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Determination of TBT in water and sediment samples along the Argentine Atlantic coast

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Cases of imposex have been reported for some organisms living in areas of the Argentine Atlantic coast. Since this is one of the known effects of the anti-fouling agent tributyltin (TBT), quantitative determinations of organotins in samples of water and sediments collected from sites along the Argentine coast were carried out. Severe cases of imposex were first reported for two gastropod species living in the Mar del Plata area, and determinations of TBT in samples collected from this site gave extremely high values and showed a close correlation between the degree of imposex and TBT concentration. Recent investigations in the area have shown a significant decrease. Surveys were also conducted in sites that exhibit highly irregular coastal profiles to examine the relevance of physical environments. Alarming concentrations of TBT were determined in most of the sites where heavy boat traffic and/or marine activities occur, demonstrating the urgent need for regulations to avoid further input of TBT. Reports from other sites in South America reveal that this should be a subject of regional concern in order to avoid severe damage to the biodiversity of regional marine organisms.

Keywords: anti-fouling additives; organotin compounds; tributyltin (TBT); imposex; Argentine gastropods

Introduction

Owing to its worldwide use as an anti-fouling agent in paints for boats and other structures immersed in aquatic environments, tributyltin (TBT) is a common contaminant of marine ecosystems [1,2]. Its wide distribution, high hydrophobicity and persistence have raised concern about bioaccumulation, potential biomagnifications in food webs, and adverse effects on human health and the environment [3]. The most frequent and acute effect of TBT is endocrine disruption (imposex); more than 150 gastropod species have been reported to be affected [2,4,5]. Another undesirable effect of TBT is that it produces deformities in oysters [6].

Once released from an anti-fouling coating, TBT is rapidly absorbed by organic materials such as bacteria and algae, or adsorbed onto particles suspended in the water [7]. Subsequently it is readily incorporated into the tissues of filter-feeding zooplankton, grazing invertebrates, and higher organisms such as fish, sharks and dolphins, where it accumulates [8]. TBT represents the first example of an environmental endocrine disrupter that promotes adverse effects from gastropods to mammals; it permanently alters developmental programming [9]. Trace tin concentrations were found in the liver tissue of polar bears from Alaska [10], while elevated

TBT concentrations were determined in bottlenose dolphins (*Tursiops truncatus*) stranded along the U.S. Atlantic and Gulf coast [11]. TBT was also found in liver tissue of Beluga whales (*Delphinapterus leucas*) from Canada [12]. The first report of the finding of TBT in eggs from natural environments was our work with *Adelomelon brasiliense*, which provided evidence of TBT transference from the contaminated mother to the ovicapsule [5]. Several *in vitro* tests confirmed strong immunotoxic effects [13]; TBT disturbs the function of mitochondria and causes impairments in growth, development, reproduction and survival of many marine species [14]. Under favourable conditions, TBT may be degraded by bacteria, algae and fungi, through successive debutylation, to produce dibutyltin (DBT), monobutyltin (MBT) and, ultimately, inorganic tin, becoming progressively less toxic [15]. The rate-limiting step is the transformation of DBT to MBT. Although the toxicity of TBT has been considered mainly with reference to marine organisms, we have previously reported the deleterious effect of TBT on *Euglena gracilis* and *Chlorella* sp., two freshwater microorganisms [16]. The observed effects (measured by growth rate and chlorophyll content) were concentration dependent; the toxicity of TBT was found to be four orders of magnitude greater than that of ionic tin compounds. As far as we know, this

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was the first study investigating the damaging effect of TBT in freshwater organisms, but other studies have been reported recently [17,18].

TBT is considered the most toxic compound delivered to the environment [19]. Since it is a problem of global concern, several developed countries have adopted national regulations to control its dissemination; some banned the use of organotin-based antifouling paints on boats less than 25 m long [20]. Although several cases of imposex have been reported in marine gastropods at sites in Brazil, Chile, Venezuela, and Argentine coasts, no Latin American country has yet adopted any regulatory action. It was therefore of interest to monitor water and sediment samples collected along the Atlantic Argentine coast; it is also relevant to compare the current levels of TBT in the Mar del Plata zone with those previously reported [5].

