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Spatial distribution and temporal trends of butyltin compounds (TBT, DBT & MBT) in short sediment cores of the SW Portuguese Shelf (western Iberian Margin, NE Atlantic)

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ABSTRACT

Spatial patterns and temporal trends of the butyltin compounds tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) were investigated in a set of sediment samples collected along the SW Portuguese continental shelf. This region did not reach the Good Environmental Status (GES) in accordance with the Marine Strategy Framework Directive (MSFD) during a first evaluation carried out in 2012. Overall, MBT and DBT were the predominant organotin species detected, but high concentrations of TBT were found in and around disposal sites for dredge sludge derived from the dredging in navigation channels, harbours, and shipyard facilities of the Tagus and Sado estuaries. Although Portuguese regulations for monitoring sediment quality in relation to dredging activities consider only PAH, PCB and HCB, they also dictate that other organic contaminants such as butyltin compounds (BTs) should be monitored if suspicion of high values exists, but no action limits are defined for these (MAOTDR, 2007). Without action limits, the monitoring recommendation given in the regulations is not put into practice. Considering their toxicity, BT derivates should be integrated in the legislation, because they represent an environmental threat in the relocation of dredged material, especially when derived from harbour and shipyards areas. Based on this study, we recommend giving more attention to the amounts and impacts of BTs in sediments at dredged material disposal sites (DMDS) and their surroundings. Or even better, in order to be more efficient, monitoring should be done at the source of the dredged materials and not at the sink. In case it is not done, the monitoring of concentrations of TBT (and other BTs) in sediments and organisms, including imposex studies, at all Portuguese sites for disposal of dredged material receiving slightly to strongly contaminated dredged material must be developed.

1. Introduction

Butyltin compounds (BTs) are organic derivatives of tin (Sn) characterized by the presence of covalent bonds between three carbon atoms and a Sn atom (Okoro et al., 2011). They are grouped into mono-, di-, tri- and tetra-organotin compounds based on the formation of bonds with alkyl or aryl groups (Hassan et al., 2019). The biological effects of these compounds increase as the number of organic groups bound to the Sn

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cation increases (Sunday et al., 2012). Butyltin compounds (BTs), such as tributyltin (TBT) and its degradation products dibutyltin (DBT) and monobutyltin (MBT), are spread through the marine environment mostly due to their extensive use in the past as biocides in TBT-based antifoulant paints on boat and ship hulls since the 1960s (Bennett, 2010). These paints were used to prevent organisms from attaching on the hull, increasing water resistance and fuel consumption. The use of TBT-based antifouling paints began in the 1960s, and they were widely used between the 1970s and 1980s. BTs are also used in other applications such as coatings, anti-odour/anti-fungal additives, pesticides, catalysts, wood treatments and preservatives. However, the great expansion of the use of BTs started already during the 1940s, when MBT and DBT were mainly used by the plastic industry in the production of polyvinyl chloride (PVC) to avoid degradation caused by heat and light (Chen et al., 2010; Dong et al., 2015; Hoch, 2001).

While the antifoulant paints were effective, the TBT slowly leached out into the marine environment where it turned out to be highly toxic to a wide range of organisms (Evans et al., 1995; Neuparth et al., 2017). TBT-containing paint particles resulting from the abrasion of antifouling paint from ship hulls also constitute an important source of TBT to the environment (Berto et al., 2007). TBT was considered as one of the most toxic substances ever intentionally introduced into the aquatic environment (Goldberg, 1986). Even at very low concentrations it can cause a range of negative effects (e.g. shell deformation in oysters, imposex in gastropods, mussel larval mortality, adipogenesis) (Bowen et al., 1984; Capitão et al., 2017; de Oliveira et al., 2020). In marine gastropods, exposure to low TBT levels (in the range of 1 ng/L) causes the development of male secondary sexual characteristics in females. This effect, known as imposex, was found in over 150 species of marine snails (gastropods). In highly polluted areas imposex was responsible for the sterility of several species (Neuparth et al., 2017; Santos et al., 2004). The cause-effect correlation between concentration of TBT in sediments and imposex incidence was identified in previous studies (Gómez-Ariza et al., 2006; Laranjeiro et al., 2015; Mattos et al., 2017). As a response to the endocrine disrupting effects of BTs, particularly in gastropods, and growth disorders affecting farmed oysters, France and the UK introduced legislation (1982 and 1987, respectively) to ban the use of TBT antifouling paints on small boats (<25 m). Later it was applied in most European countries (EC directive 89/677/EEC) (Barroso and Moreira, 2002; Santos et al., 2000). Portugal adopted proper legislation and banned the use of TBT in 1993 while the Portuguese Navy imposed a total ban on TBT on their ships in 1992 (Barroso et al., 2002). As the first regulation applied only on small boats (EC directive 89/677/EEC) was evaluated to be insufficiently effective, the International Maritime Organization (IMO) implemented a ban on the application of TBT-based antifouling paints starting from 1 January 2003, and with 1 January 2008 as the last date for having TBT-based antifouling paint on a vessel (Champ, 2000).

Although it has now been illegal for over a decade to either sell or apply TBT-based antifoulants, the remains of TBT used in the past may persist in older buried sediments. Since BTs are hydrophobic substances, they are easily adsorbed on suspended particles after entering the water, and with those accumulate in the sediments (Lee et al., 2022). TBT is considered as the most hydrophobic BT compound, strongly binding to organic matter in sediments (Furdek Turk et al., 2020). Thus, BT still constitutes a threat to the marine environment due to its toxicity and tendency to bioaccumulate. The legacy of TBT contamination is still affecting benthic communities, such as the case of the crustacean *Crangon crangon* (Parmentier et al., 2019). Recent reports indicate that TBT pollution is still a big concern in certain regions, such as the South China Sea (Zhang et al., 2022).

The degradation of BTs in aquatic systems may occur step by step via the sequential loss of butyl groups triggered by ultraviolet irradiation, and biological cleavage (Amouroux et al., 2000; Chen et al., 2017; Hoch, 2001). The sequential degradation of TBT to DBT and then MBT (Furdek et al., 2016), eventually leads to formation of stable inorganic tin compounds. Of the two degradation products, MBT is the one that lasts longest in the environment. While the half-life of TBT in marine and estuarine waters can vary from days to weeks (Omae, 2006), in sediments the degradation is prolonged, with half-lives varying from years under aerobic conditions to decades in anaerobic conditions (Matthiessen, 2013). Additionally, other factors, can influence their degradation rate such as the sediment composition (e.g., type and amount of organic matter, presence of chloride, oxides, hydroxides), the environmental conditions, and BT concentrations themselves (Filipkowska et al., 2014, 2011; Hoch, 2001; Hoch and Schwesig, 2004). BT accumulated in the sediment may be remobilized and remain bioavailable by the activity of bioturbating benthic fauna and by sediment resuspension by storm events, bottom trawling, clam harvesting in estuaries and dredging. Once resuspended into the water column, BTs can be dispersed over a wide area, with possible adverse effects on both pelagic and benthic communities (e.g., (Barroso et al., 2011; Galante-Oliveira et al., 2006; Laranjeiro et al., 2018; Sousa et al., 2009a).

