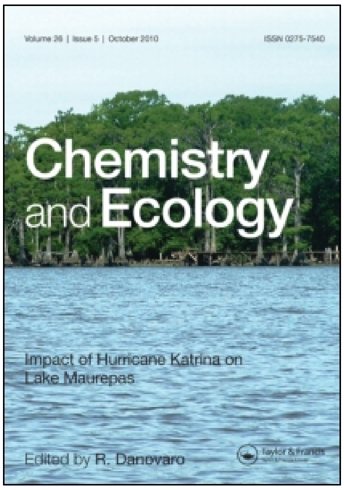

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DETECTION OF TRIBUTYILTIN (TBT) RESIDUES IN ITALIAN MARINE SEDIMENTS

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The distribution of tributyltin (TBT) in marine sediments from 16 areas of the Adriatic, Tyrrhenian, Ionian and Ligurian Seas was investigated, to obtain an extensive description of TBT residues along the whole Italian coast. The selected sites are located in three different types of marine areas: near important harbours, near river mouths and in coastal areas with moderate anthropogenic impact. The highest concentrations were measured in the harbour areas of the Gulfs of Naples and Taranto (17.81 and 21.08 ng Sn g^{-1} d.w., respectively). The lowest values were observed in coastal areas of the S. Eufemia and Policastro Gulfs (7.23 and 7.41 ng Sn g^{-1} dry weight (d.w.) respectively). On the whole, the sampled sediments may be considered as *lightly contaminated*, according to recent international classification. The statistical analysis suggests a significant combined effect of type of coastal area and marine basin on the TBT values, while the grain size does not seem to have analogous importance in the distribution of such a compound.

Keywords: Tributyltin (TBT); Antifouling; Marine sediments; Italy

1 INTRODUCTION

Pollution due to butyltin (BT) compounds is common in coastal and estuarine environments, and its effects on aquatic organisms have been of great concern in the last 20 years. Among the BT compounds, tributyltin (TBT) is the most toxic, showing measurable toxic effects on marine invertebrates at concentrations as low as a few nanograms per litre (Maguire, 1996). TBT has been used as an antifouling agent since the early 1970s, and it exists in the marine environment exclusively as a result of human activities (Pest Management Regulatory Agency, 2002). The discovery of its toxic potential led to a ban on its use by small craft in many countries in the late 1980s (Bennett, 1996). TBT poses a potential severe risk for the marine environment as a result of its toxicity, persistence and bioaccumulation capacity. It is toxic to a number of non-target marine organisms at the concentrations found in the aquatic environment (Pest Management Regulatory Agency, 2002).

The persistence of TBT in water is slight to moderate, with half-lives of a few days to a few weeks. The half-life of TBT in sediments has been experimentally estimated to be between

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100 and 800 d, depending on the aerobic/anaerobic conditions (Watanabe *et al.*, 1995). In deeper anoxic sediments, TBT's half-life may be from 1.9 to 3.8 years (Batley, 1996), while several studies indicate half-lives in sediments up to 15 years (Pest Management Regulatory Agency, 2002).

Finally, the TBT octanol–water partition coefficient (K_{ow}) indicates a potential for bioaccumulation, as the log K_{ow} ranges from 3.2 to 4.1. The bioconcentration factor (BCF) value is higher than 5000 in several marine species and ranges up to 50,000 in fish and 500,000 in clams. Although TBT does not significantly biomagnify up the food chain, it has been found in the tissues of marine mammals in the Mediterranean Sea (Focardi *et al.*, 2000) and in organisms of open ocean areas (Pest Management Regulatory Agency, 2002).

In view of marine environmental risk related to TBT use, many regulatory measures to reduce TBT concentrations in marine environment have been adopted since the 1980s. It is important to remember the phasing-out date of TBT-based antifouling paints by 1 January 2003, which prescribes, according to IMO Convention (2001), the complete prohibition of these compounds in antifouling paint formulations after 2008. Furthermore, to evaluate the potential risk in the marine environment, in Italy two important laws (D.Lgs 152/99, Law 979/82) provide for monitoring concentrations of TBT in bivalve tissues and in sediments.

At present, very little information on organotin contamination in Italian marine sediments is available. Most studies report data on organotin compounds in water and in organisms (Di Cintio, 1988; Bacci and Gaggi, 1989; Gabrielides *et al.*, 1990; Caricchia *et al.*, 1992; Amodio Cocchieri *et al.*, 1993; Rivaro *et al.*, 1997; Terlizzi *et al.*, 1998; Gallina *et al.*, 2000), but few studies take into account marine sediments (Bortoli *et al.*, 2003; Chiavarini *et al.*, 2003).

