 ml of glacial acetic acid. This mixture was shaken at 400 rpm, for 24 h and centrifuged for 15 min at 4,000 rpm. Then 2.0 ml of centrifuged extract, 20 ml of acid acetic–acetate buffer (pH 4.8) and 1 ml of isooctane were directly introduced into the derivatization reactor. Ethylation was carried out using 500 μl of sodium tetraethylborate $NaBEt_4$ (2% m/v). The mixture was immediately shaken at 200 rpm for 1 h. Subsequently 1 or 2 μl of the organic phase were directly injected into the GC-PFPD. The butyltin species were quantified using the standard addition method with TPrT as internal standard.

A similar procedure was applied for the analysis of biological species: 1.0 g (±0.1 mg) of freeze-dried sample was extracted with 2.5 ml methanol + 12.5 ml 0.1 M HCl in methanol and 200 μl of TPrT as internal standard, by shaking for 1 h at 200 rpm. The mixture was extracted by ultrasonic stirring for 2 h and then centrifuged at 4,000 rpm for 15 min. Ethylation and determination of butyltin species in the extracts by GC-PFPD was performed as for sediment samples.

The analytical method was validated by analyzing the certified reference materials marine sediment PACS-2 and mussel tissue CMR 477. The results for the analysis of Certified Reference Materials (CRM) are presented in Table 1.

Quantification for the CRM, PACS-2 and 477, for TBT and DBT, compared well with the certified values. The certified value of MBT for sediment PACS 2 has been shown to be debatable by a number of independent publications. The actual MBT concentration appears to be closer to 600 ng Sn g^{-1} (Scrimshaw et al. 2005).

Relation between organic matter and butyltin species

The relation between all parameters found in water and sediment samples from the seven sites was tested by the chemometric method of principal components analysis, using the computer software package Unscrambler 7.0 (Camo, Norway).

Results and discussion

Organic matter in surface sediments and bottom water samples from San Vicente bay

Some authors have reported that San Vicente bay presents high organic carbon contamination due

Table 1 Concentrations of TBT, DBT and MBT found in marine sediment (PACS-2) and mussel tissue (CRM 477) reference materials (Values expressed as means ± standard deviation in nanograms Sn per gram dw, $n = 4$)

CRM species	Concentration (ng Sn g^{-1})					
	PACS-2			CRM 477		
	TBT	DBT	MBT	TBT	DBT	MBT
Certified value	980 ± 130	1,090 ± 150	450 ± 50	2.20 ± 0.19	1.54 ± 0.12	1.50 ± 0.28
Obtained value	925 ± 34	1,043 ± 39	558 ± 20	2.31 ± 0.13	1.39 ± 0.11	1.31 ± 0.12

to the anthropogenic discharges and the industrial activities carried out in the area (Mudge and Seguel 1999; Rudolph et al. 2002). These studies conclude that on the bases of organic matter content in sediment and the quantity of organic discharges in the coastal area, the bay can be divided into three areas. The north-east zone of the bay, where the port is located, is the most impacted and the southern zone is the least affected.

The concentration of total organic carbon (% TOC) and the fraction of Cr(VI) oxidizable organic carbon (% COx) found in surface sediments and bottom water samples collected from different sample sites around the bay, are presented in Table 2.

As can it be observed, in sediments the % TOC is greater than those obtained by oxidation with Cr(VI; % COx). This confirms that the different sediments contain a fraction of refractory organic carbon, which is resistant to oxidation with Cr(VI). It is important to note that the % ROC in sediments from the NE zone (S1 to S5) is 7 to 334 times greater than that found in the southern zone (S6 and S7), where % ROC is less than 0.1%.

Additionally, the highest levels of % TOC and % COx in the sediments of NE zone are approximately 6 to 90 times greater than those of the southern zone. Similar behaviour was obtained for the concentration levels of COD in waters from the same sample sites; the values of COD in waters from the NE zone are 1.1 to 5.3 times greater than those from the southern zone.

The highest levels of organic matter found in the northern zone show the influence of the anthropogenic activities carried out there: in this zone is located the port and are discharged municipal and industrial fishing wastewaters. (Ahumada 1992; Ahumada and Vargas 2005). According to these authors, in the NE zone of the bay sedimentation velocity and organic matter content are greater than in other zone of the bay. The high organic matter contents may also be explained by the hydrodynamic behaviour of the bay, since water residence time and therefore that of the contaminants in the NE zone is greater than that of the southern zone (Rudolph et al. 2002; Mudge and Seguel 1999).

