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Organotins (TBT and DBT) in water, sediments, and gastropods of the southern Venice lagoon (Italy)

D. Berto [a,*], M. Giani [a], R. Boscolo [a], S. Covelli [b], O. Giovanardi [a], M. Massironi [c], L. Grassia [c]

[a] *Istituto Centrale per la Ricerca Scientifica e Tecnologica Applicata al Mare (ICRAM), 30015 Chioggia (Venezia), Italy*
[b] *Dipartimento di Scienze Geologiche, Ambientali e Marine, Via Weiss 2, 34127 Trieste, Italy*
[c] *Centro Italiano Ricerche e Studi per la Pesca, Via De' Gigli d'Oro 21, 00186 Roma, Italy*

Abstract

The release of tributyltin (TBT) from maritime traffic represents one of the main problems of direct, diffuse, and continued contamination of the marine environment.

In the present survey, the concentrations of TBT and dibultytin (DBT) in brackish waters, sediments, and the gastropods *Nassarius nitidus* were evaluated in order to estimate the contamination of the southern part of the Venice lagoon.

TBT and DBT were determined by GC–MS/MS. Recent contamination of TBT was found in brackish waters near marinas, whereas the highest concentrations of TBT and DBT were observed in surface sediments at dockyards and harbours. High content of organotin in the gastropods sampled near the dockyards, harbours, and marinas showed a mobilisation from the sediments through the food web.

The present study allowed assessment of whether, despite the ban on the use of TBT paints, waters, sediments, and biota were still being contaminated by organotin compounds in the southern Venice lagoon.

Keywords: TBT; DBT; Organotin; Antifouling paints; Venice lagoon

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1. Introduction

Butyltins, including tributyltin (TBT), are widely used as biocides in antifouling paints. Evidence of the damaging effect of organotin compounds (BTs) on the reproduction and growth of various marine organisms has prompted action by many countries to regulate or ban their use in antifouling products. The widespread use of BTs as stabilizers in the manufacture of polyvinylchloride (Blunden et al., 1984), as a biocide in agriculture (Champ and Seligman, 1996), as a fungicidal in wood preserve (Bennett, 1996), and as a biocide in antifouling paints for vessels (Hoch, 2001; Yebra et al., 2004) and for cooling pipes of thermoelectric power (Bacci and Gacci, 1989; Bressa et al., 1999) has provided several points of entry for these compounds into aquatic and terrestrial environments.

TBT gained widespread application as an effective antifouling paint biocide on pleasure boats, large ships, and docks in the 1970s and 1980s (Fent, 1996).

At present, the use of antifouling paints containing TBT is restricted in many countries. In October 2001, MEPC/IMO adopted a new International Convention on the Control of Harmful Antifouling Systems on Ships which will prohibit the use of harmful organotins in antifouling paints used on ships, and will establish a mechanism to prevent the potential future use of other harmful substances in antifouling systems. The resolution called for a global prohibition on the application of BTs, which act as biocides in antifouling systems on ships, by January 2003, and a complete prohibition by January 2008 (Reg. EC 782/2003).

Despite such restrictions, TBT persists in many areas at levels considered to be chronically toxic to the most

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[*] Corresponding author. Tel.: +39 041 5543933; fax: +39 041 5547897.
E-mail address: d.berto@icram.org (D. Berto).

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susceptible organisms (Stäb et al., 1995). The release of BTs into terrestrial and aquatic environments has decreased, but inputs still occur, and previously contaminated sites continue to act as sources (Ritsema, 1994; Stäb et al., 1995). The BTs compounds have been routinely found in both estuarine and marine waters, sediments, and biota (Tas et al., 1996).

TBT is characterised by high toxicity, environmental mobility, and a tendency to accumulate in living systems (Fent, 1996). Chronic toxic effects on oysters (shell deformation; Alzieu, 1998, 2000), and in neogastropods and mesogastropods (imposex; e.g., Ellis and Pattisina, 1990; Gibbs et al., 1991; Stewart et al., 1992; Horiguchi et al., 1994) occur at aqueous concentrations of a few ng L^{-1}, and most susceptible marine algae and zooplankton species are negatively affected at a few hundred ng L^{-1} (Huang et al., 1996). It is widely recognised that TBT, as an endocrine disruptor, compromises reproductive capacity and sexual development, increasing incidence of masculinisation, in numerous fish species (Meador, 1997; McAllister and Kime, 2003; Shimasaki et al., 2003). The phenomenon of imposex, a superimposition of male sexual organs (penis and vas deferens) on female gastropods, is reported to occur in more than 150 species belonging to 63 genera of prosobranch gastropods (Schulte-Oehlmann et al., 2000), and is positively correlated to TBT concentrations (Gibbs et al., 1987). Despite the high concentrations of toxic BTs found in aquatic invertebrates, little is known about the accumulation and toxic effects of BTs in higher trophic vertebrate predators, which may be exposed to these pollutants via food ingestion (Hoch, 2001). In general, coastal species exhibit higher butyltins accumulations than their relatives from off-shore areas (Hoch, 2001). Despite this, Borghi and Porte (2002) showed that organotin pollution in the NW Mediterranean is not limited to circumscribed coastal areas, but rather reaches the deep-sea environment and inhabiting organisms (1000–1800 m depth).

At present, scarce information on organotin contamination in Italian waters, sediments, and biota, collected simultaneously, is available; most studies report data on organotin compounds in a selected environmental matrix: seawater (Bacci and Gacci, 1989; Caricchia et al., 1993; Terlizzi et al., 1998), sediments (Cicero et al., 2004; Chiavarini et al., 2003), or gastropods (Terlizzi et al., 1998). Contamination of BTs compounds in the lagoon of Venice was reported by a few papers, focusing either on sediments (Bortoli et al., 2003) or molluscs (Binato et al., 1998; Boscolo et al., 2004; Pellizzato et al., 2004).