Experimental details

Materials and methods

Reagents

Dibutyltin dichloride (DBT, 97%), sodium borohydride powder, 98% (Sigma Aldrich, USA), tributyltin chloride (TBT >97 %) (Merck Schuchard), and absolute ethanol (J.T. Baker) were used as received. Analytical-grade sodium chloride, anhydrous sodium sulphate and hydrochloric (J.T. Baker) were used. High-performance liquid chromatography (HPLC)-grade hexane and ethyl acetate were bi-distilled. Since these solvents were used for the sample treatment, purification was repeated until no impurities were detected by gas chromatography (GC) under splitless conditions. Durene (1,2,4,5-tetramethylbenzene), (Sigma Aldrich, USA), crystallized from ethanol was used as internal standard. Individual stock solutions of DBT and TBT were prepared by dissolving adequate amounts in ethanol or hexane, and stored at 4°C in the dark. A standard solution containing known amounts of TBT and DBT was prepared daily by dilution of the individual stock solutions, and a GC run was carried out as a control of the whole system before the analysis of the unknown samples.

Equipment

HP gas chromatograph Model 5890 Plus (Agilent Technologies, Avondale, PA, USA) fitted with a split/splitless capillary injector, a flame ionization detector system and a DB-5 capillary column (Agilent Technologies) cross-linked 5% phenyl-methyl siloxane, 30 m × 0.32 mm internal diameter (0.25 μm film thickness) was used for the separation of the organotin species. High-purity nitrogen was the carrier gas; column head

pressure was controlled at 4 psi. The temperature program was: 60°C for 2 min, 15°C min⁻¹ to 140°C, then 9°C min⁻¹ to 230°C, followed by 25°C min⁻¹ to 290°C, hold for 15 min. Injector and detector temperatures were 200°C and 280°C, respectively. This program allows the simultaneous determination of DBT and TBT. For maximum sensitivity, the chromatographic analyses were made under splitless conditions for 1.5 min. Retention times: DBT: 9.3 min; Durene: 10.1 min; TBT: 13.8 min. Integration of the chromatographic peaks was achieved using the commercial HP software supplied with CG-HPLC 1100 Chem Station. When needed, the identity of the signal for TBT and DBT was confirmed by gas chromatography-mass spectrometry (GC-MS) analysis under conditions similar to those used in GC analysis; GC-MS spectra were recorded on a Shimadzu GCMS-QP5050A Gas Chromatograph Mass Spectrometer equipped with a Shimadzu gas chromatograph GC-17A, provided with a Ultra 2, (cross-linked 5% phenyl-methylsiloxane), 50 m × 0.25 mm capillary column, coated with a film of 0.11 μm thickness. In some cases, GC-MS spectra were also recorded on a BG-Trio-2 spectrometer; typical clusters of tin-containing ions were observed. In the TBT mass spectrum listed below (only the most abundant peaks are given), clusters corresponding to the molecular ion, and to the loss of 57, (2 × 57) and (3 × 57) mass units are shown between brackets. MS *m/z* (relative intensity) [292, (1.59), 289, (1.2) (M⁺); [235 (67), 234 (37.5), 233 (56.7), 232 (32.1); 231 (35.4) (M⁺-57)]; [183 (29) 181 (29.6), 180 (8.3), 179 (100), 178 (57.1), 177 (100), 176 (59.3); 175, (88.5) (M⁺-(2 × 57)) (M⁺-1-(2 × 57)); 121 (42.0), 120 (25.5), 119 (35.8), 118 (19.3), 117 (18.7) (M⁺ - (3 × 57))].

Analytical procedure

Sampling

Samples of water and sediment were collected from the beach, the coast and the harbour at different sites, following the usual procedures for reliable sampling. Figure 1 shows the location of the main sites along the Atlantic Argentine coast. Sites of intense traffic were mainly chosen; in some cases, samples from neighbouring sites, where more pristine zones were expected, were also collected and analyzed to examine the magnitude of the anthropogenic origin of TBT contamination.

Water sample treatment

In a 500 mL Erlenmeyer flask, 2 mL of 1 M hydrochloric acid and 250 mL of water was poured. To this, 75 mL of solvent (hexane/ethyl acetate 70:30) was added. The

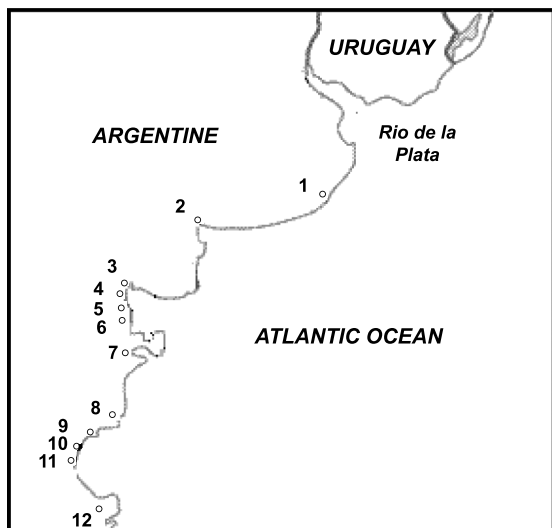


Figure 1. Sample sites.