The % TOC in sediments obtained in this study are smaller than those reported by other authors for sediments from the same bay, e.g. Rudolph et al. (2002) reported levels between 1.3 and 12.6% for sediments from the NE zone; Mudge and Seguel (1999) reported levels in the interval 6.5–23.3%; and Ahumada and Vargas (2005)

Table 2 Organic matter contents in surface sediment samples and bottom sea water collected from San Vicente Bay (*TOC* total organic carbon, *COx* carbon obtained by chemical oxidation with Cr (VI), *ROC* refractory organic carbon, *COD* chemical oxygen demand in bottom water samples, after elimination of chloride)

Site	Sediment samples			Water samples
	% TOC	% COx	% ROC	COD (mg l^{-1})
S1	8.87 ± 0.09	5.53 ± 0.04	3.34	453 ± 9
S2	6.96 ± 0.07	5.60 ± 0.08	1.36	170 ± 4
S3	2.25 ± 0.09	0.42 ± 0.04	1.83	187 ± 5
S4	1.80 ± 0.08	0.88 ± 0.06	0.92	190 ± 6
S5	0.78 ± 0.06	0.373 ± 0.006	0.407	94 ± 3
S6	0.11 ± 0.02	0.045 ± 0.002	0.065	90 ± 4
S7	0.10 ± 0.01	0.087 ± 0.0016	0.013	80 ± 3

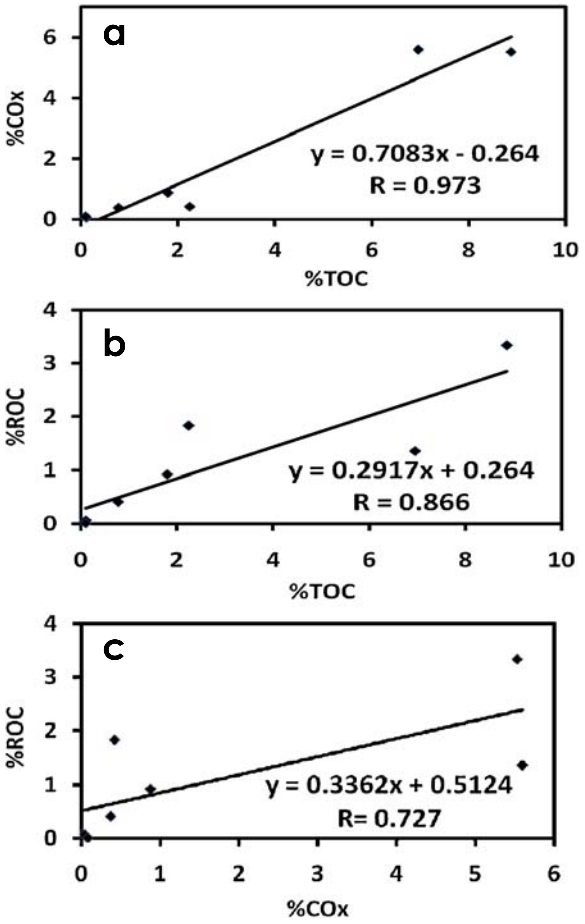


Fig. 2 Relationships between organic carbon concentrations in sediments from San Vicente bay. (TOC and ROC total and refractory organic carbon, respectively; COx carbon oxidized by dichromate)

between 0.3 and 0.8% for sediments from the south-central zone. The lower % TOC obtained in this study may be explained by the mitigating activities carried out in the area in recent years.

Furthermore, as can be observed in Fig. 2a, % COx and %TOC show a very close linear correlation, suggesting that in the bay both total organic carbon and oxidizable organic carbon shows the same distribution pattern. This conclusion is corroborated by the linear correlations obtained between % TOC and % COx with the refractory organic carbon (%ROC; see Fig. 2b and c, respectively).