The Venice lagoon is subject to intense ship traffic due to the presence of the harbours of Venice (2.32×10^6 t yr^{-1}) and of the port of Chioggia (1.0×10^6 t yr^{-1}). Small ferries, a fleet of 800 fishing boats (APAT, 2005), and the presence of many marinas, dockyards and shipyards contributed to the increase in maritime traffic, mainly in the central and southern part of the lagoon, during the last decades. In recent years, relevant dredging activities were carried out in order to create a new commercial harbour in Chioggia, and to construct the "MOSE" barriers against the flooding at Chioggia inlet (1.4×10^6 m^3 of estimated dredging materials).

The present paper aims to evaluate the TBT and dibultytin (DBT) contamination in the brackish waters, sediments, and gastropods – *Nassarius nitidus* – in the southern part of the Venice lagoon, subjected in the last decades to an increase in dockyards, shipping, and fishing activities.

2. Materials and methods

2.1. Study area and sampling

The Venice lagoon is a transitional coastal environment covering a surface area of 549 km^2, and it is characterised by low average water depth (≈1 m) and tidal range (<1 m). The lagoon is connected to the sea through three inlets (Lido, Malamocco and Chioggia), and water exchange with the Adriatic Sea is controlled by tidal fluxes.

Waters, sediments and gastropods (*N. nitidus*) were collected in late spring–summer 2003 in the southern part of the Venice lagoon, near the town of Chioggia (53,470 inhabitants). The sampling stations were defined as dockyards, harbours, marinas, centre town, and lagoon channels on the basis of their location and the activities undertaken therein (Fig. 1). Water samples were collected using Niskin water samplers (5 L capacity) at a depth of approximately 1 m in navigable areas with a minimum bottom depth of 1.5–2 m. The samples were filtered with GF/F filters, and acidified to pH 2 with concentrated ultrapure HCl.

Bottom sediments were sampled by an Ekman grab in 25 stations. The upper 2 cm were recovered and placed in acid-cleaned glass containers, then homogenised in mortar porcelain, sieved on a 200 μm mesh nylon screen, and stored at −20 °C.

A pool of 25 specimens of dogwhelk (*N. nitidus*), scavenger gastropods feeding on dead or decaying animals, were caught by wire basket in 18 of the sediment sampling sites. The shell length and the maximum diameter were measured.

The mean length of the collected specimens was 25.5 ± 1.8 mm, and the mean width was 12.0 ± 0.7 mm. All the specimens were sexually mature and were therefore presumably at least 4 years old, according to Tallmark (1980). The soft tissues of the molluscs were excised with stainless-steel scalpel blades, thoroughly rinsed with MilliQ water to remove extraneous impurities, and homogenised using a blender (Ultraturrax). The homogenised samples were stored at −20 °C. All samples were lyophilised for 72 h before analysis.

2.2. Reagents and standards

Dibutyltin chloride, tributyltin chloride, and tetrabutyltin chloride (96%, 97%, and 96% purity, respectively) were

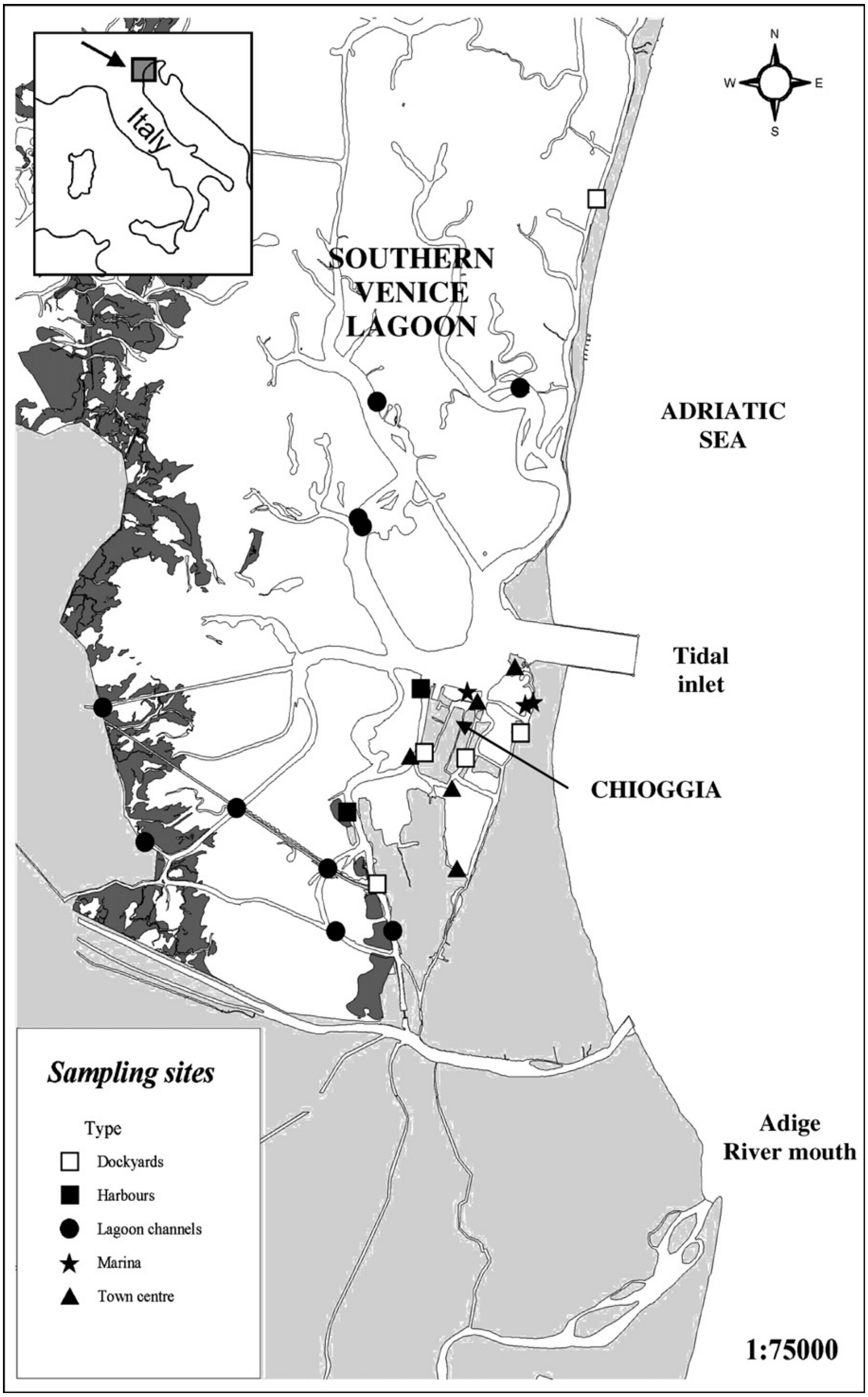

Fig. 1. Sampling stations in the southern Venice lagoon.