In Portugal, published BT data are mostly from harbour and estuarine areas (Almeida et al., 2007; Anastasiou et al., 2016; Carvalho et al., 2009; Coelho et al., 2002; Cortez et al., 1993; De Bettencourt et al., 1999; Díez and Bayona, 2009; Nogueira et al., 2003; Quevauviller et al., 1989; Santos et al., 2004; Sousa et al., 2007). These previous studies revealed the occurrence of BT contamination in sediments, mainly associated with recreational marinas, shipyards, and fishing and commercial harbours. Santos et al. (2004) investigated the effect of dredging, combining data from BTs measured in tissues of gastropods from dredged material disposal sites (DMDS) with incidence of imposex. However, very limited information is available regarding TBT compounds in the Portuguese open marine environment, with only a few not so recent studies focused on the characterization of BT in marine sediments (e.g., Díez et al., 2005; Gómez-Ariza et al., 2006; Sousa et al., 2007, 2012) and in organisms (Barroso et al., 2004; Galante-Oliveira et al., 2006). Despite the lack information about marine sediment contamination by BT compounds, there is indirect evidence of the presence of BT from recorded incidence of imposex in marine areas (Barroso et al., 2011; Barroso and Moreira, 2002; Galante-Oliveira et al., 2009, 2006; Laranjeiro et al., 2018; Santos et al., 2004, 2002, 2000; Sousa et al., 2009b, 2005). Furthermore, there is no information of BTs in Portuguese marine environments dating from after the total ban in 2008.

Sediments from ports, marinas, shipyards, and navigation channels represent the main repositories of BTs, due to the activities that took place before the use of BTs was banned by international regulations. To assure safe navigation, navigation channels need to be dredged and the dredged material is generally disposed at offshore sites. Unfortunately, the Portuguese regulation for dredged material (MAOTDR, 2007) does not dictate the monitoring of BT, except if suspicion of high values exists, but without defining the action limits for the BT assessment. In the absence of any control on the concentrations of BTs (particularly TBT) in the disposed materials there is substantial risk that these compounds are remobilized from sediments to the water phase, posing a risk to aquatic organisms.

Despite that BTs were banned two decades ago, especially due to TBT toxicity, the persistence of these compounds in the marine environment makes the present work relevant to evaluate their source and to assess the nature of BT contamination. This study is part of the CSS project (Evaluation of Contamination of Surface Sediments in the Coastal Area between Peniche and Sines, Portugal). In the CSS project, the spatial patterns, and temporal trends of sedimentary characteristics (e.g., grain size, organic carbon) and chemical contaminants (including BTs) for an area of the SW Portuguese shelf that did not reach the Good Environmental Status (GES) in the first Marine Strategy Framework Directive (MSFD) evaluation report (see in Fig. 1 the marine region named BT1.2) are investigated. In this first MSFD report the concentrations of BTs were not assessed because of the scarce published information regarding their occurrence in Portuguese marine sediments. This work intends to fill this

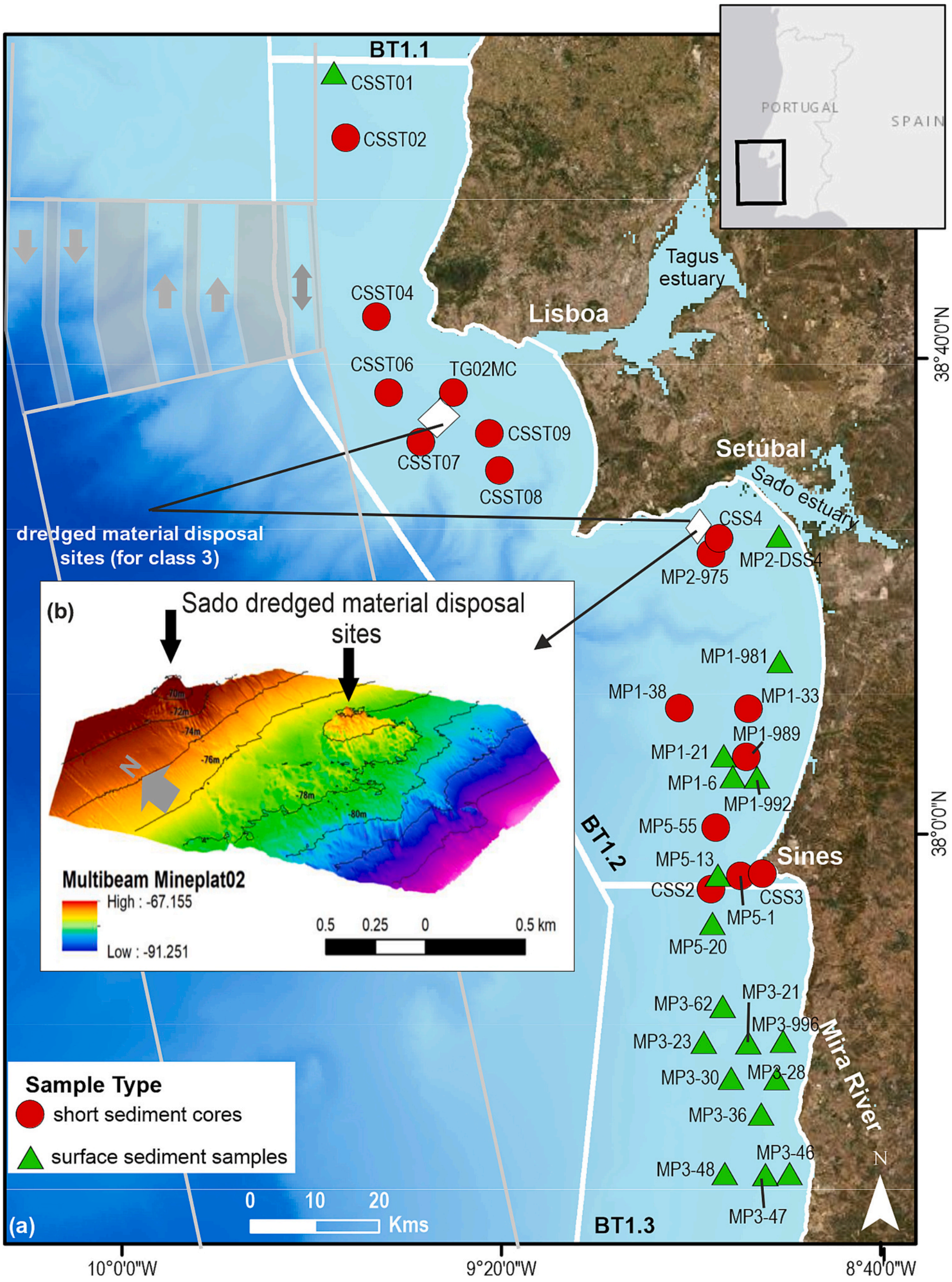

Fig. 1. (a) Map of the sediment sampling locations. White polygons represent dredged material disposal sites (DMDS) for Class 3 sediments (moderately contaminated). Thick white lines represent the limits of MSFD regions (b) Excerpt of multibeam data from the Sado DMDS obtained within the scope of the MINEPLAT project (Terrinha et al., 2020), clearly showing the disposal sites by their elevated topography. Grey lines and arrows represent maritime traffic corridors and traffic directions (source Direção Geral dos Recursos Marinhos and International Maritime Organization).

information gap and aims to assess the concentrations of TBT, DBT, and MBT in marine sediment samples and how these BT compounds are temporally and spatially distributed. The acquired data are compared with Sediment Quality Guidelines (SQG) and international sediment criteria (such as the Action Levels (ALs) of contaminants for managing the disposal of dredged marine sediment material).

