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Time trend of Butyl- and Phenyl-Tin contamination in organisms of the Lagoon of Venice (1999–2003)

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Abstract In the period 1999–2003 a monitoring study on the accumulation of organotin compounds in edible organisms in the Lagoon of Venice was conducted. Butyl and Phenyl derivatives were determined in pooled samples of *Mytilus galloprovincialis* and *Tapes spp.* with the aims of assessing organotin contamination in the Lagoon of Venice in the period just preceding their ban in Europe, monitoring the concentrations in organisms with a high commercial use, evaluating a potential hazard for human health due to seafood and identifying the possible contamination sources. Sampling stations (up to 20) were distributed around the Lagoon and particularly concentrated in the area close to the town of Chioggia. Significantly higher (analysis of variance (ANOVA), $p<0.05$) tributyltin (TBT) concentrations were found in mussels (from 38±8 to 6,666±1,333 μg kg^{-1} d.w., as TBT^{+}), than in clams (from 6±1 to 2,256±451 μg kg^{-1} d.w., as TBT^{+}). During the 3 years of the survey no increase in average concentrations of the butyltin compounds (tributyltin (TBT) + dibutyltin (DBT) + monobutyltin (MBT)) was observed (ANOVA, $p>0.05$) in either species. Furthermore, by analyzing the entire data set, it is evident that most stations show analogous concentrations in the 3 years for both species, whereas few have anomalously higher concentrations. If organotin concentrations in specimens from some sites are compared with the Tolerable Average Residue Level, a possible risk for human health must be considered.

Keywords Lagoon of Venice · *Mytilus galloprovincialis* · *Tapes spp.* · Tributyltin

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Introduction

Most organotin compounds present in the environment are anthropogenic. Only methyl derivatives can be naturally produced through biomethylation processes (Evans 1974).

In the 1950s, when the biocidal activity of some organotins was discovered, they began to be used as fungicides, bactericides and insecticides (Bressa and Cima 1985). The worldwide production of organotin compounds reached 30,000 tons per year at the beginning of the 1980s (Barnes and Magos 1986).

Uses of organotin compounds can be classified in two classes: (a) non biocide, as polyvinyl chloride stabilizers, additives and catalysts, and (b) biocide, mainly as pesticides and insecticides in agriculture and antifouling paints.

Toxicological properties of organotin derivatives depend on the number and nature of organic constituents; toxicity increases at increasing organic constituents and reaches the top level with the trisubstituted derivatives generally used as biocides (Davies and Smith 1982). Variations in toxicity with the nature of the alkyl group can be observed within the class of trisubstituted compounds: the most toxic for insects is trimethyltin, for mammals triethyltin, for bacteria tri-*n*-propyltin, for fishes, molluscs and fungi tri-*n*-butyltin, for phytoplankton triphenyltin and for acari tricyclohexyltin (Maguire 1987 and references therein).

Tributyltin (TBT) and triphenyltin (TPhT) used in antifouling paints were directly leached into the aquatic environment. Generally TPhT is used as a pesticide in agriculture but it is also added to antifouling paints as coformulant (Morcillo and Porte 1998). Other significant sources, particularly considering the contamination of harbour sediments, were due to the operations of shipping maintenance. For these reasons organotin compounds have become common pollutants and areas characterized by intensive port and industrial activities have shown the heaviest pollution.

The interest in organotin compound toxicity grew after an accident happened in 1954 in France, when 100 people died after swallowing a drug contaminated with ethyltintriiodide, triethyltin iodide, or tetraethyltin. The observed effects on patients were neurological signs and symptoms such as headache, photophobia, altered consciousness, and convulsions. Moreover for at least 4 years continuous headaches and weakness persisted (US Department of Health and Human Services 2005). More recently, at the beginning of the 1980s, evidence of TBT toxicity from antifouling paints was observed in the Arcachon Bay where oyster production was drastically reduced because of a progressive decline of reproduction and juvenile recruitment. The causes were the high levels of TBT in the environment linked to maritime traffic (Alzieu 1998). Moreover in England the phenomenon of imposex (i.e. the superimposition of male sexual characters on female of mollusc gastropods) on *Nucella lapillus* was observed with a decline of organism populations caused by sterility of females (Bryan et al. 1986).

Organotin accumulation in marine organisms can occur as active transport through the gill and/or assimilation through the diet. In all cases these pollutants are characterized by high bioaccumulation, particularly in some target organs: for instance, a higher accumulation of butyltin compounds in liver than in other organs has been observed exposing fishes to organotin contaminants (Kannan et al. 1995); a study conducted on the gastropod *Hexaplex trunculus* sampled in the Mediterranean Sea showed a generally higher load of TBT in the digestive gland and gonads than in the rest of soft body (Axiak et al. 1995). Tanabe (1999) analysed the butyltin content in several organs and tissues of cetaceans and pinnipeds. The highest concentrations were found in liver and secondarily in kidney. This has suggested that butyltin accumulation in liver, kidney and blood might be a typical feature of a wide range of animals.