1: Mar del Plata; 2: Bahía Blanca; 3: San Antonio Oeste; 4: Las Grutas; 5: Playas Doradas; 6: Punta Colorada; 7: Puerto Madryn; 8: Camarones Bay; 9: Caleta Córdova; 10: Comodoro Rivadavia harbour; 11: Rada Tilly; 12: Puerto Deseado.

mixture was placed on a magnetic stirrer and shaken for 20 min. The organic layer was dried with anhydrous sodium sulphate, then distilled by vacuum at 30°C to nearly 5 mL, and stored at -18°C before derivatization.

Derivatization

The concentrate was allowed to react for 1 h with a suspension of 85 mg of NaBH₄ in 5 mL of absolute ethanol; the solution was then washed with 10 mL of 10% sodium chloride. The organic phase was dried with anhydrous sodium sulphate; 0.2 mL of durene solution (2.62 µg L⁻¹) was added as internal standard, and the mixture was carefully distilled under vacuum at room temperature to a final volume of 0.1 mL. The TBT content was determined by GC (injection: 2 µL).

Sediment sample treatment

Sediments were freeze-dried using a Thermo Savant Molulyo Liophilizer, provided with a WLP200 Savant Pump. Approximately 1 g of solid sample, exactly weighed, was placed in a flask provided with a lid. To this was added 30 mL of solvent (hexane/ethyl acetate 70:30), and the system was shaken for 30 min, centrifuged and the solvent collected. The process was repeated successively with 30 mL and 15 mL of fresh solvent. The whole organic phase was partly distilled and derivatized for GC analysis. Although a single number is assigned to samples from each site in Table 1, several TBT concentration determinations (four to seven) were performed for each sample.

Results and discussion

Comparison of analytical methods

TBTs are present in seawater at ng L⁻¹ levels, therefore their quantification requires highly sensitive techniques [21]. The complete validation of organotin analysis in seawater samples is still far from being achieved, mainly because of reproducibility problems [22]. Since our monitoring plan involved multiple TBT determinations, a suitable and feasible method was needed. Ion pair chromatography and solid-phase microextraction methods were not suitable, due to the high cost of each determination. A suitable extraction procedure for both water and sediment samples was developed as described in the experimental section. Calibration curves were determined for a wide range of TBT concentrations in sediment and water ([Sn] 100–11,000 ng L⁻¹) and the detection limit (DL) was determined for each case (DL = 54.4 ng g⁻¹ dry wt. in sediments; DL = 156 ng L⁻¹ in water); details of the method validation and the calibration curves will be published elsewhere. The recovery of TBT dissolved and spiked to unpoluted sediments ($n = 5$) was 90 ± 5%. Aging may be an important component of the fate of TBT in sediments; therefore, in the present work, DBT was also carefully looked for in all samples.

Several HPLC methods have been published for the analysis of organotins [23]; nevertheless, since in the case of TBTs the peaks are generally broader than those found with GC, in the present work GC was chosen as the most suitable technique. Due to the low volatility of the target compounds, a derivatization step (based on *in situ* hydridization with sodium borohydride, NaBH₄) was carried out prior to GC. In order to ensure good quality control of tin speciation analysis, the recommendations given by a series of inter-laboratory studies were followed [24]. We have recently participated in an inter-laboratory study organized by the A&M University (Texas, USA) and our results were considered within 100% of confidence. In some cases, the identity of the peak at the retention time of TBT was confirmed by applying GC-MS. In all cases, the clusters corresponding to the molecular weight of TBTH (292 for ¹²⁰Sn), as well as the ions of m/e ($M^+ - 1$), ($M^+ - 1 - 57$), [$M^+ - 1 - (2 \times 57)$] and [$M^+ - 1 - (3 \times 57)$], were clearly observed.

Samples from the Mar Del Plata zone

The results of determinations of TBT carried out in samples of water and sediment from the Mar del Plata (MdP) zone, collected in 2001 (previously reported [5]) and in 2007 are all summarized in Table 1 (see site 1 in Figure 1). For the sake of simplicity, average values of TBT concentrations are given for those samples

Table 1. TBT contents in water and sediments from the Argentine Atlantic Coast.