2. Materials and methods

2.1. Study area

The choice of the study area (Fig. 1) aimed to fill the most prominent gaps in knowledge on butyltin occurrence in surface sediments of the Portuguese margin. The study area includes the area that did not reach the GES in the first MSFD evaluation report and it is subdivided in the areas BT1.2 and BT1.3. Area BT1.2 coincides with the area that did not reach the GES (MAMAOT, 2012), located in the proximities of the Tagus and Sado estuaries and the Sines harbour (Fig. 1). The two estuarine areas are characterized by dense urban (ca. 2.8 million of inhabitants in the Lisboa metropolitan area comprising the cities of Lisboa and Setúbal) and industrial occupation (e.g., shipyards, chloroalkali plant, pyrite roast plant, smelter) some of which disabled since the 1980s. Sines has the largest harbour of Portugal and one of the main harbours for the transhipment of containers in the Atlantic and Mediterranean routes as well as an oil refinery, and thermoelectric power plant which was deactivated at the end of 2021. Area BT1.2 also comprises the Tagus and Sado DMDS of slightly contaminated dredged material under the Regulatory Portuguese Legislation (Ordinance 1450/2007, 12th of November). The dredged material disposed at these sites mainly originates from harbours, shipyards, and navigation channels. Fig. 1b shows an excerpt of multibeam data in the Sado DMDS revealing the seafloor elevations produced by the dumping of dredged materials from the Sado estuary. Multibeam data for the Tagus DMDS is not available. Area BT1.1 located to the north of BT1.2 was not sampled because the seabed there is mainly composed of rock substrate and coarse-grained sediments. Area BT1.3 met the criteria of GES in 2012, but it was included in the present study with the main goal of obtaining recent information that may help to support the maintenance of the GES. This area is characterized mostly by coarse sediments and rocky outcrops, reflecting limited terrigenous sediment supply from the Mira River and removal of fines by currents.

2.2. Sediment sampling

Sediment samples for the present study were collected during two oceanographic campaigns that occurred in 2019 and 2021. For assessment of BT levels, eighteen surface sediment samples were collected using a Smith-McIntyre grab, and sixteen short sediment cores were sampled with an OSIL multicorer (with 4 core liners of 10 cm internal diameter by 60 cm long) and NIOZ boxcorer (equipped with cylindrical coring barrel of 50 cm diameter) (Fig. 1a). On-board, the sediment cores were sub-sectioned in different depth intervals: 1 cm slices in the first 4 cm core depth, 2 cm slices between 4 and 20 cm core depth, and 3 cm slices below 20 cm core depth. Subsamples for BT determination were wrapped in aluminium foil and stored at −20 °C until preparation for analysis in the laboratory. Subsamples for organic carbon (C_{org}), grain-size and ^{210}Pb and ^{226}Ra measurements were stored in plastic bags at 4 °C. In the laboratory, all subsamples were lyophilized. Subsamples for analysis of BT, organic carbon (C_{org}) and ^{210}Pb and ^{226}Ra were sieved through a 2 mm square mesh sieve to remove coarse shell material and gravel, and then milled using agate pots in a Fritsch Pulverisette 7 Classic Line planetary mill.

2.3. ^{210}Pb and ^{226}Ra determinations

Sediment chronology was based on the down-core distribution of ^{210}Pb (half-life 22.3 years) and ^{226}Ra. Total ^{210}Pb activity was determined in 12 samples per core by α-spectrometry indirectly via its granddaughter ^{210}Po, as well as in 3 samples per core by γ-spectrometry. Activity of ^{226}Ra was determined in 3 samples per core by γ-spectrometry (Costa et al., 2011). Excess ^{210}Pb activity was calculated by the difference between total ^{210}Pb activity and the average ^{226}Ra activity in each sediment core, the latter taken as proxy of supported ^{210}Pb (i.e., the background ^{210}Pb activity produced by radioactive decay of ^{234}U series radioisotopes contained in the sediment matrix. A Constant Flux and Constant Sedimentation Rate model (Carpenter et al., 1982) including a surface mixed layer (SML) CF/CS$^{(+SML)}$ was fitted on the observed ^{210}Pb profiles to estimate the sedimentation rates. This model is applicable to ^{210}Pb profiles characterized by a relatively slow downward decline in excess ^{210}Pb activity in the biologically mixed surface sediment layer followed by a more pronounced exponential downward decline in the deeper subsurface sediment layer (Boer et al., 2006). The sedimentation rate is estimated from the ^{210}Pb decline in the layer below the SML.

2.4. Organic carbon (C_{org}) and grain-size determination

Sediment C_{org} content was calculated from the difference between total carbon and inorganic carbon content, determined by high temperature combustion on a Leco Truspec micro-analyzer CHNS. For determination of inorganic carbon, samples were first heated in a muffle furnace for 3 h at 400 °C to combust organic matter. Three replicate subsamples of 2 mg of each dried and homogenized sediment sample were measured, before and after combustion. The relative precision of repeated measurements was lower or equal to 0.03 % (dry weight).

Grain-size in the range of 0.04 to 2000 μm was determined by laser diffraction using a Coulter LS-1320 after removal of coarse fraction (>2 mm) by wet sieving, organic matter destruction with H_2O_2 and dispersion with CALGON. Measurements were replicated three times to guarantee data consistency. The median value of fine-fraction content of the three measurements was considered.

2.5. Butyltin compounds analysis

Butyltin compounds (BTs) were measured by solid-phase microextraction (SPME)-GC–MS, using NaBEt4 as derivatizing agent, based on a previously optimised methodology (Carvalho et al., 2007, 2009). The analytes were extracted from ca. 1.5 g of sediment with 3 mL of a 6 M hydrochloric acid/ethanol 1:1 (v/v) mixture solution, in an ultrasonic bath (Transsonic 460/H) for 2 h, and then centrifuged at 2500 rotations per minute for 15 min. A 200 μL aliquot of the extract was then put into a vial containing 500 μL of a buffer solution of $NaCH_3COO$ (2.0 M)/ CH_3COOH (5.6 M) (pH = 4.3) and the required deionised water to accomplish a total solution volume of 10 mL per vial. Vials were closed and then 250 μL of NaBEt4 (2 %, w/v, ABCR GmbH Co. KG (Karlsruhe, Germany)) was added to each vial by means of a syringe (properly washed with methanol) to start the derivatisation of BTs.

Pre-concentration of BTs was carried out by SPME, with a fiber of poly(dimethylsiloxane) (PDMS, Supelco) with 100 μm film thickness, inserted in an autosampler CombiPal model (CTC Analytics). The extraction was done at 40 °C during 40 min in agitation. A GC–MS Varian Saturn 2000 MS coupled to a Varian 3900 GC with a split/splitless injector port, a SPME liner (0.8 μm) and a microseal septum system, and a CP-Sil 8CB Low Bleed/MS column (60 m length X 0.250 mm diameter, 0.25 μm film thickness) was used for analysis. The carrier gas was helium of high purity (99.9999 %) which had a constant flow of 1 mL min^{-1}. The column oven was initially set at 40 °C for 1.5 min, and then it was heated at a rate of 20 °C min^{-1} to 95 °C. Then, it was heated at a rate of 2.5 °C min^{-1} to 135 °C where it was held for 5 min, after which it was heated to 250 °C at a rate of 20 °C min^{-1}. The temperature of the injector was set at 250 °C.