Even at nanomolar aqueous concentrations, TBT causes chronic and acute poisoning of the most sensitive aquatic organisms such as algae, zooplankton, molluscs and larval stages of some fishes (Hoch 2001 and references therein). For this reason, TBT was defined as among the most toxic anthropogenic pollutants ever intentionally introduced into marine and fresh waters (Goldberg 1986).

The object of the present study is the Lagoon of Venice that covers an area of about 550 km^2, its maximum length is 52 km and the average water depth 1 m; it is divided in three basins, separated by watersheds, called Northern Lagoon or basin of Lido, Central Lagoon or basin of Malamocco and Southern Lagoon or basin of Chioggia. All basins are connected with the Adriatic Sea through inlets and hydraulically are completely independent from each other.

In the lagoon the water exchange with the sea, which mainly depends on tide regime and dynamic mechanisms and determines dispersion and reduction of pollutants' levels, is one of the most important factors for the quality of waters, sediments and biota.

Movement of water masses can spread pollutants in lagoon regions not directly affected by inputs, rendering more problematic the use of waters for activities such as mariculture, bathing and others. In areas where circulation and water exchange are reduced, because of particular morphologic characteristics, a rapid accumulation of pollutants is favoured.

Several substances, including organotin compounds, are transferred from water to particulate matter through adsorption. Because of reduced water turbulence, particles tend to settle onto the sediments, causing accumulation of pollutants in this matrix. Sediments are potential environmental sinks, but, because TBT adsorption to solid particles is a reversible process, they represent also a source of TBT contamination (Hoch and Schwesig 2004 and references therein): organotin compounds can move from water and sediments to the organisms, entering the trophic chain and reaching also humans.

This study is probably the last extended monitoring campaign carried out in the lagoon of Venice before the "Regulation (EC) 782/2003 of the European Parliament and of the Council of 14 April 2003 on the prohibition of organotin compounds on ships" has become effective. This regulation prohibits "the application or re-application on ships of organotin compounds which act as biocides in anti-fouling systems as from 1st July 2003. Furthermore as from 1st January 2008 ships shall either not bear organotin compounds which act as biocides in anti-fouling systems on their hulls or external parts and surfaces, or bear a coating that forms a barrier to such compounds leaching from the underlying non-compliant anti-fouling system. This Regulation shall apply to ships flying the flag of a Member State, ships not flying the flag of a Member State but operating under the authority of a Member State, and ships that enter a port or offshore terminal of a Member State but are not included in the first two categories".

Aims of this work were to: (a) assess organotin compounds contamination in the Lagoon of Venice in the period just before the European regulation had become effective; (b) monitor three times over a 5 year period the concentration of organotins in organisms with a high commercial use and evaluate a potential hazard for human health due to seafood and (c) identify the possible organotin contamination sources.

Materials and methods

Sampling

The organisms analysed in this study were selected for being poorly mobile, numerous enough to enable a significant sampling, sufficiently long living to display accumulation and non-lethally affected by organotins. Finally, being edible they might represent, if contaminated, a potential hazard for human health.

Mytilus galloprovincialis (Lamarck, 1819) and *Tapes spp.*, are very common in the lagoon and can be considered as the most representative for displaying contamination by TBT, TPhT and their derivatives. (Alzieu 1989; Morcillo et al. 1997).

Sampling stations (Fig. 1 and Table 1) were selected in areas where *M. galloprovincialis and Tapes spp*. are widespread and numerous enough to provide a good reflection of the whole lagoon and show a possible relationship between organotin concentrations and pollution sources, i.e. shipyards where maintenance is done.

In the first sampling (September–November 1999), organisms were collected in 12 stations. Results were reported in Bortoli et al. 2003. In the next two samplings (2001 and 2003) stations were increased to 20. Six of these (1, 2, 4, 19 and 20), which were supposed highly contaminated, and one (7), selected as a reference site, were seasonally monitored. Annual sampling was conducted in autumn. Organotin concentrations in the water are expected to be the highest in this period, as it corresponds to the end of the summer when the maritime traffic is concentrated.

At all stations about 200 organisms of the same size were sampled by hand from the wood poles named "bricole" signalling the edges of the main lagoon channels. After sampling, mollusks were drained, then the edible part was extracted from the shell, homogenized, frozen at −18°C, freeze-dried and stored at −20°C.

Chemical analysis

An analytical procedure, derived from Morabito (1995), was used to quantify the concentrations of TBT, TPhT and their derivatives, dibutyltin (DBT), monobutyltin (MBT), diphenyltin (DPhT), and monophenyltin (MPhT).