purchased from Aldrich (Milwaukee, USA). Tropolone and analytical grade solvents *n*-hexane, methanol, and dichloromethane, were purchased from Carlo Erba (Milan, Italy). Diethyl ether, hydrogen peroxide, anhydrous sodium sulphate (Na_2SO_4), ammonium chloride (NH_4Cl), and ultrapure HCl were obtained from Carlo Erba (Milan, Italy). Na_2SO_4 and Florisil 60–100 mesh were activated at 450 °C for 1 h and 160 °C for 24 h, respectively, before use. The Grignard reagent (2.0 mol L^{-1} solution of methyl magnesium bromide, CH_3MgBr, 3 mol L^{-1} in diethyl ether) was purchased from Aldrich (Milwaukee, WI,USA). The internal standard tetrabutyltin chloride in methanol, the tropolone solution (0.05 wt.%) in dichloromethane, and the aqueous solution of NH_4Cl (20 wt.%) were prepared weekly and stored refrigerated at 4 °C.

2.3. Analytical procedures

Sediments were treated with concentrated hydrogen peroxide for 48 h, organic debris and shell fragments were removed by sieving (<2 mm), and grain-size analyses were performed by a laser diffraction sizer (Malvern Mastersizer 2000 coupled with Hydro 2000s sampler unit). Sediments were classified in accordance with Shepard (1954). Organic carbon (C_{org}) and nitrogen (N_{tot}) were determined in sediments by using a CHNS–O elemental analyser, Fison (Italy) model EA1108, calibrated with acetanilide as a standard. C_{org} was determined after removal of carbonates with concentrated HCl, 1 N (Hedges and Stern, 1984). Weight percentages of N_{tot} were determined following the same procedure, but without acidification. Analytical precision of measurements was <2% for both C_{org} and N_{tot}. Reference material BCSS (CNRC, Canada) was used to assess the accuracy of the analytical data.

TBT and DBT were determined in filtered waters (1 L), sediments (500 mg), and molluscs (1000 mg) according to Binato et al. (1998) and Caricchia et al. (1993). A gas chromatograph (Trace GC, Thermo Finningam, USA) equipped with an automatic injector was connected to an AS2000 (Thermo Finningam, USA) and fitted with a capillary column Rtx-5MS (i.d. 0.25 mm, length 30 m, film thickness 0.25 μm, Altech, USA). Gas chromatographic separation was performed at 60 °C (1 min) with a heating rate of 15 °C min^{-1} to 270 °C. The splitless injector port was kept at a temperature of 270°C, and the transfer line was kept at 280 °C. The carrier gas was helium at 1 mL min^{-1}, and the injected sample size was 1.5 μL.

The fragmentation was obtained by Ion Trap (Polaris Q, Thermo Finningam, USA) with the electron impact (EI) source at a temperature of 270 °C, electron energy of 70 eV, and accelerating voltage of 1.1 kV. Full scan and mass to mass (MS/MS) were operated under a programme described in the literature (Binato et al., 1998). The fragmentation ions chosen were 193, 137, and 120 m/z, and 153, 135, and 120 m/z, respectively, for TBT and DBT. The method involved extraction, derivatization, and clean up steps before the GC–MS/MS analysis.

The extraction efficiency was evaluated by analysing spiked, uncontaminated, filtered, brackish water (5, 10 and 20 ng L^{-1}) and certified reference materials for biota and sediments (CRM 477 and CRM 462), regularly analyzed together with the samples.

The recovery of TBT and DBT in spiked brackish water samples was 97 ± 9% and 101 ± 12%, respectively. The recovery levels of TBT and DBT in the CRM 477 and CRM 462 were 81 ± 16% and 82 ± 15%, respectively, for the certified values.

The detection limits were approximately 5 ng Sn L^{-1} for TBT and DBT in brackish water samples, and 4 ng g^{-1} for TBT, and 8 ng Sn g^{-1} for DBT in sediments and biota. TBT and DBT concentrations were expressed as ng Sn L^{-1} for water and ng Sn g^{-1} dry weight for sediments and gastropods, respectively.

3. Results and discussion

3.1. Sediments characteristics

Sandy silt and silt were prevalent in the southern lagoon. Clay (<2 μm) was present in reduced amounts (<7%) in all sediment samples. Grain size progressively decreased from the tidal inlet towards the inner areas of the lagoon and in the lower energy zones. Very fine to medium sands were found only in the marine area and in some sites near Chioggia town. Most of the samples were characterised by a high percentage of 2–8 μm particles (very fine silt). The C_{org}/N_{tot} molar ratios calculated on the basis of the C_{org} (0.3–3.1%) and N_{tot} (0.02–0.38%) contents ranged from 5.3 to 13.7. Sandy silty sediments in dockyards were the most enriched in C_{org}, whereas the sandy sediments of harbours showed the lowest values of C_{org} (Table 1). It cannot be excluded that the highest C_{org}/N_{tot} values found in dockyards and centre town sediments were caused by a local source of organic matter, such as the micro-fragments generated by the use of antifouling paints (Yebra et al., 2004).

The positive correlation between pelitic (<62.5 μm) contents, C_{org} ($R^2 = 0.79$, $p < 0.05$), and N_{tot} ($r^2 = 0.85$, $p < 0.05$) suggests a prevailing association of organic matter within the finer fraction of the sediments, as reported for other North Adriatic coastal environments (e.g. Faganeli et al., 1991).