The transfer line and ion trap temperatures were set at 230 °C and 200 °C, respectively. In the MS mode it was considered the precursor ions (*m/z*) 235, 263 and 291 for MBT, DBT and TBT respectively, and the product ions m/z) 179, 207 and 179 for MBT, DBT and TBT respectively (Table S1 and Fig. S1 in supplementary material). For measuring the 3 compounds, three segments were set, one for each compound, with a specific time and ion mass (m/z) range for each (Table S1 in supplementary material). Each segment had a scan time of 0.550 s, an emission current of 40 μA, a multiplier offset of 220 V, a threshold of 1 count, a target TIC of 5000 counts, a prescan ionization time of 1500 ms and a RF dump value of 300.0 m/z. Linear response range was from 6 to 750 ng g^{-1} for MBT, 3–750 ng g^{-1} for DBT and 3–750 ng g^{-1} for TBT. The method validation showed and acceptable precision (RSD < 15 %). The accuracy of the method was established by Carvalho et al. (2007) using the certified reference materials BCR-646 and PACS-2. According to these authors, standard addition method should always be used in the BTs quantification due to differences in sediment matrix between samples. All samples were analysed in triplicate. Thus, standard addition was done to one of the samples replicates and the calibration curve (after subtracting sample replicate signal) was used to quantify the other two replicates. This procedure was used also for samples with similar matrix to reduce analytical workload and time.

Quality control was assured through the analysis of blank solutions, quality control solutions (<10 % variation among independent days) and spike of control sediment samples. BTs spiked control sediment samples were used to evaluate the recovery of the analysed compounds and the method accuracy. The detection limits (calculated through signal to noise ratio (S/N), three times S/N) varied with the samples due to matrix effects, being always lower than 1.5 ng g^{-1} for TBT and 3 ng g^{-1} for the other two BTs. The Limit of Quantification (LoQ, calculated as ten times S/N) for TBT was always lower than 5 ng g^{-1} and for DBT and MBT 10 ng g^{-1}, being always the highest value the one considered.

3. Results and discussion

3.1. ^{210}Pb chronology

The down-core profiles of excess ^{210}Pb activity in the studied sediment cores typically show a SML reaching depths of 2 to 20 cm (Table 1). The presence of the SML can be attributed to sediment mixing caused by natural (e.g., hydrodynamic, and biogenic) and anthropogenic processes (e.g., bottom trawling, anchoring, dredging, and dumping operations). Among the bioturbating benthic fauna, the burrowing crustacean *Callianassa subterranea* which is common in the sandy mud bottom sediments of the Portuguese shelf (Sampaio et al., 2016) produces burrows of several tens of cm deep (Ziebis et al., 1996). This biological activity may explain the relatively large thickness of the SML in core CSST06. In core CSS2 the relatively short length of the sediment core together with a thick SML makes the estimation of sedimentation rate subject to speculation. Core CSS3 collected in the Sines harbour has an anomalous excess ^{210}Pb profile, with relatively high values throughout the core without a clear decrease with depth. This may be interpreted as indicative of very high sedimentation rate or of deep and thorough sediment mixing. All these sediment mixing processes can disturb the geochemical profiles of the contaminants released by anthropogenic activities and influence the biogeochemical processes that may affect their accumulation or degradation.

The sediment cores located in the vicinity of the Tagus estuary showed the highest sedimentation rates (cores TG02MC, CSST07 & CSST09), reflecting high sediment supply derived from the Tagus River (Table 1).

3.2. Surface sediment characteristics

Surface sediment samples from the Tagus shelf area had relatively high contents of fine fraction and C_{org}, ranging from 22 to 94 % and 1.0 to 1.8 %, respectively. These values are distinctly higher than those from the Sado and Sines shelf areas, where fine fraction and C_{org} contents varied between 0.10 and 23 % and 0.10 and 0.83 %, respectively (Fig. 2), with exception of core CSS3 collected inside the Sines harbour. The higher values observed for the Tagus shelf area reflect the major outflow from the Tagus River compared to the Sado River, and the associated higher export of particulate matter. The mean annual discharge of the Tagus River close to the river mouth in Lisboa is about 500 $m^3 s^{-1}$ (Benito et al., 2003), while that of the Sado river is >10 times lower with a mean annual discharge of 40 $m^3 s^{-1}$ (Vale et al., 1993). The positive correlation between fine fraction content and C_{org} (Spearman correlation coefficient $r = 0.84$; $p < 0.05$) indicates a general association of C_{org} with the finer sediment fraction.

Table 1
Length of the sediment cores, thickness of the surface mixed layer (SML) and sedimentation rate (SR in cm yr^{-1}). N.P.E. means not possible to estimate.

Cores	Length (cm)	SML (cm)	SR (cm yr^{-1})
CSST02	32	10	0.16
CSST04	26	9	0.42
CSST06	26	20	0.06
TG02MC	35	6	0.72
CSST09	28	9	0.71
CSST07	26	2	0.98
CSST08	23	6	0.26
CSS4	12	9	0.11
MP2-975	16	6	0.14
MP1-33	16	7	0.09
MP1-38	17	9	0.05
MP1-989	21	7	0.15
MP5-55	18	6	0.12
CSS2	14	11	0.03
CSS3	21	N.P.E.	N.P.E.

3.3. Down-core sediment characteristics

A similar difference in fine-fraction and C_{org} contents that distinguishes surface sediments from the Tagus and Sado regions is also noted in the down-core samples (Fig. 3). Down-core fine fraction and C_{org} contents in cores from the Tagus shelf range from 75 to 96 % and 0.66 to 2.41 %, respectively. In cores from the Sado shelf, downcore fine fraction and C_{org} contents range from 3 to 33 % and 0.16 to 1.25 %. The fine fraction contents of the surface samples of these cores (e.g., CSS4, MP1–989, MP1–33, CSS3) are generally much higher than those obtained at depth (Fig. 3b).

The C_{org} and fine fraction contents of the down-core samples are also positively and significantly correlated (Spearman correlation coefficient $r = 0.79$; $p < 0.05$). The limited down-core variability in grain-size and C_{org} distribution may reflect the absence of significant changes in the hydrodynamic conditions of the area.

3.4. Characterization of butyltin compounds in sediments

A summary of the occurrence of BTs in the studied sediments is presented in Table 2. Where BTs are found in concentrations above the Limits of Quantification (LoQ) compounds are counted as present. In only 8 out of 168 sampled locations all three BTs were detected simultaneously. The most abundant BT was MBT, present in 27 % (39 samples of which 6 are surface samples) of the samples analysed, followed by DBT in 17 % (25 samples of which 3 are surface samples) and TBT in 13 % (19 samples of which 5 are surface samples) of the samples analysed. Of the three BTs, the highest concentrations were found for DBT: 300 and 190 ng g^{-1} in core MP5–55 at, at respectively, 2–4 cm (corresponding to the age of 2005 Common Era (CE)) and 1–2 cm (2012 CE), and 200 ng g^{-1} in core CSS4 at 2–4 cm (2011 CE) (Fig. 4). The highest concentrations of MBT of 100 and 80 ng g^{-1} were found in core CSS4 at, respectively, 4–6 cm (1982 CE) and 10–12 cm (1927 CE), respectively. The highest concentrations of TBT of 41 ng g^{-1} were found in core CSST09 at 2–3 cm (2016 CE), and 40 and 30 ng g^{-1} in CSST04 at, respectively, 3–4 cm (2015 CE) and 4–5 cm (2014 CE), followed by 30 ng g^{-1} in the top 2 cm of core MP2–975 and 11 ng g^{-1} in the surface level of core CSS4. Of particular interest are the relatively high concentrations of TBT in cores collected in the vicinities of the Sado DMDS (cores MP2–975 and CSS4) where the contents of fine fraction sediment and C_{org}, the main carriers of adsorbed BTs, are relatively low (average contents of fine fraction 6.3 % and 7.3 %, C_{org} 0.64 % and 0.46 %, respectively). This suggests that the fine sediment fraction and organic matter in that area are enriched in TBT compared to the other studied areas. Alternatively, the sediment may contain TBT-containing old paint particles produced by the abrasion of antifouling paint from ship hulls.