500 mg of dry tissue were twice extracted with 15 mL of a tropolone solution in methanol (0.03%) and 1 mL of HCl in an ultrasonic bath and centrifuged. Supernatants were combined in separatory funnels containing 100 mL of NaCl in deionised water (10%) and extracted twice with 15 mL of CH_2Cl_2; the organic phases were then mixed and dried with anhydrous Na_2SO_4 activated overnight by

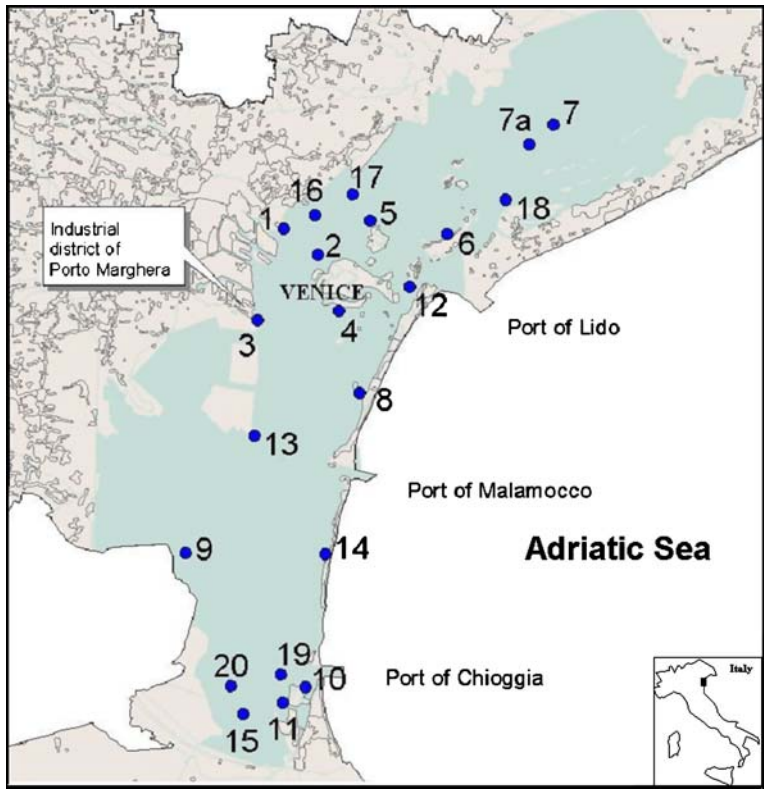

Fig. 1 Map of the Lagoon of Venice and sampling sites

heating. The solvent was changed by adding 1 mL of isooctane to CH_2Cl_2 and gentle evaporating with nitrogen blowing.

After derivatization with 1 mL of Pentilmagnesium bromide 2M in diethylether, the internal standard (tripropylpentyltin) was added and the excess of the Grignard reagent hydrolyzed with 2 mL of deionised water and 5 mL of H_2SO_4 1M. Pentilated organotin compounds were twice extracted with 2 mL of *n*-hexane and the extracts washed with 3 mL of $NaHCO_3$ 0.1M. The organic phase, reduced to 1 mL under nitrogen blowing, was purified with 3 g of Florisil and eluted with 8 mL of *n*-hexane-toluene 1:1. Final extracts were concentrated to 1 mL and analyzed by HRGC-LRMS.

Chromatographic conditions were the following: capillary column, HP-5 (5% phenyl methylsiloxane, i.d. 0.25 mm, length 25 m, film thickness 0.4 μm); injector temperature, 260°C; temperature programme, 80°C for 2 min, then 10°C min^{-1} up to 280°C, post run 10 min at 280°C; transfer line temperature, 280°C, splitless injection; carrier gas helium at 70 kPa head pressure. MS detection was conducted using electron impact ionization (70 eV) and an ion trap detector using full scan mode. Procedure recovery yields were tested by analysing the certified reference material CRM 477: TBT=89%, DBT=92%, and MBT=92%. Detection limits obtained by analysing ten blanks were: TBT=12, DBT=12, MBT=12, TPhT=5, DPhT=7, MPhT=12 μg kg^{-1}d.w. Concentrations were expressed as microgram of cation per kg of tissue, dry weight. For comparison, literature concentrations expressed as Sn were converted using the following factors: 2.44 for TBT, 1.96 for DBT, and 1.48 for MBT.

Data were processed using the computer software Statistica (Statsoft, USA) and SIMCA-P 8.0 (Umetrics, Sweden).