3.2. Organotins in the lagoon waters

Fig. 2 reports TBT and DBT concentrations in lagoon waters at the different sampling sites. High levels of TBT and DBT were detected in areas adjacent to vessel repair facilities and shipyard hull washing/refinishing activities, such as harbours and marinas, whereas lower, but consid-

Table 1
Sediment characteristics

Parameter	Dockyards ($n = 7$)	Harbour ($n = 2$)	Town centre ($n = 6$)	Marina ($n = 4$)	Lagoon channels ($n = 11$)
Sand (%)	23.5 ± 15.8	87.3[a]	38.9 ± 37.0	40.1 ± 35.3	31.9 ± 15.1
Silt (%)	71.2 ± 15.2	11.5[a]	56.6 ± 34.2	55.7 ± 32.7	63.2 ± 14.2
Clay (%)	5.3 ± 0.9	1.2[a]	4.6 ± 2.9	4.1 ± 2.7	4.9 ± 1.1
C_{org} (%)	2.0 ± 0.8	0.3 ± 0.2	1.6 ± 1.1	1.2 ± 1.1	1.6 ± 0.8
N_{tot} (%)	0.21 ± 0.11	0.05 ± 0.04	0.20 ± 0.14	0.16 ± 0.11	0.25 ± 0.08
C_{org}/N_{tot} (mol/mol)	11.4 ± 1.7	6.3 ± 1.3	9.9 ± 2.1	9.0 ± 2.9	7.4 ± 1.7

Average concentrations and standard deviations are reported.

[a] Grain-size analysis $n = 1$.

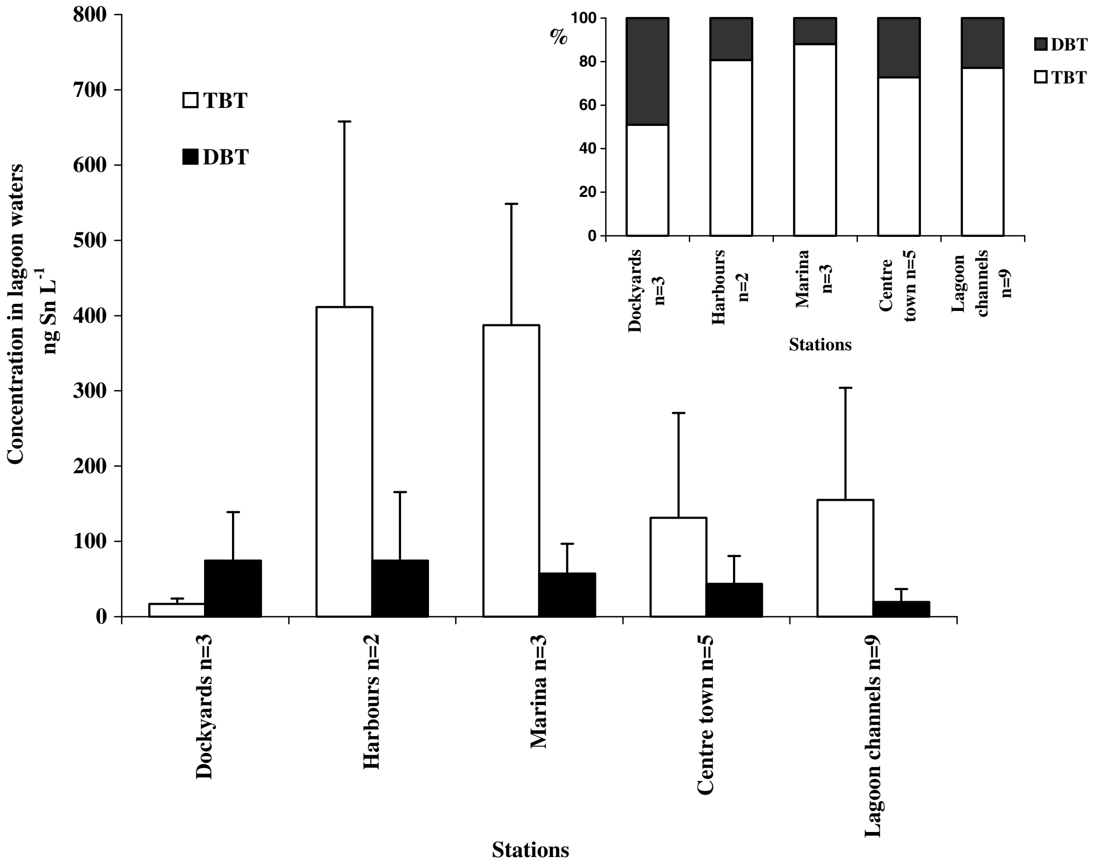

Fig. 2. Concentration (average and standard deviation) of TBT and DBT, expressed as ng Sn L^{-1} and percentage of TBT and DBT (right top corner) in the lagoon waters at different sites.

erable, concentrations were found at centre town and lagoon channels (Fig. 2).

The content of TBT and DBT in harbours and marinas sites is considerably high, even if comparable to those reported for other harbour areas (Table 2).

Table 2
Comparison of TBT concentrations in waters of contaminated sites

Sites	Year	TBT (ng Sn L^{-1})	DBT (ng Sn L^{-1})	References
Southern Venice lagoon dockyards, Italy	*2003*	*10–24*	*75–139*	*Present study*
Southern Venice lagoon harbours, Italy	*2003*	*237–586*	*<5–139*	*Present study*
Southern Venice lagoon marinas, Italy	*2003*	*273–572*	*16–95*	*Present study*
Lucija marina, Slovenia	2002	500–600	30–125	Nemanič et al. (2002)
Marmugao harbour, India	2001	145–345	8–43	Bhosle et al. (2004)
Antwerp harbour, The Netherlands	1993	765–1000	217–283	Reported by Hoch (2001)
Cote d'Azur ports, France	1995	7–459	<0.5–221	Tolosa et al. (1996)
European harbours	1980	10–1500	nd	Alzieu (1998)

Though regulations have reduced the levels of environmental TBT in many countries, hull cleaning and painting sites can still act as potential localized TBT sources (Page et al., 1996). In fact, the measurements taken prior to restrictions on TBT use in antifouling paints have shown high levels of contamination in north American and European marinas (Bacci and Gacci, 1989; Alzieu, 1998), and extremely high concentrations have been found in the waters of harbours of countries where no regulations have been adopted (Hassan and Juma, 1992; May Ming Lau, 1991).