The ratio of TBT to ΣBTs (ΣBTs = TBT + DBT + MBT) was calculated as indicator of substantial TBT input. Where concentrations of any of the compounds were below the limit of quantification (LoQ of TBT = 5 ng g^{-1}, DBT and MBT = 10 ng g^{-1}), half of this LoQ value was used to calculate the table-value for the samples in which at least one of the three BT was identified. A TBT to ΣBTs ratio higher or equal to 0.50 was found in only 9 samples (6 % of the total number of samples analysed). This suggests that there is no recent input of TBT or that input is derived from sources containing mainly DBT and MBT, both used in higher quantities in plasticizers. The surface samples with TBT to ΣBTs ratios higher or equal to 0.50 were MP2–975 (0.56) located in the vicinity of the Sado DMDS, TG02MC (0.50) and CSST09 (0.70) located nearby the Tagus River mouth. The highest ratios of TBT to ΣBTs (≥ 0.50) were observed in down-core samples from the Tagus area, cores CSST09 (0.80 at 2–3 cm (2016 CE)) and CSST04 (0.57, 0.80 and 0.75 at, respectively, 2–3 cm (2017 CE), 3–4 cm (2015 CE) and 4–6 cm (2013 CE)), indicating a lower state of degradation of TBT in these sediments than found at the surface.

The butyltin degradation index (BDI) can be used to evaluate the degradation of TBT in aquatic systems (Díez et al., 2002). This index is

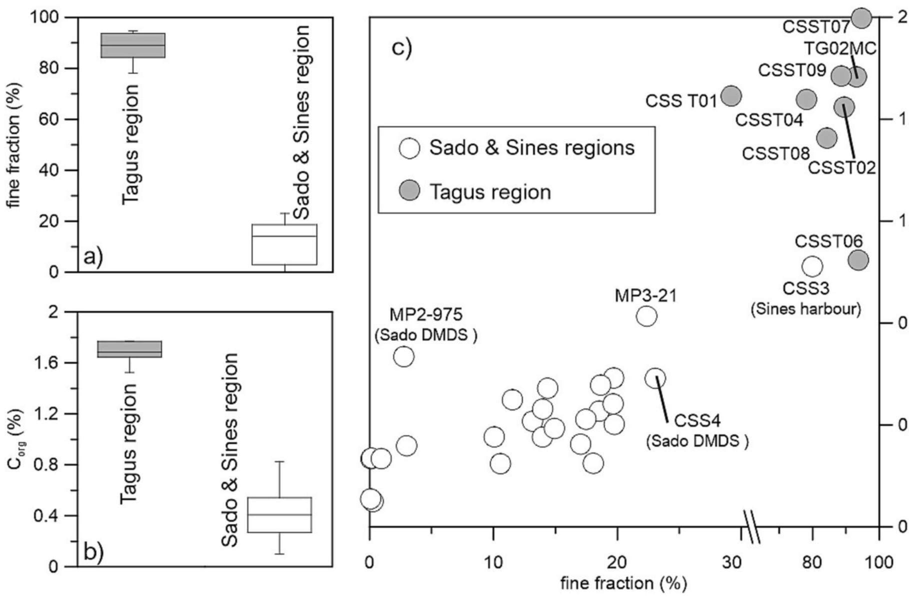

Fig. 2. Fine-fraction and organic carbon contents of surface sediments collected in the Tagus and Sado and Sines regions. (a, b) Box-whisker plots showing minimum, maximum, and median values and lower and upper quartiles. The box represents the interquartile range that contains 50 % of the values. The whiskers are the lines that extend from the box to the highest and lowest values. The line across the box indicates the median. (c) Scatterplot showing the relationship between fine fraction and the organic carbon contents in the studied surface sediment samples.

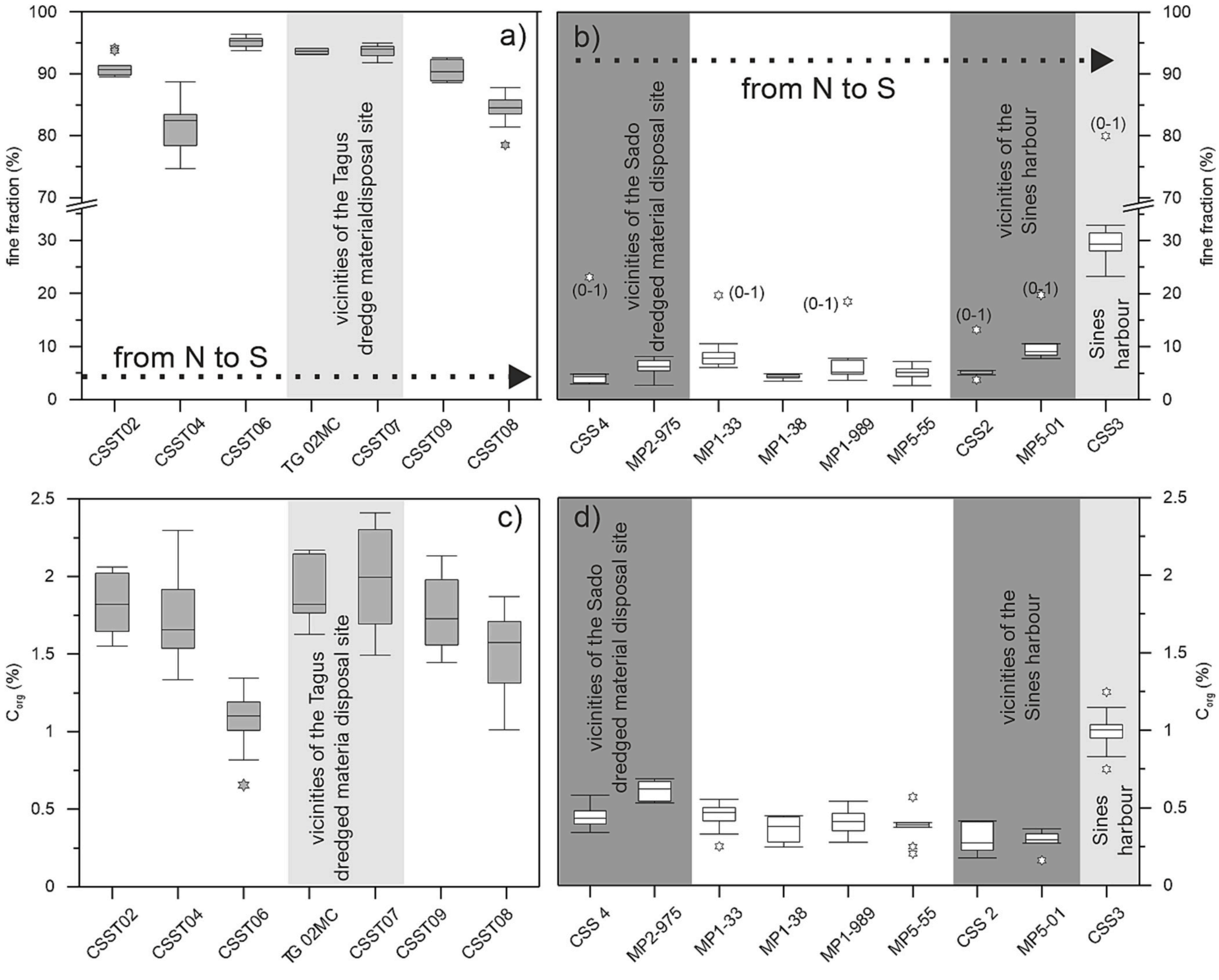

Fig. 3. Box-whisker plots for the fine fraction (a & b) and organic carbon (c & d) contents in the studied sediment cores, geographically ordered from north (left) to south (right). Sediment cores from the Tagus region are presented in a and c, cores from Sado and Sines regions are presented in b and d. The star symbol represents the samples considered as outliers that are defined as 1.5 X inter-quartile range.