In 1999, the Italian Central Institute for Marine Research (ICRAM) carried out an extensive survey program, with the twofold aim of assessing marine coastal water trophic conditions and characterising the coastal sediments for some organic and inorganic compounds (PAHs, POPs, TBT, heavy metals). This large-scale study included areas affected by a wide range of anthropogenic impacts (like industrial ports and riverine areas) and areas with moderate or no apparent anthropic impacts, used as 'reference'.

This paper focuses on the TBT results obtained from this extensive survey along the Italian coast to provide recent data on the contamination by such a compound in marine sediments. In particular, we present the results obtained from 40 sediment samples collected in 16 areas from distinct marine basins, selected according to different environmental conditions and potential inputs of TBT; sites were grouped into three main area typologies: harbours, river mouths and coasts with moderate anthropic influence. The analytical results on grain size and TBT were processed by means of statistical analysis, taking into account also the type of area and marine basin of belongings, to single out the main variables that influence the TBT distribution along the Italian coast.

1.1 Marine Basins' Main Characters

The selected areas belong to distinct marine basins, which have different morphological and sedimentological features that could influence the TBT distributional patterns and must be taken into account in evaluating analytical and statistical results.

1.1.1 Adriatic Sea

The Adriatic Sea is an epicontinental semi-enclosed basin connected to the Ionian Sea through the sill of the Otranto Strait. It is characterised by a wide, gently sloping shelf in the northern sector, reaching a depth of about 100 m at the latitude of Ancona; it becomes abruptly deeper, until 200 m, in the central part, while the southern part is a deep basin that reaches 1200 m at its centre (Poulain, 1999).

As regards grain-size distribution, Jorissen (1988) reports Pleistocene sandy sediments in the northern and central sectors, while clayey bottoms characterise the southern basin. In addition, a mud belt parallel to the Italian coast is present at a depth of about 20–60 m. The Po River runoff mainly characterises the shelf area of the northern Adriatic sector along the Italian coast, with freshwater and sediment contributions.

1.1.2 Ligurian Sea

The Ligurian continental shelf is a very narrow shelf, mainly consisting of rocky bottoms in the inner part and plio-quaternary sediments in the outer part, the margin of which is incised by submarine canyons. It may be divided into two sectors, with distinct morphological and sedimentological features. The Holocene pelitic sediments are localised mainly near the river mouths in the western sector, while in the eastern sector, a rather continuous Holocene covering is present (Corradi *et al.*, 1980). The continental shelf in front of Genoa harbour is covered by plio-Quaternary sediments; the finest sediments are deposited west of the harbour, while in the eastern sector, sandy sediments may be found, owing to the suspended loading that follows the general west-trending water circulation of the Ligurian Sea (Fanucci *et al.*, 1974).

1.1.3 Tyrrhenian Sea

The Tyrrhenian Sea originated from different geological events, which occurred during the middle-late Miocene; this is a complex and articulated basin that may be summarily divided into two main basins, the boundary of which conventionally corresponds to 41° N. The northern basin belongs to a zone of continental margin and comprises the studied deltas of the Ombrone and Tiber Rivers. The Arno River mouth should be considered to belong to the Ligurian Sea if we assume the lineage Cape Corso, Capraia, Elba as a southern boundary. In spite of this, from a structural viewpoint, many features indicate that this area may be considered as the northern continuation of the Tyrrhenian Sea (Fanucci and Nicolich, 1984).

The three deltas, which lie on a relatively wide continental shelf, had similar evolutions during the last glacioeustatic semi-cycle. During the transgressive phase, they were entrapped in a barrier-lagoon system that retreated landward. At the begin of the low-stand phase, they filled their lagoons and flowed directly into the Tyrrhenian Sea, building their modern delta complexes, in which the littoral sands are limited to the first few metres (max 10–15 m) of water depth (Bellotti *et al.*, 1994; Tortora, 1999; Carboni *et al.*, 2000; Pranzini, 2001). The transgressive and low-stand deposits are also recognised in the Holocene sedimentary sequences that deposited on the wide continental shelves of the Naples (Milia *et al.*, 1998) and Salerno Gulfs (Buccheri *et al.*, 2002). The southern Campanian and Calabrian Tyrrhenian shelf is indeed generally narrow and inclined, draped by fine holocene sediments, and its margin is often incised by submarine canyons along which recent sediments are displaced (Ulzega *et al.*, 1981; Ortolani *et al.*, 1997).

1.1.4 Northern Ionian Sea

The northern Ionian Sea has a triangular shape, limited by a very narrow continental shelf and a steep slope, incised by many submarine canyons (Colantoni *et al.*, 1984).