Additionally, in order to prove if the concentration of organic carbon in sediments and bottom water of the same sites are related, indices of linear and exponential correlation were evaluated. The respective equations and correlation indices are presented in Table 3. The best linear and exponential correlations were obtained between % COD and % ROC. From these high correlations, it may be postulated that the dissolved organic carbon in the water column comes from the degradation products of the complex organic matter present in sediments. Relative to this behaviour, it has been reported that the composition of sediment organic matter not always reflect the dissolved organic carbon of the water column. The composition of organic matter in sediments depends on a series of complex factors, such as, the relative proportion of particulate organic carbon (POC; of slow degradation) and refractory organic carbon, the degree of POC decomposition and solubility during the sedimentation process, their relative adsorbability on inorganic particles, and the chemical composition and biological activity existing in the layer overlaying the sediments (Buffle 1990).

Butyltin compounds in surface sediments from San Vicente bay

Results of TBT, DBT and MBT concentrations in sediments, expressed in nanograms Sn per gram dry weight, from the seven selected sites are presented in Table 4.

Table 3 Relationships between organic matter concentrations in bottom water and in surface sediments from San Vicente bay

Function	Equation	Correlation index
Y (COD mg/L); X (% TOC)	$Y = 16,114X + 74.65$	$r = 0.725$
	$Y = 92.96\exp(0.784X)$	$r^2 = 0.647$
Y (COD mg/L); X (%COx)	$Y = 13.624X + 131.13$	$r = 0.499$
	$Y = 1,192.38\exp(0.075X)$	$r^2 = 0.347$
Y (COD mg/L); X (% ROC)	$Y = 33.898X + 49.272$	$r = 0.956$
	$Y = 87.695\exp(0.2856X)$	$r^2 = 0.949$

Table 4 Concentration of Butyltin species in surface sediments from San Vicente Bay (in nanograms Sn per gram ± SD dried weight; $n = 4$)

Site	TBT ng Sn g^{-1}	DBT	MBT	Ratio TBT/DBT
S1	1,560 ± 160	1,170 ± 100	< 27	1.33
S2	1,350 ± 160	766 ± 10	470 ± 67	1.76
S3	540 ± 250	342 ± 10	< 27	1.58
S4	800 ± 40	255 ± 51	< 27	3.10
S5	68 ± 3	46 ± 5	< 27	1.48
S6	900 ± 40	410 ± 26	223 ± 30	2.19
S7	14 ± 2	< 20	< 27	–

The highest concentrations of TBT and DBT correspond to sediments S1 and S2 collected from the port. In sediments from site S1 the concentrations of TBT and DBT are 111 and 59 times greater, respectively, that those from site S7, sediments containing the least concentration values for all three species. As can be observed in the distribution of the species presented in Fig. 3, TBT is the predominant species in the different sediments (≥50%).

From the predominance of TBT and its low degradation rate it may be postulated that the species comes from the continuous discharge of this contaminant, especially from the port of the bay. Stuer-Lauridsen and Dahl (1995) have proposed that the concentrations ratio TBT-DBT can be used to evaluate the TBT contamination degree of a particular site. These authors suggest that when the TBT-DBT ratio is higher than 1.5, the site may be considered as highly contaminated. Applying this criteria sediments from San Vicente bay are highly contaminated, excepting that of site S7 (DBT concentration was found to be less than the LOD). Furthermore, it was demonstrated that in these sediments the DBT concentrations are linearly correlated to the TBT concentrations: DBT (ng Sn g^{-1}) $= 0.659$ TBT (ng Sn g^{-1}) $- 64.162$, with a correlation index of 0.942. This strong correlation confirms that DBT is a degradation product of TBT.

For comparative purposes, in Table 5 are summarized the concentrations of butylated species for some sediments worldwide. In spite of the variability on the butyltin levels, generally these are ranged between 0.4–11 × 10^3 ng Sn g^{-1}, excepting the highest values reported by Ceulemans et al. (1998) in sediments from dry docks in Belgium. The concentration of butyltin species in sediments from San Vicente bay is within the range found through-out the world.