Table 2
Summary of occurrence of butyltin compounds (MBT, DBT and TBT) in the studied sediments. LoQ – Limit of Quantification.

Butyltin Compounds	LoQ (ng g^{-1})	Samples above the LoQ	Samples above the LoQ (%)	Range (ng g^{-1})	Spearman Correlation with C_{org} and fine fraction ($p < 0.05$)
MBT	10	39	27	10–100	Not correlated
DBT	10	25	17	10–300	Not correlated
TBT	5	19	13	5–41	0.65 & 0.51

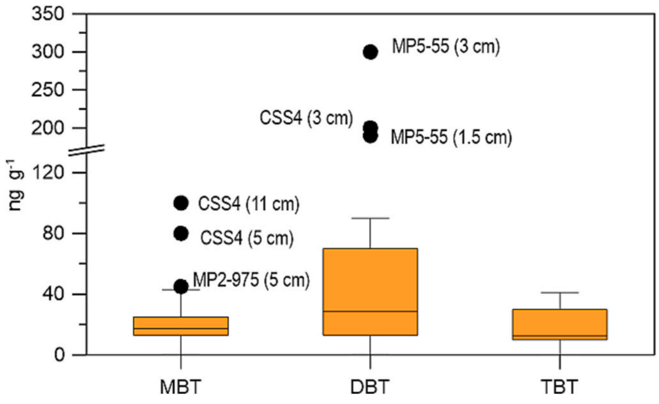

Fig. 4. Box-whisker plot of concentrations of butyltin compounds above the Limit of Quantification.

calculated by dividing the sum of MBT and DBT by TBT [(MBT + DBT)/TBT]. A BDI value of <1 indicates a recent TBT contamination, assuming that the decomposition of TBT is the only source of DBT and MBT (Díez et al., 2002) or a low TBT degradation rate that may be found under certain conditions (e.g., hypoxia, darkness, low temperature, low microbial activity, and high levels of TBT). BDI values larger than one would suggest prograded degradation of TBT deposited in the past. In coastal areas adjacent to river mouths and estuaries, however, DBI should be used with caution because DBT and MBT may enter directly from other sources (e.g., discharge of domestic and industrial effluents). In our study, the BDI values were lower than or equal to 1 in seven samples (surface samples of cores TG02MC, CSST09 and MP2–975, and depth levels between 2 and 6 cm of cores CSST04 and CSST09). In general, the BDI shows great down-core variability, except in cores TG02MC (top 8 cm) and MP2–975 (top 10 cm) where BDI displays a general increase with depth consistent with the degradation of TBT to DBT and MBT.

The samples with the highest levels of butyltins (ΣBTs = MBT + DBT + TBT) are those with the highest concentrations of DBT. ΣBTs ranges from 13 ng g^{-1} to 323 ng g^{-1}. Of the three BTs, only TBT shows a moderately positive correlation ($p < 0.05$, $n = 19$) with fine fraction sediment and C_{org} content (Table 2). This may be explained by sorption of TBT on negatively charged surfaces of organic matter and fine-grained particles. In these samples, C_{org} is also inversely correlated with BDI (Spearman correlation $r = -0.66$; $p < 0.05$, $n = 19$) suggesting that organic matter strongly influences the TBT degradation in sediments in addition to adsorption. Through the control of TBT adsorption, organic matter is responsible for regulating TBT partitioning in the sediment-porewater system. As the compounds present in interstitial waters are considered bioavailable for microorganisms (Burdige, 2006), organic matter in sediments can influence the degradation of TBT by defining its bioavailable fraction in interstitial water (Furdek et al., 2016). Once present in the porewater, TBT can migrate from deeper to surface layers, where much more efficient degradation under oxic conditions can occur (Filipkowska et al., 2014). The other two BTs (MBT and DBT) are significantly correlated with each other (Spearman Correlation $r = 0.52$; $p < 0.05$, $n = 23$), but not with either TBT, C_{org}, or fine fraction. The absence of correlation between TBT and DBT may suggest that DBT is for some part derived from other sources than by degradation of TBT. Another explanation for the absence of correlation between TBT and its degradation products (MBT and DBT) may be that these degradation products are less hydrophobic and more mobile than TBT, and thus under conditions of very slow TBT degradation have time to diffuse to other sediment layers, leaving TBT behind (Furdek et al., 2016).

3.5. *Spatial distribution of butyltin compounds*

TBT concentrations in surface sediments were highest in cores TG02MC, CSST09, MP2-975 and CSS4 in the vicinities of the Tagus and Sado DMDS (Fig. 5a). These samples show concentrations of TBT that are higher than the concentration of its degradation products, with TBT/DBT ratio greater than one, suggesting the dispersion of TBT from disposed sediment derived from the harbours, shipyards, and navigation channels of the estuaries. The fact that these sediment samples were collected in the vicinity of dumping sites suggests that contaminants present in the disposed dredge material are subsequently being dispersed by currents and become mixed with marine uncontaminated sediments. The disposal sites of the dredged materials thus might represent an active source of contaminants to biotic and abiotic compartments. Relatively high concentrations of DBT and MBT in the surface sediments of core CSST04, which is not close to any DMDS, may be associated with the Tagus River plume. Especially during winter when high river runoff favours the export of sediment enriched in BTs and other contaminants out of the Tagus estuary, the plume tends to spread in westerly and northerly direction driven by the prevailing southerly winds in that season (Fernández-Nóvoa et al., 2017; Vaz et al., 2018).

In the Sines offshore area, core CSS2 is the only one with measurable TBT concentrations, ranging from 8 to 11 ng g^{-1} in the top 2 cm, which may be explained by the intense maritime traffic in the vicinity to the Sines harbour. However, the predominance of MBT over TBT in these samples suggests relatively low recent TBT input in the marine environment and/or a rapid TBT degradation, or recent inputs of MBT (or/and DBT) in the water column and surface sediments of the harbour and adjacent coastal areas (Fig. 5c). This agrees with results obtained by Díez and Bayona (2009) two decades ago.

3.6. *Vertical distribution of butyltin compounds*

Most of the subsurface samples had TBT concentrations lower than the LoQ. Quantifiable values were found only in cores nearby dredged material disposal sites (e.g., TG02MC, CSST09, MP2-975 and CSS4) at depths within the SML reached by bioturbation (Fig. 6). This suggests that sediment reworking by burrowing benthic fauna plays a role in the downcore distribution of BTs, which could also explain the down-core variability. The highest concentrations of TBT were observed in samples from cores CSST04 and CSST09, characterized by high fine-fraction and C_{org} contents, confirming the preferred accumulation of TBT in association with sedimentary organic carbon.