The highest concentration of TBT found in the waters at the marinas sites (572 ng Sn L^{-1}), associated with a higher percentage of TBT than DBT (Fig. 2), pointed to a recent input, probably due to the illegal addition of TBT in antifouling paints in boats smaller than 25 m, as also found along the Portuguese coast (Santos et al., 2002, 2004). Thus, the low aqueous solubility (1–10 mg L^{-1} for tributyltin oxide and under 20 mg L^{-1} for more soluble salts, such as halides), low mobility of triorganotins compounds in the aquatic environment, and the easy adsorption onto suspended particulate matter could facilitate the direct transport and deposition of the contaminant in the sediment. Regardless, TBT half-life in water is highly variable depending on the environmental conditions of pH, temperature, turbidity, and light, and it is estimated to range approximately from days to weeks (Alzieu, 1998). The TBT/DBT ratio greater than 1 that we found in the waters at all sites, and the absence of linear relationship ($r^2 = 0.091$, $p = 0.327$) between TBT and DBT concentrations pointed to a widespread and recent TBT contamination in the southern Venice lagoon.

3.3. Organotins in sediments

The presence of detectable TBT and DBT in all locations demonstrated its widespread diffusion (Table 3). The highest levels of TBT (39,300 ng Sn g^{-1}) and DBT (12,623 ng Sn g^{-1}) have been found in sediments at one dockyard site showing a recent input, probably due to the use of TBT-based antifouling paints applied on boat hulls, and a low control of the wastewater treatment in the adjacent shipyard hull washing/refinishing activities. The concentrations in the marinas, centre town, and lagoon channels in this study were relatively higher for the channels of the southern part of Venice lagoon (below 20.5 ng Sn g^{-1}), compared to the values reported by Bortoli et al. (2003), but similar for the sites located in the central Venice lagoon. A low but diffuse contamination of TBT in coastal areas located in the Ligurian, Tyrrhenian, Ionian, and Adriatic seas was found in sediments by Cicero et al. (2004), and in the North-Western Sicilian coasts and Ustica (3–27 ng Sn g^{-1} d.wt.) by Chiavarini et al. (2003). The high concentrations of TBT and DBT in the dockyard and harbour sediments found in this study are similar to those measured in sediments of heavily industrialized areas and harbours around the world (Page et al., 1996; Axiak et al., 2000; Díez et al., 2002; Shim et al., 2002).

The relationships between TBT and DBT shows that TBT prevails over its degradation product. In fact, the relative percentage of TBT towards the sum of TBT and DBT concentrations ranged up to 72% (marinas) and 98% (harbours).

The rate of TBT degradation in sediments was evaluated to be much slower with respect to the water column. The half-life of TBT in sediments depends on the nature of the sediments (Stewart and de Mora, 1990) and on the form of TBT (e.g. oxide, hydroxide, halide, carbonate, or sulphate) (Hoch, 2001). For example, if TBT was present in sediments from TBT-containing paint particles, it would be very resistant to biodegradation (Page et al., 1996). Moreover, where TBT is present from TBT-containing paint residue, the release of the toxic component from copolymer paints is controlled by percolation (free association antifouling paint) or by gradual erosion (self-polishing antifouling paint) through the coat of paint (Hoch, 2001). The use of antifouling TBT paints was widespread in the past in the dockyards and shipyards around the lagoon (ARPAV, 2004). While TBT concentrations in waters around the world have declined since restrictions on TBT use in paints, TBT contamination in sediments, in consequence of its long half life which ranges from 4 months to more than 8 years, has remained relatively high (Page et al., 1996; Alzieu, 1998, 2000).

The ratio of the TBT concentration in sediment to TBT concentration in water (TBT_{sed}/TBT_{water}) was calculated to evaluate an apparent sediment–water distribution coefficient (Fig. 3). Much higher values of the TBT_{sed}/TBT_{water} ratio than that determined in Boothbay Harbour and Portland sediments by Page et al., 1996 (2.8 L g^{-1}) have been found in dockyards and harbour sites of the southern Venice lagoon (Fig. 3), whereas the lowest values were found in the marinas (0.1–0.4 L g^{-1}). Therefore, the elevated sediment–water distribution coefficients observed in the field reflect the presence of TBT containing paint particles from hull refinishing.

A positive relationship ($r^2 = 0.725$, $p < 0.001$) was found between TBT concentrations and C_{org} in sediments with a content of C_{org} higher than 0.9%. The highest contents of TBT and DBT, 26,962 ± 17,449 ng Sn g^{-1} and 7212 ± 7653 ng Sn g^{-1}, respectively, were found in two sites of dockyard sediments and not included in the relationship, but correspond to higher values of C_{org}. We hypothesize that the high C_{org} and TBT concentrations in the sediments near the contaminated sites could be due to the presence of microparticles of antifouling paint residues in the sediments. These could be generated by self polishing antifouling paints which are made of a polymer matrix, such as vinyl, epoxy, acrylic, or chlorinated rubber polymers (CEPE, 1999), to which TBT is chemically bonded. Since the levels found in sediments at dockyards sites were two or three orders of magnitude higher that those found in harbour sediments, they could acts as a potential source for future TBT contamination of the lagoon. In fact, pollutant residues associated with undisturbed buried sediment are not readily bioavailable until resuspended into the water by natural or human activities (Hoch et al., 2003). There is evidence that the resuspension, either via mechanical resuspension or by dredging operations in dockyards and marinas sediments, can release TBT into the water col-