The western continental shelf is prograding, due to the terrigenous contribution of rivers; in the eastern continental shelf, in which sedimentation is almost exclusively carbonatic (organic and bioclastic), three orders of terraces referable to the Wurmian regression may be recognised. The continental slope is controlled by quaternary faults and incised by several canyons along which there is a strong displacement of coastal material (Belfiore *et al.*, 1982).

2 MATERIAL AND METHODS

2.1 Sampling

The areas investigated are located in the Adriatic Sea (Trieste, Venice, Ancona, Pescara and Manfredonia); in the Northern Ionian Sea (Gulf of Taranto, Sinni-Basento and Crati Rivers); in the Tyrrhenian Sea (Arno, Ombrone and Tiber Rivers; Gulfs of Naples, Salerno, Policastro and S. Eufemia) and in the Ligurian Sea (Genoa).

Sampling sites (Fig. 1 and Tab. I) were selected according to different inputs of contamination, and the sampling cruise was performed during July 1999.

We selected areas subjected to strong shipping activities (Trieste, Ancona, Manfredonia, Taranto, Genoa, Salerno and Naples; harbour areas in Tab. I), areas subjected to riverine impact (Arno, Ombrone, Tiber, Crati, Sinni-Basento; river mouth areas in Tab. I) and areas with moderate or limited anthropogenic influence (Venice, Pescara, Policastro, Sant'Eufemia; coastal areas in Tab. I).

In each area, two sampling stations were selected, with the exception of the Gulfs of Genoa and Naples, where six sampling stations, placed on three transects, were considered. All the sampling stations were located along inshore–offshore transects, placed within the

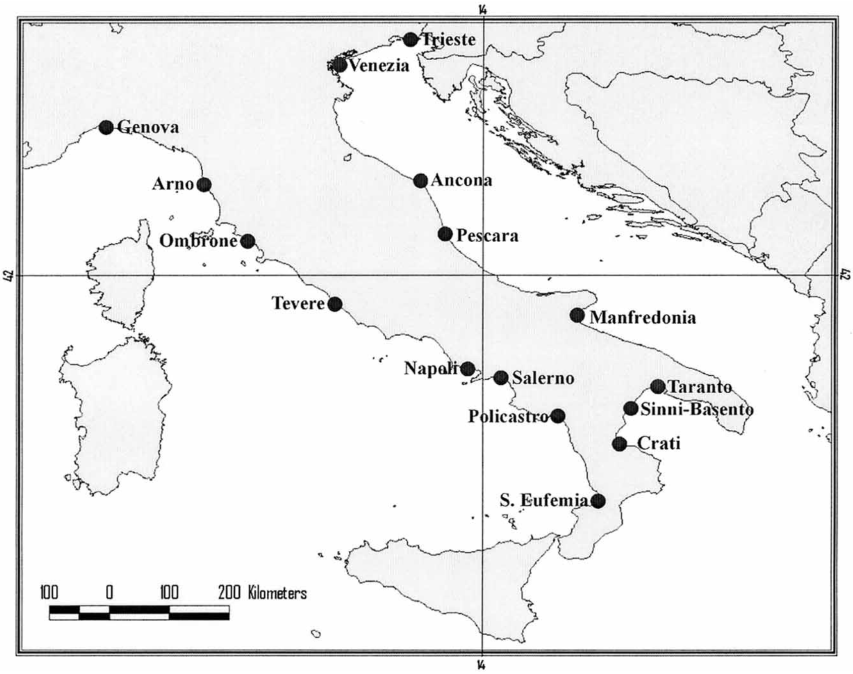

FIGURE 1 Location of the investigated areas.

TABLE I Location of sampling stations, TBT concentrations (ng Sn g^{-1} d.w.) and results of grain-size analysis (%).