Results and discussion

Data collected from the 20 stations distributed over the lagoon of Venice at three different times from 1999 to 2003 give an insight on the organotin contamination in the period of time preceding the

Table 1 Sampling sites

Number of station	Name and location of stations
1	Canale Salso
2	Ponte della Libertà (area north-west of Venice)
3	Confluence of the Naviglio del Brenta and Canale dei Petroli
4	Area south of the city of Venice
5	Area north-east of the city of Venice
6	S. Erasmo
7	Area north-east–Reference station
8	Lido, Lagoon side
9	Punta Fogolana
10	Chioggia (Area in front of the Hydrobiology station, University of Padua)
11	Chioggia
12	Island Le Vignole
13	S. Leonardo
14	Pellestrina
15	Canale delle Trezze (in front of the state road Romea)
16	Campalto
17	Tessera
18	Treporti
19	Chioggia (mussel farming area)
20	Mouth of Canale Nuovissimo

European banning of these compounds from marine paints. In Fig. 2 average butyltin and phenyltin concentrations in *M. galloprovincialis* and *Tapes spp.* sampled in autumn from all stations are shown. Phenyltins are on average one order of magnitude less concentrated than butyltins, being many samples below detection limits. Triphenyltin has been used as a low concentration co-formulant in antifouling paints and no other sources can be identified in the Lagoon of Venice.

As this observation holds true in all the three sampling times only butyltin data will be considered in the following discussion.

Tables 2 and 3 report the results of butyltin in *M. galloprovincialis* and *Tapes spp.* sampled in the autumnal sampling periods. During this period of time average butyltin concentrations in both species were invariant (analysis of variance (ANOVA), $p>0.05$).

Considering the sum of butyltin, no significant differences in the contamination extent of the two species (ANOVA, $p>0.05$) were observed, although the variation range in *Mytilus* was greater.

On the contrary, considering only TBT contamination, a higher concentration in *Mytilus* than in *Tapes* was observed (ANOVA, $p<0.05$). Given that DBT and MBT are metabolites of TBT, it can be hypothesized that the two organisms have a different

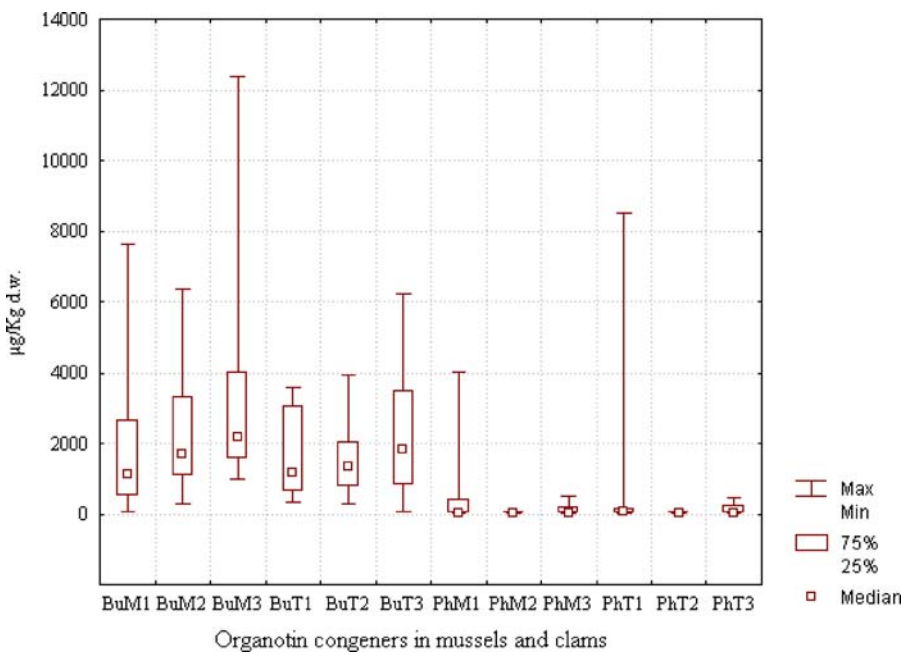

Fig. 2 Box plot of butyltin and phenyltin concentrations in *M. galloprovincialis* and *Tapes spp.* for 3 years observations (*BuM1*, *BuM2*, *BuM3*, *BuT1*, *BuT2*, *BuT3*: total concentration of butyltin compounds in *M. galloprovincialis* (M) and *Tapes spp.* (T) in first, second and third campaign; *PhM1*, *PhM2*, *PhM3*, *PhT1*, *PhT2*, *PhT3*: total concentration of Penyltin compounds in *M. galloprovincialis* (M) and *Tapes spp.* (T) in first, second and third campaign)

Table 2 Concentrations of butyltin in *Mytilus Galloprovincialis* (μg kg^{-1} d.w.) sampled in autumnal campaign