Table 3
TBT and DBT concentrations at the surface sediments

Sites	TBT (ng Sn g^{-1})					DBT (ng Sn g^{-1})			
	N	Average	Min	Max	St. Dev.	Average	Min	Max	St. Dev.
Dockyards	7	8057	87	39,300	14,752	2213	20	12,623	4632
Harbours	2	1857	966	2747	1259	37	29	44	11
Marinas	5	159	43	517	201	202	2	950	418
Centre town	5	267	21	817	325	9	2	18	7
Lagoon channels	11	280	22	1001	289	18	2	142	42

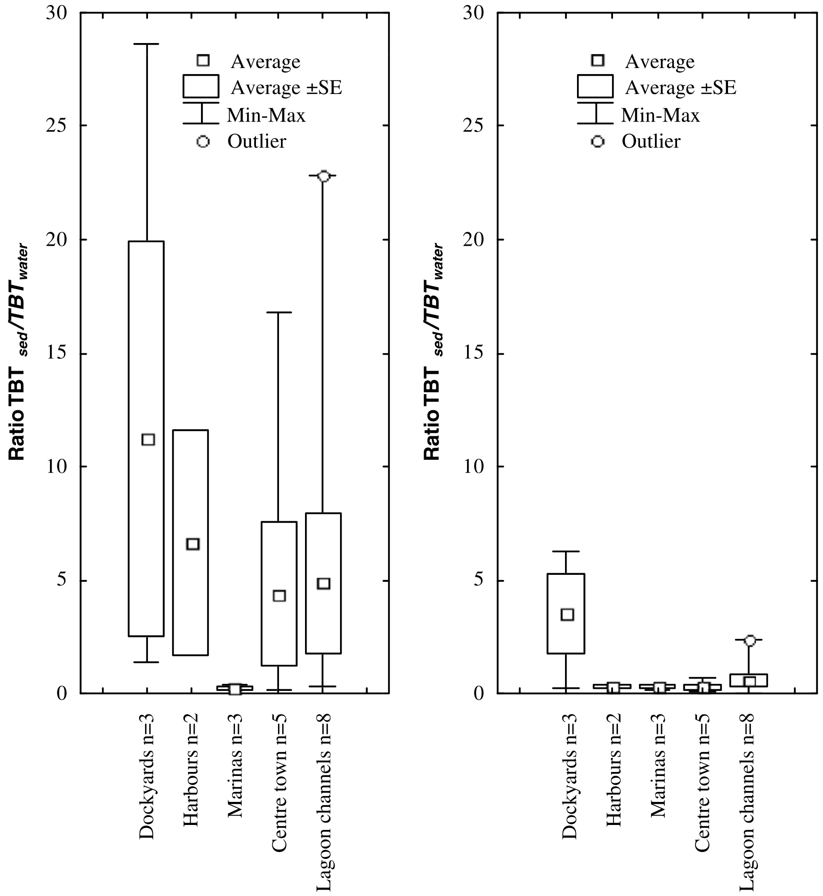

Fig. 3. Ratio of sediment–water distribution coefficient. Sediment TBT concentration to the water TBT concentration (TBT_{sed}/TBT_{water}) and sediment DBT concentration to the water DBT (DBT_{sed}/DBT_{water}) concentration.

umn with possible adverse effects on the biota (Page et al., 1996). The strong relationship ($r^2 = 0.944$, $p < 0.001$) between TBT and DBT, in particular at the dockyards, may indicate that both the TBT and DBT in the highly contaminated sediments originate from the same sources, such as antifouling paints, with respect to the other sites. The mean TBT/DBT ratio evaluated for dockyards sites was 4.1 ± 3.6, similar to that reported by Tolosa et al. (1996) in the anoxic sediments of highly contaminated Spanish harbours (4.3 ± 2.9).

High TBT/DBT ratios and no significant relationship between TBT and DBT for lagoon channels and centre town sediments may reflect the presence of a recent input of TBT from the water column. However, the tendency of TBT to accumulate in sediments implies that the degradation processes will have greater importance in determining the persistence of the TBT in marine environments. Sediments are a sink for TBT, and TBT has been found to accumulate to concentrations which can probably inhibit biological degradation (Stewart and de Mora, 1990).

A TBT_{sed}/TBT_{water} ratio much higher than the DBT_{sed}/DBT_{water} ratio (Fig. 3) points to a stronger association of TBT with sedimentary compartments than DBT. The absence of a relationship between TBT concentration in sediments and TBT concentration in waters, and the positive relationship between TBT concentrations and higher content of organic carbon in the sediments suggests that adsorption in the sediments could be driven by the hydrophobic character of TBT (Hoch et al., 2003). The positive relationship ($r^2 = 0.63$, $p < 0.01$) between DBT content in water and DBT in sediments at the contaminated sites, such as the harbours, marinas, and centre town (Fig. 4), suggests that desorptive processes occur differently than for TBT, for which no correlation was found between the concentrations in sediment and waters. DBT is lost to overlying waters from sediments more easily than TBT due to its higher solubility in water (Hoch, 2001).

The major release of DBT into the water phase could also be a consequence of extreme and near-continuous anthropogenic disturbances to the sediments resulting from a combination of dredging, salt marsh reclamation, and local techniques in clam harvesting, even if natural processes, such as tidal flushing, were not excluded. The higher release of DBT in water favoured by the resuspension processes could explain why the ratios of DBT_{sed}/DBT_{water} found in our work are lower than those reported by others authors (Hoch, 2001; Hoch et al., 2003).