Sample	Zone	Site ^b	[TBT] ^a	
			Water (ng L ⁻¹)	Sediment (ng g ⁻¹)
	Mar del Plata	1		
1	Beach		190 ^c 160 ^d	200 ^c 175 ^d
2	Coast		300 ^c 400 ^d	nd ^e
3	North Pier		4400 ^c 400 ^d 600 ^d	1300 ^c nd
4	Harbour		6700 ^{c, f}	5200 ^c
5	Naval Base		770 ^d	700 ^d
	Rio Negro Province			
6	San Antonio Oeste Pier ^g	3	3700	125
7	Las Grutas	4	1370 ^h 800 ^h	77
8	Playas Doradas	5	650	nd ^e
9	Punta Colorada	6	6200	60
	Puerto Madryn	7		
10	Luis Piedrabuena Pier		250	200
11	Aluar Pier		580	655
12	Heavy Transit Zone		1500	1780 ⁱ
13	Harbour			565 ^j
	Southern zones^m			
14	Camaronas Bay	8	na	60 ^k 200 ^l
15	Caleta Córdova Platform	9	na	550 ^l 245 ^k
16	Comodoro Rivadavia Harbour	10	na	400 ^l 100 ^k
17	Rada Tilly Beach	11	na	180 ^l
18	Puerto Deseado Harbour	12	na	850 ^l

^a[TBT] reported as Sn, in accordance with [12]. ^bSee sites in Figure 1. ^cSamples collected in 2001. ^dSamples collected in 2007. ^end: Not determined. ^fSupernatant liquid of deep sediment. ^gImposex zone. ^hValues from two different sites in Las Grutas. ⁱTraces of DBT. ^j[DBT = 780 ng g⁻¹. ^kSamples collected in September 2007. ^lSamples collected in September 2006. ^mContamination by polycyclic aromatic hydrocarbons prevents satisfactory determination of TBT in water samples from this zone. ^{na}na: no data available.

collected in 2001; individual values for each site have been reported elsewhere [5]. The data for [TBT] in the range 190–400 ng L⁻¹ (expressed as tin) for samples 1–3 in water were similar to the value of 480 ng L⁻¹ determined in 1994 in Aburatsubo Bay (Japan) [25]. Higher values ([TBT] = 3340 ng g⁻¹ in sand and 600 ng g⁻¹ in silt) were reported for samples collected in the vicinity of the shipyard in Arcachon Harbour (France) [26]. Many leisure boats anchor at the MdP coasts, and this might be the cause for the higher TBT levels in comparison with the beach area. Interestingly, determination of the total tin concentration in the water and sediment samples by hydride generation atomic absorption spectrometry indicated that the TBT made up almost 100%

of the tin, suggesting that anthropogenic organotins represented the major source of tin in these areas.

In the samples collected in 2001 and 2007, the TBT levels in beach sediments (sample 1) are not much higher than those observed in the seawater, suggesting that the appearance of TBT in this area could be relatively recent (probably arising from TBTs coming from the more contaminated, crowded areas). In contrast, in samples from the North Pier (sample 3, area of intense boat traffic and restricted water exchange) and the harbour (sample 4, where large commercial vessels and small fishing boats operate), TBT levels determined in water, sediments and the supernatant phase of sediment samples were very large, particularly for the samples

collected in 2001. The sediments from the Naval Base (sample 5) were very dark; the data indicate that this is the most contaminated site of those recently surveyed. Comparison of the TBT concentrations determined in 2001 and 2007 showed, in all cases, significant decreases, especially for the samples from North Pier. It is interesting to note that the samples in 2001 were collected shortly after the land had been reworked to build the Pier; this is probably the cause of the high values observed, revealing accumulation of TBT for probably more than 15 years.

Samples from the Bahia Blanca zone

An important harbour has operated near Bahia Blanca (site 2, Figure 1) for many years; nevertheless, measurements in samples from this zone showed no significant amounts of TBT in sediments; consistent with this, no imposex was found in gastropods collected from this site [27].