Station	TBT (μg/kg)			DBT (μg/kg)			MBT (μg/kg)		
	1st year	2nd year	3rd year	1st year	2nd year	3rd year	1st year	2nd year	3rd year
1	1148±230	793±159	3838±768	823±165	621±124	526±105	705±141	148±30	187±37
2	1177±235	2022±404	2041±408	1043±209	765±153	990±198	977±195	249±50	251±50
3	1628±326	3684±737	2804±561	555±111	1189±238	550±110	217±43	1026±205	376±75
4	4501±900	1880±376	2703±541	1269±254	549±110	1129±226	1863±373	173±35	459±92
5	835±167	3163±633	1521±304	193±39	752±150	454±91	97±19	270±54	198±40
6	255±51	1456±291	1051±210	81±16	300±60	376±75	39±8	80±16	203±41
7	38±8	605±121	1138±228	10±2	123±25	267±53	12±2	28±6	117±23
8	577±115	895±179	1728±346	160±32	390±78	460±92	52±10	138±28	211±42
9	n.d.	179±36	440±88	n.d.	85±17	485±97	n.d.	40±8	62±12
10	384±77	2016±403	6666±1333	83±17	1626±325	4187±837	41±8	258±52	1538±308
11	909±182	4307±861	6049±1210	373±75	1520±304	3084±617	206±41	511±102	1047±209
12	526±105	2396±479	1305±261	116±23	674±135	495±99	33±7	243±49	378±76
13		796±159	874±175		220±44	233±47		61±12	139±28
14		1811±362	4164±833		825±165	1154±231		206±41	570±114
15		187±37	1175±235		80±16	234±47		31±6	192±38
16		730±146	2331±466		269±54	306±61		100±20	62±12
17		933±187	845±169		191±38	121±24		95±19	6±1
18		530±106	1088±218		127±25	461±92		35±7	80±16
19			1483±297			377±75			208±42
20			932±186			235±47			107±21

n.d. Not detected

Table 3 Concentrations of butyltin in *Tapes spp.* (μg/kg d.w.) sampled in autumnal campaign

Station	TBT (μg/Kg)			DBT (μg/Kg)			MBT (μg/Kg)		
	1st year	2nd year	3rd year	1st year	2nd year	3rd year	1st year	2nd year	3rd year
1	1471±294	336±67	1154±231	701±140	119±24	462±92	890±178	113±23	277±55
2	835±167	677±135	1535±307	1635±327	299±60	728±146	649±130	373±75	1219±244
3	962±192	646±129	1930±386	221±44	242±48	2956±591	133±27	202±40	756±151
4	769±154	2100±420	1231±246	636±127	518±104	198±40	557±111	498±100	409±82
5	352±70	n.d.	1519±304	73±15	n.d.	644±129	80±16	n.d.	575±115
6	309±62	1576±315	n.d.	99±20	312±62	n.d.	221±44	149±30	n.d.
7	n.d.	703±141	n.d.	n.d.	135±27	n.d.	n.d.	57±11	n.d.
8	556±111	1029±206	753±151	280±56	290±58	236±47	38 ± 8	291±58	151±30
9	113±23	142±28	395±79	84±17	74±15	158±32	147±29	53±11	202±40
10	650±130	1426±285	2256±451	194±39	1216±243	2456±491	135±27	1025±205	1501±300
11	895±179	1072±214	1771±354	1246±249	1030±206	2259±452	1437±287	1830±366	1191±238
12	n.d.	813±163	1182±236	n.d.	233±47	377±75	n.d.	90±18	289±58
13		518±104	565±113		183±37	146±29		81±16	107±21
14		1383±277	6±1		304±61	6±1		135±27	50±10
15		1339±268	1066±213		654±131	311±62		305±61	217±43
16		223±45	n.d.		73±15	n.d.		51±10	n.d.
17		1106±221	n.d.		273±55	n.d.		137±27	n.d.
18		201±40	630±126		55±11	155±31		30±6	140±28
19			344±69			6±1			60±12