As the BTs, and particularly TBT, are associated to the sediments and have a long residence time, they could diffuse far from their sources by the relevant anthropogenic

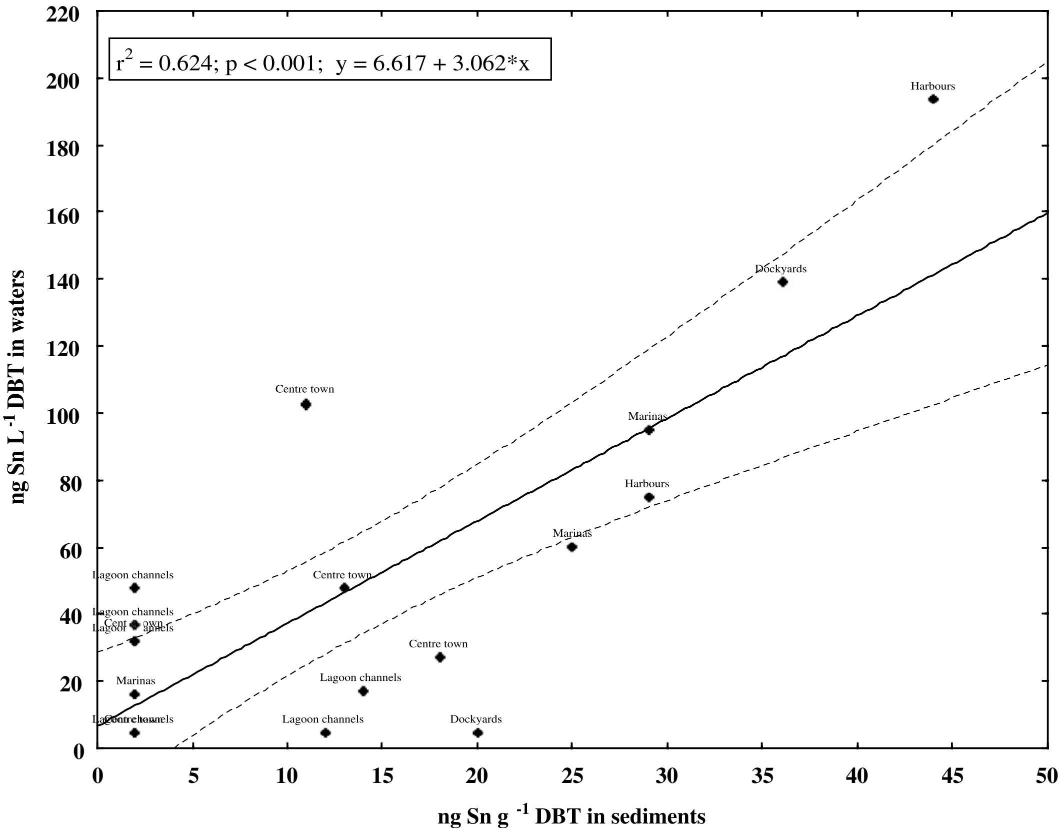

Fig. 4. Relationship between DBT in sediments and DBT in lagoon waters in most contaminated sites. The dotted lines represent the confidence interval ($p < 0.05$).

disturbances to the sediments, such as dredging, salt marsh reclamation, and local techniques of clam harvesting of *Tapes philippinarum*. This activity causes re-suspension of huge amounts of small-sized particles with direct consequences on sediment morphology and indirect damage to benthic organisms (Pranovi and Giovanardi, 1994; Pranovi et al., 1998; Sorokin et al., 1999; Sfriso et al., 2001; Pellizzato and Da Ros, 2005). Moreover, the strong net loss of sediment, the retreat of marsh, and the increase of the fetch and mean depth of the lagoon (Day et al., 1999) could enhance the resuspension due to storms.

3.4. Organotins in gastropods

Desorbed TBT is not the only bioavailable form, and it is important to stress that the presence of TBT in sediments does not necessarily imply safe removal from the system. TBT can be directly ingested from contaminated sediments by scavanger organisms such as gastropods.

TBT in body burden of *N. nitidus* content varied between <4 and 976 ng Sn g^{-1}, whereas DBT ranged from <4 to 1428 ng Sn g^{-1}. The lower concentrations of TBT and DBT have been found in the lagoon channels with respect to the other sites examined (Fig. 5). The relative incidence of DBT on the sum of TBT and DBT in gastropods tissues was significantly higher (Test *U* Mann–Whitney, $p < 0.001$) in harbours, town centre, and lagoon channels than in dockyards and marinas, suggesting an older input in these latter sites. Thus, *Nassarius reticulatus* collected from Portuguese coast yielded tissue concentrations of TBT varying between 20 and 1368 ng Sn g^{-1} at harbours, enclosing ports, marinas, and shipyard sites (Barroso et al., 2000), whereas at the polluted sites of SW England were measured to have concentrations of TBT from several hundred up to a maximum of 3000 ng Sn g^{-1} in *N. nitidus* before the partial ban (Bryan et al., 1993). TBT concentrations in gastropods from contaminated sites of the lagoon are comparable or slightly higher than those found in other countries (Bryan et al., 1993; Barroso et al., 2000; Barreiro et al., 2001). The absence of a linear correlation between BT content in gastropods and BTs concentration in waters, and the absence of correlation between BT content in gastropods and BTs content in the sediments, suggest that the contamination of gastropods occurs mainly through the food chain, rather than directly from water or sediments. The diet of these predatory gastropods, that may include organotin contaminated prey organisms such as animal carcasses and bivalves (Binato et al., 1998; Bortoli et al., 2003; Boscolo et al., 2004; Cacciatore, 2007), could explain the high TBT and DBT content found in *N. nitidus*.