Relationship between butyltin species and organic matter

The distribution of contaminant species throughout the different phases of the marine ecosystem is strongly influenced, among other processes, by their sorption on the sediment particles, which is

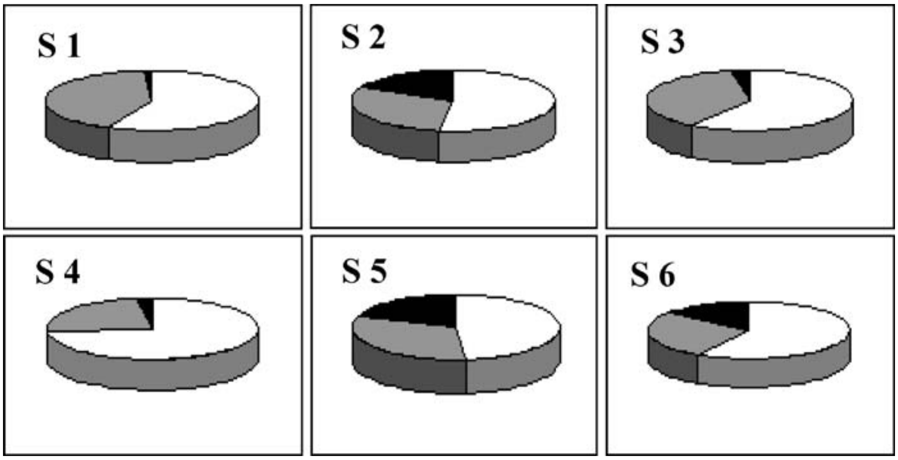


Fig. 3 Distribution of butyltin species in sediments from S1–S6 sites in San Vicente Bay. ☐ TBT; ▨DBT and ■ MBT species

Table 5 Levels of butyltin species in sediments worldwide

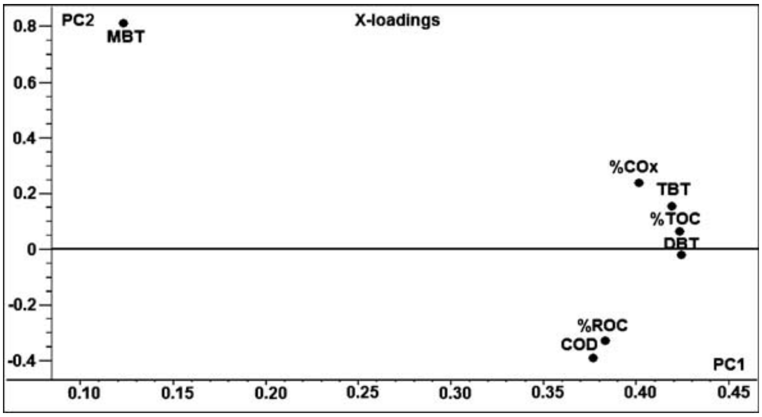
Location	Concentration range of butyltin species (ng Sn g^{-1};dw)	Reference
German North Sea	11.0–179	Shawky and Emons (1998)
Belgium	1–141 μg g^{-1}	Ceulemans et al. (1998)
Korea, Chinae Bay	2.52–24.66	Hwang et al. (1999)
Different countries	1.2–10,780	Hoch (2001)
Denmark and Sweden	$< 1 - 19$ (only TBT)	Strand et al. (2003)
Antarctic, Ross Sea	28–2,110	Negri et al. (2004)
Vietnam, north and central coasts	0.4–34	Midorikawa et al. (2004)
Brazil, Sao Paulo Coast	17–482	Godoi et al. (2005)
Portugal, rivers	4–12	Mzoughi et al. (2005)
Northern Spain	18–177	Díaz et al. (2007)
Chile, San Vicente Bay	14–1,560	This study

one of the principal mechanisms responsible on the decreasing of the contaminants concentration in water (Sigg et al. 2000b). The sorption capacity of sediment depends, for most of contaminants, on the content of organic matter and the sediment particle size. Therefore it may be postulated that sedimentary organic matter influences the mobility and availability of OTCs in coastal marine ecosystems.

With the aim of generating more evidence of the influence of organic matter on the spatial distribution of butyltin species in San Vicente Bay the chemometric method of principal components analysis was performed on the whole data obtained (organic carbon concentrations and butyltin concentrations). All information was compressed into a data matrix in order to determine the structure present in these components by estimating latent variables (see Fig. 4). Using cross-validation it was determined that two principal components represents the quasi totality (88.8%) of the total variance (51.1% the first component and 37.7% the second one), fitting the bi-lineal model. Analysis of the loadings shows that the variables %TOC, %COx, TBT, DBT and the ΣBTs, which constitute the first principal component, present high correlation.