Investigated areas typology	*Station*	*Depth (m)*	*Location*	*TBT*	*Gravel*	*Sand*	*Silt*	*Clay*	*Shepard's classification*
Coastal areas									
Venezia	BV 1A	10	45°19.070 12°21.250	10.81		100.0			Sand
	BV 1C	20	45°16.890 12°28.900	10.32		88.4	5.3	6.3	Silty sand
Pescara	PE 1A	11	42°28.730 14°14.680	10.30		95.3	4.7*		Sand
	PE 1C	26	42°30.850 14°17.940	10.66		8.7	56.9	34.4	Clayey silt
Gulf of S. Eufemia	SE 1A	14	38°52.715 16°12.841	7.33		83.4	14.5	2.3	Sand
	SE 1C	34	38°52.619 16°11.989	7.23		50.7	36.9	12.4	Silty sand
Gulf of Policastro	PO 1A	14	40°03.346 15°31.053	8.02		10.6	63.5	25.9	Clayey silt
	PO 1C	40	40°02.999 15°31.516	7.41		1.4	62.3	36.3	Clayey silt
Harbour areas									
Trieste	TS 1A	21	45°38.680 13°43.880	13.05		9.8	27.6	62.6	Silty Clay
	TS 1C	23	45°39.680 13°36.890	11.80		6.6	27.1	66.3	Silty Clay
Ancona	AN 2A	12	43°36.460 13°34.700	11.09		84.7	15.3*		Sand
	AN 2C	30	43°39.810 13°39.700	10.67		1.1	60.0	38.9	Clayey silt
Gulf of Manfredonia	MN 1A	10	41°35.290 15°54.554	14.37		21.2	36.9	41.9	Loam
	MN 1C	14	41°34.895 15°58.563	13.05		3.8	42.7	53.5	Clayey silt
Gulf of Taranto	TA 1A	13	40°29.858 17°01.100	21.02		91.9	5.5	2.6	Sand
	TA 1C	32	40°29.115 17°01.044	18.18		19.8	59.3	20.9	Clayey silt
Gulf of Salerno	SA 1C	33	40°34.311 14°50.301	10.47		14.5	58.0	27.5	Clayey silt
	SA 2C	32	40°23.618 14°56.192	10.80		13.0	57.0	30.0	Clayey silt
Gulf of Naples	NA 1A	10	40°48.553 14°12.744	17.81	0.2	99.7			Sand
	NA 1C	34	40°48.630 14°12.841	15.79		65.0	30.4	4.6	Silty sand
	NA 2B	25	40°48.782 14°13.574	15.31		93.1	*6.9		Sand
	NA 2D	52	40°49.000 14°14.300	16.28	4.4	52.0	34.9	8.7	Silty sand
	NA 3A	17	40°48.884 14°19.370	14.84		91.8	8.2*		Sand
	NA 3D	52	40°48.490 14°19.090	15.03	2.0	52.9	37.9	7.2	Silty sand
Gulf of Genoa	GE 1B	23	44°24.015 8°41.770	8.68	0.7	66.4	29.4	3.5	Silty sand
	GE 1D	45	44°23.959 8°42.198	9.35		4.5	70.4	25.1	Clayey silt
	GE 2B	22	44°25.145 8°44.940	8.80		65.5	31.0	3.5	Silty sand
	GE 2D	45	44°24.416 8°44.891	9.57		4.5	65.0	30.5	Clayey silt

(*continued*)

TABLE I Continued.

Investigated areas typology	*Station*	*Depth (m)*	*Location*	*TBT*	*Gravel*	*Sand*	*Silt*	*Clay*	*Shepard's classification*
	GE 3B	20	44°23.048 8°58.904	10.08	16.8	83.2			Sand
	GE 3D	57	44°22.189 8°58.843	11.16		22.5	38.2	39.3	Loam
River-mouth areas									
Sinni River	SB 1A	12	40°14.003 16°45.472	7.43		79.2	10.4	10.4	Sand
	SB 1C	34	40°13.209 16°48.307	7.26		75.2	16.9	8.7	Sand
Crati River	CR 1A	13	39°45.811 16°29.615	10.57		75.8	17.4	6.8	Sand
	CR 1C	32	39°45.855 16°30.305	11.04		11.4	56.7	31.9	Clayey silt
Tiber River	TV 1A	13	41°43.743 12°13.511	12.22		78.0	18.6	3.4	Sand
	TV 1C	32	41°42.118 12°11.959	11.92		42.2	38.7	19.1	Silty sand
Ombrone River	OM 1A	12	42°38.708 10°59.781	10.08		94.4	5.6*		Sand
	OM 1C	32	42°38.078 10°59.082	9.53		11.4	42.3	46.3	Silty clay
Arno River	AR 1A	13	43°42.439 10°15.644	12.56		3.2	63.1	33.7	Clayey silt
	AR 1C	29	43°42.530 10°07.562	12.29		1.8	55.5	42.7	Clayey silt

*Pelite: sum of silt and clay.

marine transition belt. This belt is situated between the submerged beach and the internal continental shelf, into the bathymetric range of 10–50 m. This range is significant because it represents the shallowest bathymetric belt in which the finest sediments, generally associated with contaminants, are found (Brondi and Ferretti, 1986).

Sediments were sampled by box-corer or Van Veen grab. The superficial layer (0–2 cm) was collected from each sample, which was thoroughly homogenised and divided into two portions: the first for grain-size analysis, and the second for chemical analysis.