Cores CSST08, CSST07, CSST06 and core MP5-55 (located north of Sines harbour) are characterized by the presence of high DBT and/or MBT in subsurface samples between 1 and 6 cm, suggesting faster TBT degradation in these sediment depths. This may also explain the occurrence of high DBT concentrations (50 to 300 ng g^{-1}) and MBT (20 to 23 g^{-1}) between 1 and 6 cm in core MP5–55 collected north of Sines harbour. Of the BTs, MBT was the only one identified in core CSS3 collected inside the Sines harbour, suggesting a recent entrance of MBT, or the absence or low recent MBT and TBT inputs in the harbour and/or a rapid TBT degradation in the water column of the harbour. The presence of quantifiable levels of BTs at depths below the SML and dated as prior to the 1960s, before the widespread application of BTs as

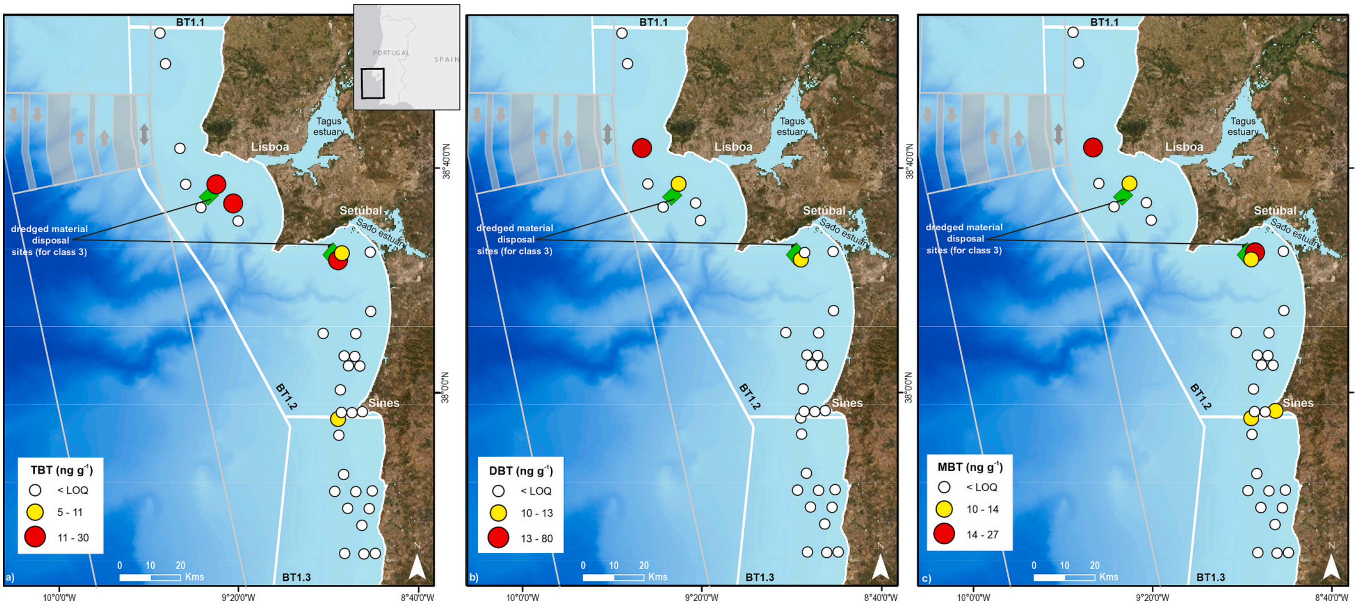

Fig. 5. Spatial distribution of TBT, DBT and MBT in the collected surface sediments.

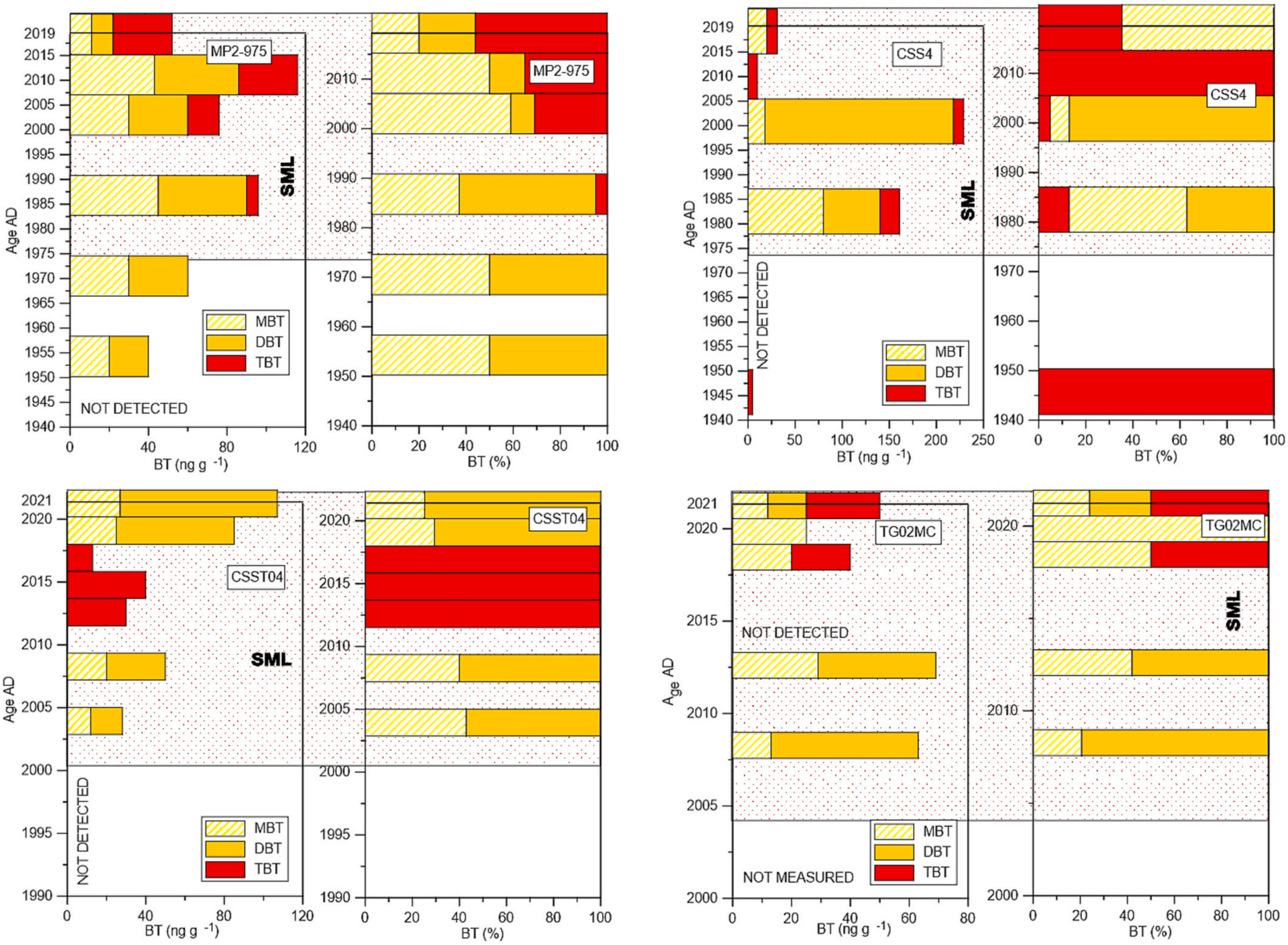

Fig. 6. Down-core distribution of TBT, DBT and MBT in ng g^{-1} and as % relative to ΣBTs in selected sediment cores in relation to age. SML is short for Surface Mixed Layer.

antifoulant, may be explained by dispersion of traces of BTs along isolated burrows of macrobenthos, penetrating older sediment below surface mixed layer depth.