n.d. Not detected

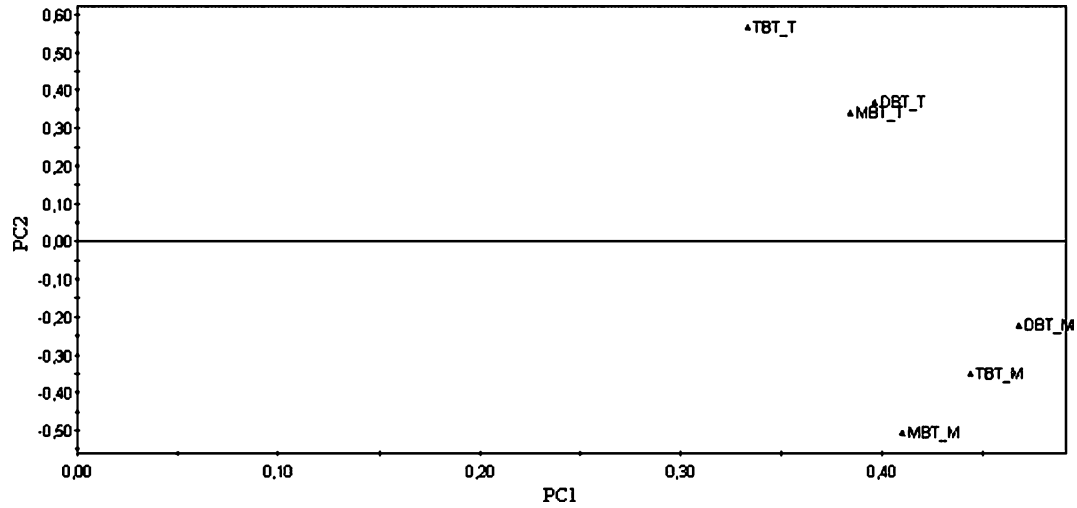

Fig. 3 Plot of Loadings of the first two Principal Component (*TBT_M*, *DBT_M*, *MBT_M*: butyltin level in *M. galloprovincialis*; *TBT_T*, *DBT_T*, *MBT_T*: butyltin level in *Tapes spp.*)

metabolic ability and probably *Tapes* degrades TBT into DBT and MBT faster than *Mytilus*.

Butyltin concentrations in mussels, in particular those from the area around the city of Chioggia (TBT=187–6,666; DBT=80–4,187; MBT=31–1,538 μg kg^{-1} d.w.), are not very different from those of Gallina et al. (2000), who reported, in the same area of the Southern Lagoon and in the same season in 1996 the following cation concentrations: TBT between 342 and 8,039 μg kg^{-1} d.w.; DBT between 608 and 5,298 μg kg^{-1} d.w.; MBT between 252 and 1,674 μg kg^{-1} d.w. Along the Portuguese coast Barroso et al. (2004) found TBT^{+} levels in mussels between 27 and 1,928 μg kg^{-1} d.w. and Nemanič et al. (2002) in the Bay of Piran, Northern Adriatic Sea, found between 1,268 and 8,444 μg kg^{-1} d.w. as cation[1].

A Principal Component Analysis (PCA) was performed on the whole set of data (TBT, DBT and MBT in *Mytilus* and in *Tapes* during the three sampling periods in all stations). Two components, explaining 69% and 15% of the variance, respectively, were extracted, corresponding to a total explained variance of 84%. On the first component all variables had high loadings, whereas on the second one loadings of butyltin for *Tapes* were high and positive, for *Mytilus,* high and negative (Fig. 3); it is apparent that all variables regarding *Tapes* and *Mytilus* are separated along the second principal component, whereas along the first one they have a similar trend. If plots of loadings and scores are observed together some interesting observations can be made: from Fig. 4 it is evident that most stations show similar concentrations in the 3 years for both species, whereas few are different. Among these, it can be noted that stations 10, 11 and 14 are situated in the southern Lagoon near Chioggia (stations 10, 11) and Pellestrina (station 14), where shipyard activity is predominant and stations 3 and 4 are close to the industrial area and the town centre, respectively.

On the basis of the first sampling results, six stations were selected for being monitored seasonally: stations 1, 2 and 4, localized in Central Lagoon and expected highly polluted, and 7 in a relatively clean site. Two additional stations (19 and 20) were positioned in the Southern Lagoon, in the same area as stations 10 and 11, but nearer to mussel farming facilities to check if these activity could be adversely affected by the high contamination of the area.

From this monitoring some stations demonstrated seasonal fluctuations (e. g. station 1), whereas others had similar concentrations (e.g. station 7). This can be observed in Figs. 5 and 6, where the average butyltin concentrations in the two species are presented. Considering the sum of butyltins, the positive peaks were observed in autumn–winter, the negative ones in spring–summer. Probably the high concentrations found in autumn–winter were rather due to shipping maintenance activities, a very common practice in this period, than to the high maritime traffic of the summer.

[1] Concentrations modified using the conversion factors reported in "Material and methods"