Samples for grain-size analysis were stored at 4 °C in a plastic container; those for TBT analysis were maintained in aluminium decontaminated foil, at −20 °C in the dark, until analysis (Nonnis and Maggi, 2001) to preserve TBT degradation (Gòmez-Ariza *et al.*, 1999).

2.2 Chemical and Physical Analysis

The grain-size analysis was performed according to Romano and Gabellini (2001). The coarse fraction was analysed by wet sieving while the fine fraction (<63 μm) was determined by X-ray Sedigraph. The sample fine fraction was not analysed when it was below 5% or if the sample was <2.5 g. The analytical results were subsequently used to classify the typology of sediment according to Shepard (1954).

TBT was extracted from samples by shaking about 2 g of dried sediment with 10 ml of HCl 6 N, 20 ml of CH_2Cl_2 and 5 g NaCl for 4 h. Samples were then centrifuged for 10 min at 1500 rpm, and the phase with CH_2Cl_2 was taken with a Pasteur pipette and evaporated in a rotavapor at 30 °C. Three millilitres of hexane and 3 ml of 3% (v/v) NaOH were added to the residue to eliminate inorganic tin, mono and dialchiltin. Two millilitres of hexane were successively put into 5 ml tubes and evaporated to dryness with N_2. The residue was digested with 1 ml of 69% HNO_3 for 1 h at 120 °C. After the acid had evaporated, 2 ml of a saturated boric acid solution in 1% HCl was added to the samples (Focardi, 2001). To prevent contamination, during each extraction cycle, more than one blank sample was obtained by using only the reagents. The solutions obtained were finally analysed by atomic absorption spectrometer with a graphite furnace and Zeeman background correction (ZETASS 4100 ZL, Perkin-Elmer), with the hydride generation technique. This technique involves the reaction of the acidified aqueous samples with a reducing agent, such as sodium borohydride. The sodium borohydride/acid reduction generates a tin volatile hydride, which is transported into the preheated graphite tube by means of an argon carrier gas. The hydride is then decomposed and tin is trapped on the inner surface of the graphite tube where atomisation takes place. Pretreatment of the graphite tube, to obtain the optimal trapping efficiency with a suitable modifier, is necessary. Therefore, for three times, 40 μl of iridium solution is dispensed into the conditioned graphite tube and heated for 20–30 s at 1200 °C.

In the tin analyses, the carrier solution was saturated boric acid (approx. 50 $g\,l^{-1}$) in 1% HCl, and the reducing agent was 0.4% $NaBH_4$ in 0.05% NaOH. The accuracy of the results was verified by analysing Certified Reference Material PACS-2 (marine sediment) from the National Research Council of Canada. Uncertainty related to sample homogeneity, extraction and analysis was assessed by replicate determination of samples and was found to be below 10%. The detection limit was 3 ng Sn g^{-1} d.w.

2.3 Statistical Treatment of Data

The results obtained were analysed using an unbalanced three-way ANOVA method, to detect the presence of effects due to typological characteristics of the sampling site (i.e. harbour areas, river mouth areas, coastal areas); basins of the investigated areas (i.e Adriatic, Ligurian, Tyrrhenian and Ionian Sea) and sediment to grain size, expressed as Shepard's classification, on the TBT concentration. The results are reported in Table II.

TABLE II Statistical analysis: results by unbalanced three-way ANOVA method.

Source	*Type IV sum of squares*	*d.f.*	*Mean square*	*F*	*P*	*Observed power**
Model	5689.182[†]	22	258.599	44.687	0.000	1.000
Typological characteristic of sampling site	60.505[‡]	2	30.252	5.193	0.017	0.758
Basin	108.676[‡]	2	54.338	9.327	0.002	0.953
Shepard's classification	3.643[‡]	3	1.214	0.208	0.889	0.082
Typological characteristic of sampling site × Basin	80.581[‡]	2	40.291	6.916	0.006	0.873
Typological characteristic of sampling site × Shepard's classification	28.134[‡]	5	5.627	0.966	0.464	0.266
Basin × Shepard's classification	19.206[‡]	4	4.802	0.824	0.527	0.212
Typological characteristic of sampling site × Basin × Shepard's classification	6.107	3	2.036	0.349	0.790	0.105
Error	104.868	18	5.826			
Total	5794.050	40				

*For $\alpha = 0.05$.

[†] $R^2 = 0.982$.

[‡] Type IV hypotheses.