It can be seen that the % ROC and the %COD are slightly distanced from the other variables; this probably due to a slight loss of linearity present in the correlation. The strong correlations between DBT and TBT species and the organic matter may be explained by the hydrophobic character of the chain of these species which favours adsorption on the organic matter present on the surface of the sediment particles; mechanism that would also occur in OTC bioaccumulation processes (Veltman et al. 2006). Moreover, Poerschmann et al. (1997), based on the sorption coefficient values found for different OTCs on particulate

Fig. 4 Loading of variables onto the first two principal components



organic matter, postulate the existence of simultaneous contribution of hydrophobic and polar interactions for the sorption process. Additionally, Arnold et al. (1998) postulate that the trisubstituted TBT^+ cation, in media with pH 3 to 9, may be complexed by negatively charged ligands from the humic acids present in sediments. Berg et al. (2001), based on laboratory experiments, proposed that sorption of OTCs in sediments is rapid, reversible and in its first stage it occurs due to the reversible complex formation between the cation and the phenolate and carboxylate ligands present in the organic matter.

The MBT levels explain the second principal component, showing that its concentration is only marginally correlated to the organic matter present in the analysed matrices. These results may be explained by taking into account that MBT, due to its low hydrophobic nature and high polarity is preferentially associated with the sediment inorganic fraction. Studies have been carried out on this subject demonstrating that MBT presents a relatively high affinity for iron oxides in comparison to that shown by TBT and DBT (Randall and Weber 1986).

In order to demonstrate if the considered variables present similar chemical behaviour in all sampling stations, a Scores graph was obtained (see Fig. 5). The stations clearly present two tendencies, demonstrating the differing associations between the species and sediment material. On one hand, the sediment from sites S2 and S4, with the highest concentrations of MBT, are found to lie in a direction formed by both components. On the other hand, the rest of the sampling stations are oriented in another direction, with S1 being the furthest point, which presents the highest % of TOC, COx and ROC.

These analyses demonstrate that the sedimentary matter have significant influence on the OTCs distribution. Taking into account the high levels of organic matter present in sediment and the correlations obtained with OTCs it may be stated that the butyltin species, especially TBT, present high persistence in sedimentary material, with the implied ecotoxicological risks. This statement may explain the fact that no biota was found in the sampling sites located in the northern zone of the bay.

Butyltin concentrations in some marine organisms

Complementary information on the presence of butyltin species in the San Vicente Bay ecosystem was obtained analysing marine biota collected from the site S7, located in southern zone of the bay, at the mouth of the Lenga stream. This was the only site where some species of human consumption were found. The collected samples were the bivalve molluscs *S. solida* (clam) and *P. purpuratus* (mussel), the *P. chilensis* (tunicate) and the alga *R. iridaea*. This alga is a raw material in the production of agar–agar, which is used as thickener and binder in the food industry. It is important to remark that bivalves are currently used as sentinel organisms in monitoring of TBT and its degradation products in harbours, mariculture

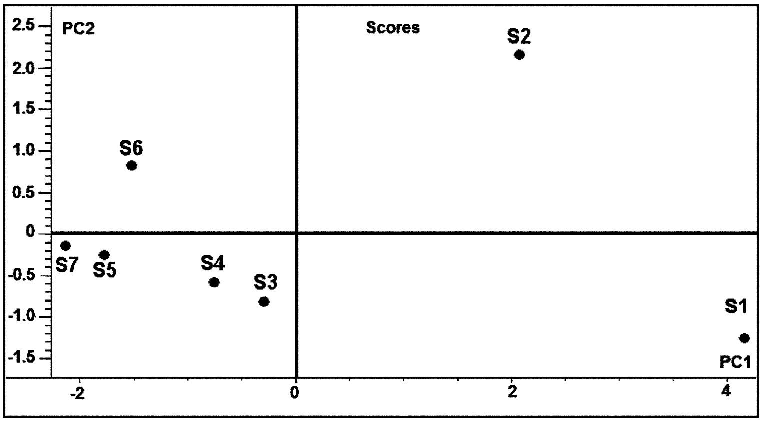


Fig. 5 Scatter plot of the scores onto the first two principal components

areas and other coastal enclosures (Uhler et al. 1993; Tolosa et al. 1992).

The concentration of TBT expressed as ng Sn g^{-1} dw in *S. solida* 220 ± 30; in *P. purpuratus* 150 ± 30 and *P. chilensis* 120 ± 20 was found to be, respectively, 3.7, 2.5 and 2.0 times higher than that of *R. iridaea* (60 ± 10 ng Sn g^{-1}). The highest concentration in *S. solida* may be due to the fact that it is the only species, among those analysed, which lives in sediments. The difference in TBT concentration among the filtering organisms and the alga may be attributed to feeding habits and the incidence of the TBT levels determined in the sediment of the bay, since the filtering organisms are more exposed to organic matter.