Concentrations of TBT and DBT observed in our study of *N. nitidus* were comparable or slightly higher than those found for *Hexaplex trunculus* (Neogastropoda, Muricidae)

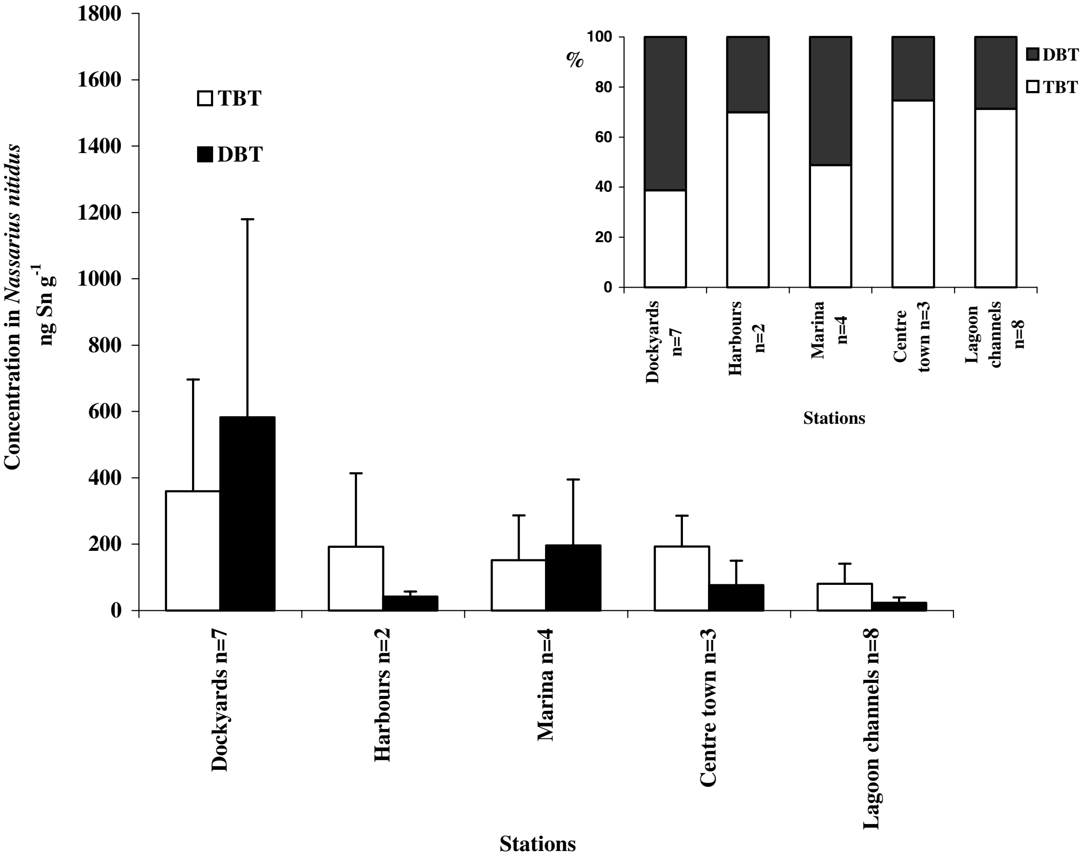

Fig. 5. Concentrations of TBT and DBT, expressed as ng Sn g^{-1} and percentage of TBT and DBT (right top corner) in the gastropods *N. nitidus* in different sites.

in the northern Venice lagoon reported by Pellizzato et al. (2004). The predominance of TBT with respect to DBT in the bivalve mussel *Mitylus galloprovincialis* was reported, by Boscolo et al. (2004), for a site close to the shipyard activities in the same area of study. The persistence of the TBT form in mussels at marina sites could suggest the limited capability of bivalves to metabolise TBT with respect to gastropods and their ability to accumulate it (Laughlin and Linden, 1985; Wade et al., 1988). Although the highest toxicity of the butyltins compounds is due to the trisubstituted species, it should be considered that DBT and MBT are also toxic compounds for aquatic organisms (Kannan and Falandysz, 1997; Stäb et al., 1995; Hoch, 2001). Higher stages of the imposex affect *N. nitidus* in the study area (unpublished results) and similarly high imposex stages were found in *H. truculus* from the central Venice lagoon (Pellizzato et al., 2004).

The significant relationship ($r^2 = 0.755$, $p < 0.001$) found between the TBT and DBT concentrations in gastropods suggests that most of the DBT residues in *N. nitidus* tissues have originated from TBT. However, the ratio of concentrations of TBT and DBT found in biota with respect to those found at the sediments (TBT_{biota}/TBT_{sed} and DBT_{biota}/DBT_{sed}, respectively) showed ratios higher than 1 in all sites analyzed. The highest accumulation of DBT compared to TBT could be explained by an elevated metabolisms of TBT in molluscs, though little is known about the biodegradation in these organisms. A possible exposure to DBT from different sources other than maritime activities could not be excluded a *priori.* A higher contamination of DBT compared to TBT can originate from industrial applications, since MBT and DBT are extensively used as polyvinyl chloride (PVC) stabilizers and catalysts for polyurethane foams and silicone resins (Fent, 1996). However, in the southern Venice lagoon, the industrial activities are very scarce with respect to those in the north. Also, the urban sewage discharged in the southern part of the Venice lagoon cannot be excluded to contribute to the contamination of the aquatic environment (Fent, 1996), though more data are needed to test the importance of this source.

4. Conclusions

Notwithstanding the increasing efforts to outlaw the TBT in antifouling paints, there is evidence of a persistent contamination in the aquatic environment. The results of this study showed that in the southern Venice lagoon there is still evidence of high TBT and DBT contamination in waters and sediments due to the increase of dockyards, shipping, and fishing activities. Natural and anthropogenic factors, such as tidal fluxes, clam harvesting, the capital dredging for the construction of both the new Chioggia harbour and the mobile barriers against flooding at the Chioggia inlet, may well facilitate the diffusion of pollutants in uncontaminated sites.

The accumulation of TBT in sediments appears to be favoured by the accumulation of organic matter in the contaminated sites. Resuspension processes probably enhance a higher release of DBT than TBT from sediments into the water.

Significant contamination of TBT and DBT in the scavenger gastropod, *N. nitidus*, at dockyards, harbours, and marinas testifies to the continuous, even if not massive, input of BTs in the southern part of the lagoon. The higher content of DBT than TBT in gastropods is probably due to the greater mobility of DBT than TBT in the aquatic systems. The persistance of BTs in sediments and their diffusion, through resuspension by storms and by the enhanced anthropogenic activities, could facilitate the mobilization of these contaminants and their transfer to invertebrates and fish. There is a need to investigate, in future research, the release of BTs from sediments and their accumulation in the trophic chain.

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