3 RESULTS

The grain size of sediments emphasises the geological, morphological and sedimentological heterogeneity of the investigated areas (Brondi *et al.*, 1979). Most sampling transects showed a general increase in fine fractions (silt and clay) with regard to depth (Tab. I). The observed trend was particularly evident in the riverine areas, where the terrigenous river input increased the muddy sedimentation, as well as in some sheltered areas, like the Gulf of Manfredonia. In the inshore area, at a water depth of 10 m, we observed mainly sandy sediments, while the bathymetric belt of 30 and 40 m showed a predominance of clayey silt. Finally, some areas like the Gulf of Genoa and Gulf of Naples were characterised by coarse sedimentation as far as the deeper stations.

In spite of the wide heterogeneity of the samples analysed, the levels of TBT in sediments are quite homogeneous; the results show a TBT range concentration of 7–21 ng Sn g^{-1} d.w. (Tab. I) with a medium value of 11.60 ng Sn g^{-1} d.w.

The highest concentration values were observed in the Gulf of Naples (17.8 ng Sn g^{-1} d.w.) and in the Gulf of Taranto (21.0 ng Sn g^{-1} d.w.), whereas the lowest concentration values were measured in the Gulf of Policastro, in the Gulf of Sant'Eufemia and in the coastal area off the Sinni River (from 7.2 to 7.5 ng Sn g^{-1} d.w.). Because of the higher number of sampling stations, in the Gulfs of Genoa and Naples the distribution of TBT concentration along the coast was observed. In particular, in the Genoa Gulf, we noticed a moderate increase in TBT concentration according to the west–east direction and with increasing water depth; the transect with the highest concentration is placed near the Genoa harbour entrance.

In the Gulf of Naples, a moderate increase is observed along the east–west direction; we did not observe any increase in TBT concentration with water depth, nor with respect to the fine fraction.

4 DISCUSSION

The concentrations were compared with those published from the Italian coastal area, where very few recent studies are available.

The concentrations measured are consistent with those reported by Bortoli *et al.* (2003), who found, in the Lagoon of Venice, values below 50 ng g^{-1} in nine of the 12 sampled sites and values of 50 ng g^{-1} or higher in the remaining three sampled sites; these TBT concentrations were defined as 'relatively low level'.

Chiavarini *et al.* (2003) reported low organotin concentration levels (between 3 and 27 μg Sn kg^{-1} d.w.) in sediment collected in Sicilian areas characterised by different shipping densities. In contrast, Caricchia *et al.* (1992) reported a high concentration of TBT in the Gulf of La Spezia (400–1500 ng g^{-1} d.w.).

Waite *et al.* (1991), Dowson *et al.* (1992) and Cortez *et al.* (1993) introduced a classification for TBT concentrations in sediments, characterising concentrations below 3 ng g^{-1} as *uncontaminated*, 3–20 ng g^{-1} as *lightly contaminated*, 20–100 ng g^{-1} as *moderately contaminated*, 100–500 ng g^{-1} as *highly contaminated* and above 500 ng g^{-1} as *grossly contaminated.*

Taking into account the above-mentioned classification, we noticed a low contamination level in all the investigated sites (7–20 ng g^{-1} d.w.), for which values are included in *lightly contaminated* class; the only exception is represented by the Gulf of Taranto, where the observed TBT concentration of 21 ng g^{-1} d.w. is included in the *moderately contaminated* class.

In general, TBT levels found in this study are lower than those detected in many different areas of the world (Fig. 2), such as in Thailand (9–4500 ng g^{-1} d.w.) (Kan-Atireklap *et al.*,