Samples from Rio Negro province

Sites 3 to 10 are located in the huge area known as Patagonia. The city of San Antonio Oeste (site 3 of Figure 1) is located in San Antonio Bay, at the north of the San Matías gulf, in Rio Negro Province. San Antonio Bay and the surrounding area constitute an important bird conservation site, forming part of the Western Hemisphere Shorebird Reserve Network International, WHSRNI [28]. The high value of TBT even in water samples indicates recent input. It is worth noting that it has been recently reported that imposex affected between 21 and 71% of the females of *Buccinanops globulosum* (*Prosobranchia*, *Nassariidae*) populations in San Antonio Bay [29], (site 3) where the highest TBT concentration of this zone was determined (sample 6). In contrast, the open sea areas of Las Grutas (site 4) and Playas Doradas (site 5) showed lower TBT concentrations (samples 7 and 8). Samples from the site called Punta Colorada (site 6) exhibited extremely high contamination by TBT. This is an area where the population engages in small-scale fishing of hake with artisanal boats, sport fishing and recreational coastline activities. Although these could be considered activities of low TBT impact, the TBT concentration is even higher here than in the harbour, showing probable recent TBT input. In fact, we have identified information regarding the operation of the Sierra Grande mine, located in the pier of Punta Colorada. The output of the Sierra Grande mine is exported through the port of Punta Colorada.

Samples from the Puerto Madryn zone

Puerto Madryn is a city located in Golfo Nuevo (Figure 1, site 7). In this zone, one of the major tourism

attractions is the ‘whale show’, which can be easily observed from the coast during the spring season. Due to the clear water, large numbers of whales gather here for reproduction and for protection for their newborns. Nevertheless, the results gathered in Table 1 show significant amounts of TBT in water and sediments from different sites in the area. It must be taken into account that near Puerto Madryn harbour, Argentina’s biggest aluminium plant, ‘Aluar’, has built its own pier, and the large vessels that bring bauxite (the raw material for manufacturing aluminium) are anchored there. The most contaminated sample (sample 12) corresponded to the heavy transit zone, while the less-contaminated samples corresponded to the Luis Piedrabuena Pier (sample 10). With regard to the value obtained for the water sample from this site in September 2006, it is worth noting that several tourist vessels, as well as others from the Argentine Navy, usually anchor in this dock. It is interesting to note that traces of DBT were found in sample 12; the sediment from the harbour (sample 13) shows [DBT] even higher than [TBT]: these results indicate that TBT inputs are longstanding. Current regulations have limited recent inputs, probably because of the tourism attracted by the ‘whale show’.

Samples from southern zones

Samples from sites located in southern zones were mainly collected in the surroundings of Comodoro Rivadavia. Comodoro Rivadavia is an important city and harbour of the Patagonian Province of Chubut, located in the San Jorge gulf, (an inlet of the Atlantic Ocean) in the centre of one of the largest oil basins in South America. The main activities are related to oil exploitation. The sampling sites are shown in Figure 1 (sites 8–12). The data in Table 1 showed significant concentrations of TBT, except for in Camarones Bay (sample 14, site 8) which is located at the opening of the gulf and is an area of relatively open sea. Analysis of the samples collected in 2006 showed that the more contaminated areas are Caleta Córdova (sample 15, site 9, a fuel-loading platform), and the harbour (sample 16, site 10). Samples from other sites showed [TBT] <200 ng g⁻¹. Due to the intense oil exploitation across the whole area, contamination with polycyclic aromatic hydrocarbons prevents precise determinations of TBT concentration in water samples from this zone. The sediment samples, in several cases, were also contaminated by hydrocarbon residues that interfere with the GC determination. TBT is probably adsorbed on the surface of the coarse sand and stones, and it was difficult to carry out a reliable and thorough extraction. To improve TBT extraction, the sample was kept in contact with the solvent for several days, and an ultrasonic bath was used to improve mixing.

It is worth noting that the samples collected 1 year later showed a significant decrease in TBT concentrations in all cases. Thus, in Camarones Bay, the concentration was near the detection limit of TBT in sediments (DL = 55 ng g⁻¹). Samples collected in Caleta Córdoba (site 9) and the harbour (site 10) also showed a significant decline, probably due to increased precautionary protective measures adopted by the companies responsible for the oil exploitation in the zone. Rada Tilly Beach (site 11) is a 'clean' beach with strict regulations, as it is a tourist attraction. As can be seen in Table 1, the [TBT] of sample 17 was the smallest of the samples collected in 2006 in the Chubut province. Puerto Deseado (sample 18, site 12), a fishing harbour in Santa Cruz Province, on the estuary of Rio Deseado, is another area very contaminated by TBTs.