The partition coefficient between organisms and sediment was calculated by dividing the TBT concentrations in the organism tissue by the TBT concentration in the sediment from the same site. The values obtained were 15.7, 10.7, 8.6 and 4.3 for *S. solida, P. purpuratus, P. chilensis* and *R iridaea*, respectively.

Comparatively, these values are greater than those obtained by Midorikawa et al. (2004) for the clam *Meretrix* spp. from the northern part of Vietnam, who reported partition coefficients in the range of 0.5–5.5, with a mean of 2.01. These values are also greater than the range 4–7 reported by Hwang et al. (1999) for the filtering species *Crassostrea gigas* and *Mitylus edulis galloprovincialis*. These results indicate that over time, sediments appear to act as secondary sources of contamination for these organisms, either because TBT adsorbed previously may be desorbed or re-suspended into the water column and become available again or because TBT ingested with food is assimilated. Thus, *S. solida*, which lives directly in the sediment, presents a higher partition coefficient than *P. purpuratus* and *P chilensis* species, which inhabit the rocky intertidal zone; the low-

Table 6 TBT Concentration in marine organisms from different countries

Location	TBT concentration (ng Sn g^{-1}dw)	Biological species	Reference
Greece, Aegean Sea	<1.6–24	*Mytilus galloprovinciallis*	Chandrinou et al. (2007)
	<1.6–45	*Modiola barbatus L.*	
	<1.6–43	*Venus gallina*	
	16–25	*Pecten jacobeus*	
	6	*Callista chione*	
Hungry, Danube river	2.24–3.17	*Unio pictorum*	Üveges et al. (2007)
Iberia peninsula, western	48	*Hexaplex trunculus*	Gómez-Ariza et al. (2006)
	32.3	*Cymbium olla*	
	35–45	*Bolinus brandaris*	
Tunisia, Bizerte Lagoon	27–50	*Mytilus galloprovinciallis*	Mzoughi et al. (2005)
Taiwan, oysters cultures	101–113	*Cassostrea gigas*	Lee et al. (2005)
Denmark, coastal zones	9.9–11	*Mytilus edulis*	Strand and Jacobsen (2005)
	9.0	*Arctica islandica*	
	1–1.2	*Zostera marina*	
	1.2–2.2	*Fucus vesiculosus*	
Vietnam, North	1.4–56	*Meretrix spp.*	Midorikawa et al. (2004)
Antarctic, Terranova Bay	31–133	*Adamussium colbecki*	Magi et al. (2004) 37
Denmark and Sweden	452–1,316	*Nuculana pernula*	Strand et al. (2003)
	8.1	*Buccinum undatum*	
	34	*Musculus niger*	
Korea, Chinae Bay	100–1,800	*Cassostrea gigas*	Hwang et al. (1999)
	120–1,210	*Mytilus edulis galloprovinciallis*	
Germany, North Sea	26–179	*Mussel samples*	Shawky and Emons (1998)
Chile, San Vicente bay	220	*Semelle solida*	This work
	150	*Perumytilus purpuratus*	
	120	*Pyura chilensis*	
	60	*Rodoficea iridaea*	

est partition coefficient was obtained for the alga *R. iridaea* (4, 3) which inhabits the intertidal sandy zone.

The TBT concentrations for marine organisms from different countries are shown in Table 6. It can be observed that these concentrations are variable depending on their location. It is also possible to deduce that the TBT levels in the filtering organisms and in the alga from San Vicente bay are higher than those summarized in Table 6, with the exception of those reported by Hwang et al. (1999) for the species *C. gigas* and *M. edulys galloprovinciallis* from Korea.

Results reported for the marine matrices of San Vicente bay demonstrate the contamination degree of TBT present in the area and the implicit ecotoxicological risk. Therefore it is important to maintain the monitoring of butyltin species over time with the aim of evaluating their persistence and/or degradation.

Acknowledgements The authors gratefully acknowledge the financial support of FONDECYT (project 1050417) and Pontificia Universidad Católica de Valparaíso (project 125.728). C. Tessini also thanks CONICYT for the fellowship granted.

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