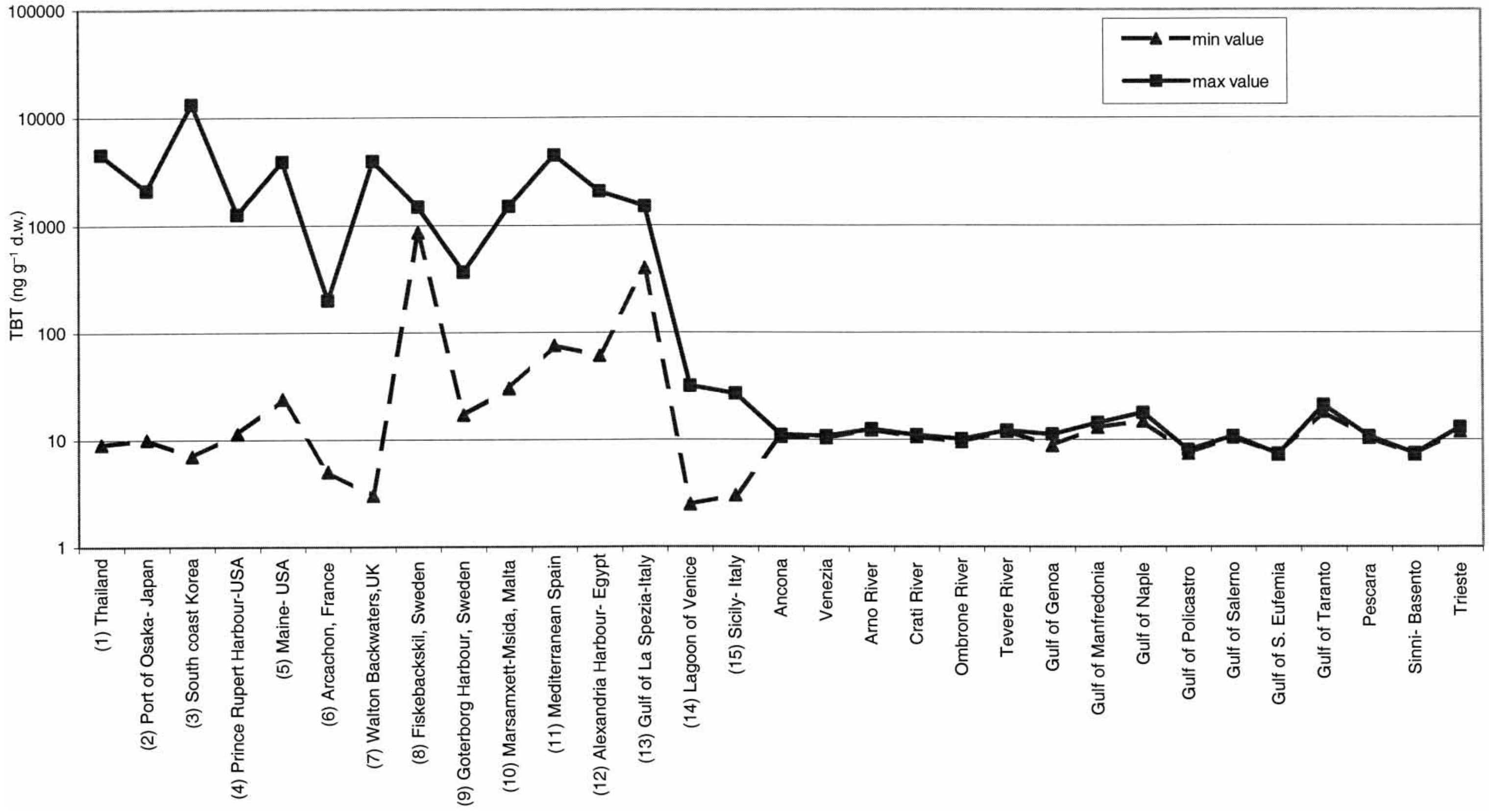

FIGURE 2 Comparison among data presented in this study and those from international references (1) Kan-Atireklap *et al.*, 1997; (2) Harino *et al.*, 1998; (3) Shim *et al.*, 2002; (4) Thompson *et al.*, 1998; (5) Page *et al.*, 1996; (6) Stuer-Lauridsen and Dahl, 1995; (7) Brack, 2002; (8) Sarradin *et al.*, 1994; (9) Dowson *et al.*, 1992; (10) Axiak *et al.*, 2000; (11) Diez *et al.*, 2002; (12) Barakat *et al.*, 2001; (13) Caricchia *et al.*, 1992; (14) Bortoli *et al.*, 2003; (15) Chiavarini *et al.*, 2003.

1997), Japan (10–2100 ng g^{-1} d.w.) (Harino *et al.*, 1998), Korea (7–13,300 ng g^{-1} d.w.) (Shim *et al.*, 2002), USA (11.4–1262/24–3900 ng g^{-1} d.w.) (Thompson *et al.*, 1998; Page *et al.*, 1996), France (5–200 ng g^{-1} d.w.) (Sarradin *et al.*, 1994), UK (3–3935 ng g^{-1} d.w.) (Dowson *et al.*, 1992), Sweden (860–1480/17–366 ng g^{-1} d.w.) (Stuer-Lauridsen and Dahl, 1995; Brack, 2002), Malta (30–1500 ng g^{-1} d.w.) (Axiak *et al.*, 2000), Spain (76–4487 ng g^{-1} d.w.) (Diez *et al.*, 2002) and Egypt (61–2067 ng g^{-1} d.w.) (Barakat *et al.*, 2001).

The high concentrations found in the cited literature may be expected, considering that all these studies are referred to sediments collected into harbours and marinas with high commercial and yachting traffic. The results from the application of the ANOVA method (Tab. II) show that the model of three-way variance analysis is significant ($F(22,18) = 44.39$, $P < 0.001$).