Comparison of the present results with studies from various regions of the world

As TBT has been widely used in anti-fouling paint formulations used on boats, ships, vessels, docks, cooling systems immersed in water, etc. for almost three decades, it is widely distributed throughout the world. Concern about its ecotoxicological impact was clear in the 1990s, and there have been many reported determinations of TBT levels, in particular from many developed countries. Values of TBT (in ng ion/g dry wt.) as high as 12,400 were determined in sediments of Portland and Boothbay Harbor (USA) [30]; 9260 in the Western Mediterranean [31]; 108,336 in New Zealand [32]; 8540 in the Coastal of Poland [33] and 3900 in the East Coast Estuaries, UK [34], to mention just a few examples of reports of the last decade. Strict legislative regulations on the use of TBT in anti-fouling paints and other industrial usage have produced a significant decline of TBT concentrations in samples from these sites in the present decade. Thus, recent determinations at more than 100 sampling points in Japan showed important decreases, and the maximum value was 9.8 ng L⁻¹ [35]. In contrast, an increase of TBT in bottom sediments in developed countries has been reported, as hot spots have been identified associated with ship channels, ports, harbours, and marinas, in different places, such as the occurrence of TBT in the sediments of Barcelona harbour [36].

Regarding developing countries in the Asia-Pacific region, one of the first comprehensive reports on butyltin pollution monitoring was published in 2002 [37]; butyltin compounds (TBT, DBT, MBT) were determined in green mussels (*Perna viridis*) from various developing countries in Asia, such as Cambodia, China (Hong Kong and southern China), Malaysia, India, Indonesia, the Philippines and Vietnam. Samples from polluted areas in Hong Kong, Malaysia, India, the Philippines and

Thailand revealed levels comparable with those in developed nations. Recent determinations in sediments from Malaysian marine environments showed the presence of TBT in all samples, ranging to values as high as 1400 ng g⁻¹ dry wt. [38]. TBT was also found in green mussels and in muscle of 10 species of fish from coastal waters; in some cases the TBT levels in mussels and fish from the polluted areas exceeded the threshold for toxic effects on organisms and tolerable average residues levels as seafoods for human consumption.

In the Latin American region, despite some cases of imposex having been reported in marine organisms of this region, [28,29,39,40], not a single country has yet established any legislative regulation to limit the use of TBT-based anti-fouling paints and industrial usage. A few studies have been reported in surface sediments from the São Paulo State coast (Brazil), in which the observed values of [TBT/(DBT+MBT)] showed more degradation than that determined in Guanabara Bay in Rio de Janeiro in 2005 [39]. Imposex has also been observed in the southern Caribbean, around Margarita Island, and on the continental coast of Venezuela [40]. Comparison of the values of TBT determined in the Argentine Atlantic coast revealed that samples from the more contaminated sites have concentrations comparable with those found in samples from some developing Asian countries. The present results also show that the more polluted areas are those of heavy marine traffic. These results also highlight that data from samples collected in different years from places where some local regulations have been applied indicate a decline in TBT concentrations. This is consistent with conclusions from polluted areas in Asian countries that revealed levels as high as 14,000 ng g⁻¹ in sediments, but showed significant reductions when legislative regulations were applied [41].

Although in Argentina dietary intake of seafood is low, the finding of TBT in gastropods and in muscle tissue of several fish species is of concern with regard to human health; this is more important for Latin American countries where daily dietary fish consumption is higher. There are also relevant economic consequences for countries such as Chile, where the export of seafood is a major economic activity. Several marine organisms, such as *X. cassidiform*, *Ch. Giganteus*, *N. crassilabrum*, among others, that are highly appreciated as seafood, have shown high population declines due to imposex levels ranging from 85–100%, in some sites of the Chilean Pacific coast [42].

Conclusions

Determination of TBT levels in samples of water and sediments collected from several sites along the Argentine Atlantic coast showed very important

concentrations of this highly toxic endocrine disruptor of anthropogenic origin. Consistent with the analytical results, the data show that there is a close correspondence between the observed degree of imposex and the TBT concentration determined in water and/or sediment. In some critical sites, species have shown considerable declines in population, indicating the need for rapid legislative regulation and effective control to preserve the biodiversity of the zone. TBT has been found in seafood, and this is of particular concern with regard to human health, in particular for Latin American countries where the dietary intake of seafood is relatively high; it also has relevant economic consequences for countries that have dependence on the export of seafood. The present results also show that data from samples collected in different years from sites where some local regulations have been applied indicate a reduction in TBT levels. Therefore, the adoption of legislative regulations recommending replacement by regular application of other anti-fouling paints is urgently required. The presence of organotin compounds in water and deep bed sediments cannot be ignored; periodic monitoring is needed to determine the full extent of TBT contamination and its biological implications, in order to preserve regional biodiversity.

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