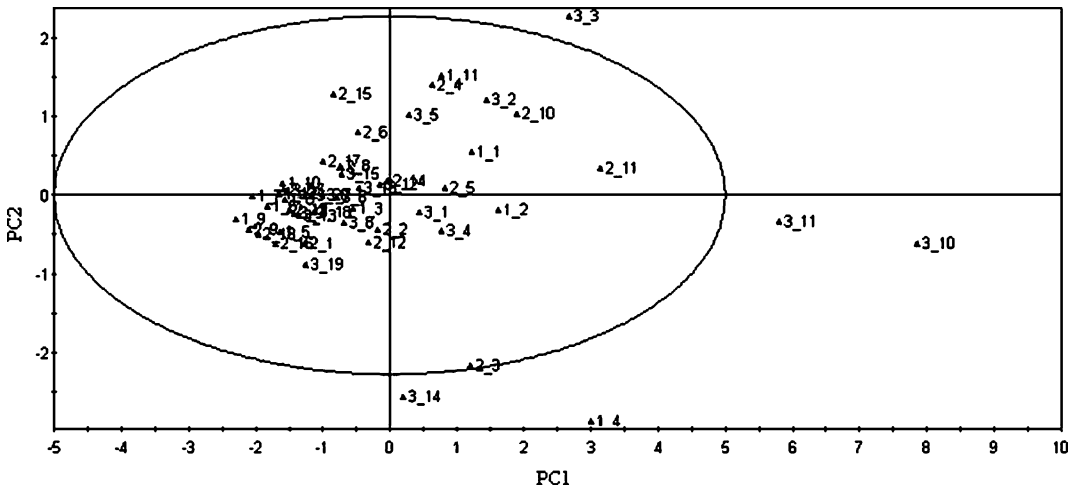

Fig. 4 Score plot of the first two Principal Component (every observation is indicated as follows: the first digit is the year of sampling, first, second or third, and the second is the number identifying the station)

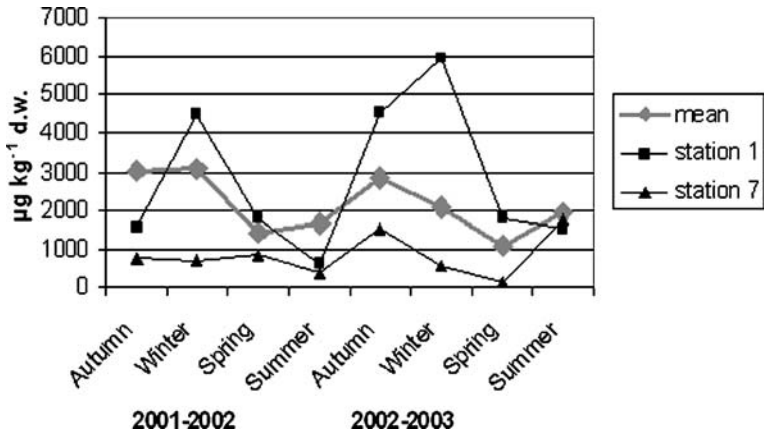

Fig. 5 Seasonal trend of butyltin concentration in *M. galloprovincialis* in stations 1 and 7

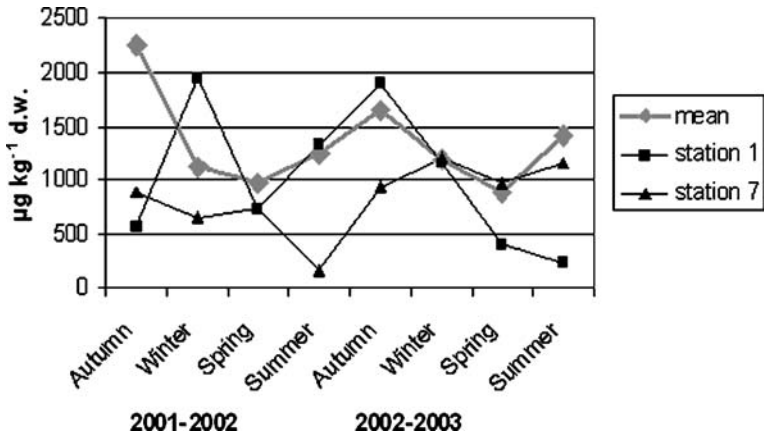

Fig. 6 Seasonal trend of butyltin concentration in *Tapes spp.* in stations 1 and 7