The TBT concentration values depend significantly on the specific typology of the areas investigated ($F(2,18) = 5.193$, $P = 0.017$) as well as on the sampling basins ($F(2,18) = 9.327$, $P = 0.002$). In contrast, no significant effect was observed between TBT concentration values and sediment texture, expressed as Shepard's classification. Furthermore, a significant effect due to the interaction between area typology and sampling basins was observed ($F(2,18) = 6.196$, $P = 0.006$).

By applying post-hoc multiple comparisons on the single significant main effects (typology of the investigated areas and sampling basins) we observed the following results. In the harbour areas, the TBT concentrations measured in the Ionian sampling sites (19.6 ng Sn g^{-1} d.w.) were significantly higher than those detected in the Tyrrhenian (12.4 ng Sn g^{-1} d.w.) and in the Adriatic Seas (12.3 ng Sn g^{-1} d.w.) (Dunnett's test (T3), $P < 0.05$). In the river mouth areas, the TBT concentrations measured in the Ionian sampling sites (9.07 ng Sn g^{-1} d.w.) were significantly lower than those measured in the Tyrrhenian sampling sites (11.4 ng Sn g^{-1} d.w.) ($T(8) = 2.29$, $P = 0.05$). In the coastal areas, the TBT concentrations measured in the Adriatic sampling sites (10.5 ng Sn g^{-1} d.w.) were significantly higher than those measured in Tyrrhenian sites (7.5 ng Sn g^{-1} d.w.) ($T(6) = -13.8$, $P < 0.001$).

To summarise, the Ionian harbour areas are impacted more by TBT residues than the Tyrrhenian and Adriatic harbour areas, and the Adriatic basin has coastal areas with higher TBT residues values than those in the Tyrrhenian Sea.

If we compare the specific impact of TBT residues measured in all the sampling basins with respect to the typology of the sampling areas, we can observe a general behaviour of TBT contamination. In the Tyrrhenian Sea, there is an increasing TBT impact moving from the coastal areas (7.5 ng Sn g^{-1} d.w.) to riverine areas (11.4 ng Sn g^{-1} d.w.) and to harbour areas (12.4 ng Sn g^{-1} d.w.) (Dunnett's test (T3), $P < 0.05$). The same trend can be observed in the Ionian Sea, where the harbour areas were more contaminated than the riverine areas (19.6 ng Sn g^{-1} d.w. and 9.07 ng Sn g^{-1} d.w., respectively) ($T(4) = 6.05$, $P = 0.004$). A similar trend is also observed in the Adriatic sampling stations where, in the harbour sites, the TBT values are significantly higher than the coastal values (12.3 ng Sn g^{-1} d.w. and 10.5 ng Sn g^{-1} d.w., respectively) ($T(8) = 2.52$, $P = 0.036$).

5 CONCLUSIONS

This study has discussed the contamination level of organotin in 16 areas located in the Ligurian, Tyrrhenian, Ionian and Adriatic Seas. Forty sediment samples were collected to evaluate the concentration of tributyltin (TBT) residues in national coastal areas characterised by different typological and sedimentological characteristics. In particular, we considered industrial harbours, riverine outflow-influenced areas and areas with moderate or no apparent anthropic impact, used as a reference.

The butyltin pollution was evident in all the considered samples. The TBT contamination appears to be diffused along the national coast, with higher values near two of the main industrial harbours, such as Naples and Taranto, even though no sampling station was located directly in the harbours. TBT concentrations were rather homogeneous, lying within the narrow range of 7–21 ng Sn g^{-1} d.w.

By comparing the measured concentration values with the national and international data, it is possible to assess a low contamination level. In particular, the data obtained showed that the measured concentration range corresponds to *lightly contaminated* sediments; the only exception is in the Gulf of Taranto, where the TBT concentration of 21 ng g^{-1} d.w. is included in the *moderately contaminated* class.

The statistical analysis revealed that the most relevant variables influencing the TBT concentration along the whole Italian coast can be referred to the features of the marine basin and to the typology of the sampled areas. On the contrary, sediment texture does not appear to influence the TBT concentration. This may be explained taking into account the regional distribution of the studied areas and the different features of marine basins, corresponding to a wide variety of sedimentary environments. The statistical relevance of such factors may have hidden the effect of single environmental parameters such as grain size.

Finally, it is worth stressing the importance of finalised research in the national marine coastal environment to increase the amount of data able to evaluate the efficacy of legislative restrictions on the use of antifouling paints containing TBT, as well as to evaluate the contamination status of the marine environment by TBT residues.

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