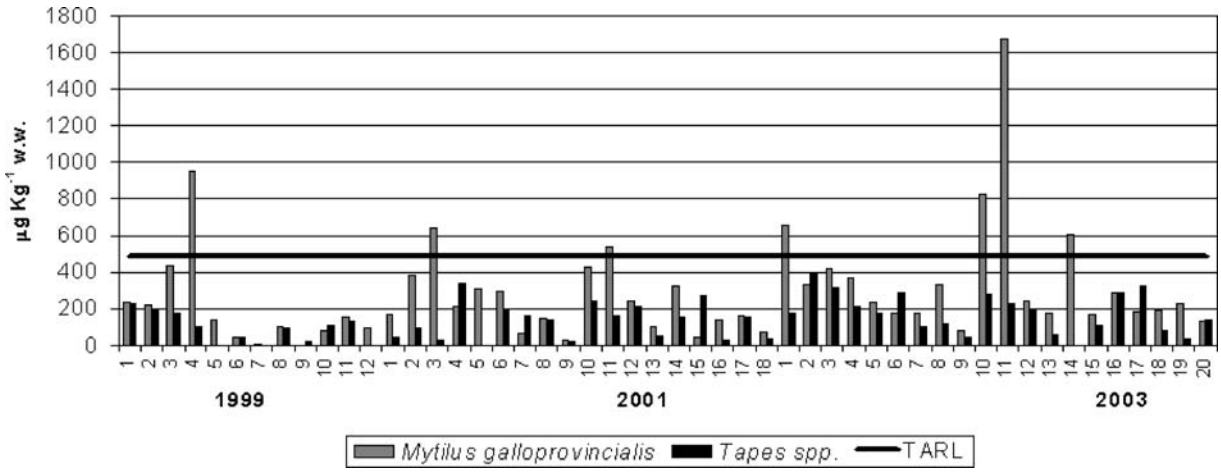

Fig. 7 Comparison between TBT concentration level in all stations during autumn campaign in the 3 years and TARL

Butyltin concentrations found in *M. galloprovincialis* during the spring–summer period in the area of Chioggia (TBT=528–986, DBT=294–678 ng g^{-1} d.w., as cations) were higher than those reported in Boscolo et al. (2004) who obtained TBT and DBT concentrations of 124–597 and 74–128 ng g^{-1} d.w. as cation, respectively, in two lagoon sites close to Chioggia in 2003. As reported by Cáceres-Martínez and Figueras (1998), who studied reproductive cycles of *M. galloprovincialis* in the Ria de Vigo, spring conditions (i.e. increase in temperature and chlorophyll-a concentration) are suitable for larvae development, so this is the period when *Mytilus*' spawning usually occurs. Lubet et al. (1985) reported that mussels show high amounts of lipids in the digestive gland in the period before spawning. In gastropods *N. lapillus* an accumulation of tributyltin in females has been observed and Bryan et al., (1987) related it to increasing lipid levels in the body in the period just before laying eggs. Sedano et al. (1995) observed that the principal energy stock in eggs of *M. galloprovincialis* is due to protein (45% of total dry weight) and lipid (22% of total dry weight). Furthermore, it has been also suggested that organotins have a higher affinity to proteins than to lipids, even if an in-depth study about this statement is needed (Antizar-Ladislao, 2008 and references therein). From these observations and our results, it could be hypothesized that mollusks release some contaminants during spawning.

In stations 19 and 20, lower concentrations than in stations 10 and 11 were found, indicating that mussel farming facilities probably had not been affected by organotin contamination in the monitored period.

Because *M. galloprovincialis* and *Tapes spp.* are edible organisms, it is important to estimate the associated risk for human health. As reported in the literature, on the basis of animal experiments, potential adverse effects of organotin compounds in humans involve endocrine, immune, respiratory, and neurological systems (Antizar-Ladislao 2008 and references therein). The tolerable daily intake for TBT is equal to 0.25 µg Kg-body $weight^{-1}$ day^{-1} (Penninks 1993).

The tolerable average residue level (TARL), is defined as the level of TBT in seafood that is tolerable for the average consumer with an average weight of 60 Kg (Belfroid et al. 2000):

$$\mathrm{TARL} = \frac{\mathrm{TDI} \times 60\,\mathrm{Kg\,body\,weight}}{\mathrm{average\,daily\,intake}}$$

For the population of Venice, an average daily intake of 70 g-seafood day^{-1} was estimated, but, considering that mollusks are about 44% of the total catch (COSES[2]), the average daily intake is about 31 g-mollusks day^{-1} and the TARL is equal to 487 µg Kg^{-1} *w.w.*

In Fig. 7 a comparison between values of TARL and TBT concentrations in *Mytilus* and *Tapes,* wet weight, is shown. It can be observed that in most stations concentrations are below the limit, whereas in

[2] http://www.coses.it/masterpubblica.html

some they are largely above it (e.g. stations 4 in 1999; 3 and 11 in 2001; 1, 10, 11, and 14 in 2003), especially for *M. galloprovincialis*. This definitely indicates a potential risk for human health. As the number of stations characterized by TBT levels above TARL has increased over time an important reason exists for continuing to monitor organotin levels in edible organisms.

Conclusions

This research was carried out between 1999 and 2003 with the aim of investigating organotin contamination in the Lagoon of Venice ecosystem. Concentration of butyltin compounds were significant in all samples, whereas phenyltin levels were often below the limit of detection.

Results of parametric analysis (ANOVA) show that contamination levels of butyltin for most stations were not significantly different between species during the period of monitoring. However, by processing the data through a PCA, it was observed that in some stations located close to shipyards, the industrial area or the town centre *Tapes* and *Mytilus* had considerably different pollutant concentrations.

In a number of stations TBT concentrations were higher than the estimated TARL, indicating a potential risk for human health from mussel eating. It is therefore important that, even though the organotin compounds containing antifouling paints have been banned in 2003, the periodic monitoring of contamination levels in the cultivated mussels of the Venice lagoon will not be discontinued.

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