3.7. Comparison with previous studies in the Portuguese margin

The butyltin levels found in this study are of the same order of magnitude as those reported in previous studies in the Portuguese margin (Table 3) one or two decades ago, and lower than those found in fishing ports and marinas. Díez and Bayona (2009) detected relatively low concentrations of BTs in sediments from the Portuguese coast (Viana do Castelo marina, Douro, Mondego, Lisandro, and Guadiana River mouths, Aveiro, Lisboa, Setubal and Sines commercial harbours, Cape St Vincent), with the highest concentration of TBT found in the Lisboa commercial harbour (12.4 ng g^{-1}). At that time, the Tagus estuary was the only area with BDI lower than 1, suggesting contemporary TBT inputs and/or low TBT degradation rate. Gomez-Ariza et al. (2006) in a study on BTs in sediments and gastropods along the Portuguese and southern Spanish coast found high TBT values in areas with higher maritime traffic densities such as Lisboa and Sagres. These areas were marked by high incidence of imposex in marine snails. In both affected areas the BDI was lower than 1. This can be explained by recent input of TBT, and/or alternatively indicate that degradation of TBT in these areas is very slow. The present study demonstrates that BT contamination is not restricted to coastal areas.

3.8. Sediment Quality Guidelines (SQG) and evaluation of the potential ecological toxicity of TBT in marine sediments

According to Portuguese environmental legislation, the management of dredged materials is based on a 5-category scheme with increasing trace metal (As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn) and persistent organic pollutant (PAHs, PCBs and HCH) concentration ranges, from Class 1 (clean dredged material) to Class 5 (heavily contaminated dredged material). In this regulation, BTs could be monitored but are not considered due to the absence of action limits. Dowson et al. (1992) proposed the following classification for sites with sediments contaminated with TBT: concentrations below 3 ng g^{-1}: uncontaminated; 3–20 ng g^{-1}: lightly contaminated; 20–100 ng g^{-1}: moderately contaminated; 100–500 ng g^{-1}: highly contaminated, above 500 ng g^{-1}: grossly contaminated. Based on these criteria, the surface sediments in 29 of the sampled locations can be classified as uncontaminated, in 2 locations as lightly contaminated and in 3 as moderately contaminated.

Table 3
Butyltin compounds in sediments from the Portuguese coast, comparison with previous studies.

	Sampling year	MBT (ng g^{-1})	DBT (ng g^{-1})	TBT (ng g^{-1})	References
	2019 & 2021	10–100	10–300	5–41	This study
Lisboa (1A; shipping route)	2000	6.4	6.4	14.7	(Gomez-Ariza et al. 2006)
Sines (open seacoast)	2000	4.1	5.3	4.9	(Gomez-Ariza et al. 2006)
Sagres (Shipping route)	2000	7.4	34.7	127	(Gomez-Ariza et al. 2006)
Tejo-coast (41S)	1990–2000	No data	No data	12.4	(Díez et al., 2005)
Mouth of the Sado river (44S)	1990–2000	No data	No data	6.7	(Díez et al., 2005)
Sines harbour (47S)	1990–2000	No data	No data	7.7	(Díez et al., 2005)
Nazaré canyon	2005	<5.1–14	<0.5–2.7	<0.1–0.8	(Sousa et al., 2012)
Nazaré fishing port	2006	370	340	470	(Sousa et al., 2012)
Peniche fishing port	2006	54	47	39	(Sousa et al., 2012)
Peniche marina	2006	78	63	140	(Sousa et al., 2012)

Our study reveals in general the presence that TBT is present in sediments in the vicinity of disposal sites for dredged material, indicating dispersion of contaminated dredged materials after being dumped. Although no sediments were analysed in their study, Santos et al. (2004) observed a similar pattern of accumulation of BTs in gastropod tissues in the vicinities of the Oporto DMDS.

The TBT concentrations found in the present study may be compared with Action Levels (ALs) developed in several other countries (e.g., United Kingdom (UK), Belgium, Finland, Denmark) (Table 4). Those ALs have been mainly derived from comparisons of contaminant levels in polluted sediments and in reference areas or local background concentrations (Alvarez-Guerra et al., 2007). The TBT ALs defined by UK are thresholds used for determining whether dredged material is acceptable for disposal at sea, and provide a proxy risk assessment for potential impacts to biota such as fish and benthic invertebrates (Mason et al., 2022; Warford et al., 2022). This type of approach is based on two ALs (AL1 & AL2) and three categories. Sediments with contaminant concentrations lower than AL1 are generally considered acceptable for disposal at sea, while if higher than AL2 they are unacceptable for uncontrolled dumping at sea without special handing and control. Sediments with contaminant concentrations between AL1 and AL2 are evaluated using a weight of evidence approach (Mason et al., 2022). From Table 4 it is obvious that the ALs established by different countries are widely different. TBT levels found in Portuguese sediments would be considered of low risk according to the UK ALs (AL1 of 100 ng g^{-1} and AL2 of 500 ng g^{-1} while they would be considered unacceptable for disposal according to Belgian ALs (AL1 of 3 ng g^{-1} and AL2 of 7 ng g^{-1} (MCWG, 2022)). The difference in ALs in different countries can be explained by the level of precaution with which toxicity of TBT is evaluated.

Despite the limitations in using sediment quality guidelines for evaluation of the ecological toxicity of TBT, this approach is a practical tool for screening possible ecological risks (Chapman and Mann, 1999; Dong et al., 2015). Because of the affinity of BTs with organic matter, C_{org} is commonly used for normalizing BTs in marine sediments (Michaud and Pelletier, 2006). The normalized BTs (BTs*) is based on 1 % C_{org} using the equation $BTs^* = BTs \text{ x } 1\ \%/\%C_{org(sample)}$. According to the Norwegian SQG which use TBT concentrations normalized to 1 % C_{org} (Bakke et al., 2010), the Portuguese sediments can be classified as moderately (Class 3; Toxic effects following chronic exposure; 5 < TBT < 20 ng g^{-1}) to badly (Class 4; Toxic effects following short term exposure; 20 < TBT < 100 ng g^{-1}) contaminated. The Australian sediment quality guidelines make use of Low Trigger Value (LTV) and High Trigger Value (HTV), set at 9 and 70 ng g^{-1} (normalized to 1 % C_{org}), respectively (Simpson et al., 2013). Considering the Australian guidelines, TBT levels in the analysed Portuguese surface sediments were between the low and high trigger values indicating possible adverse effects on benthic biota. The United States Environmental Protection Agency introduced two screening TBT values for sediments (USEPA, 1996). A lower screening value (LSV) of 5.2 ng g^{-1} and a higher screening value (HSV) of 72 ng g^{-1}, normalized to 1 % C_{org}. In our study, the TBT concentrations normalized to 1 % C_{org} varied between 8 and 49 ng g^{-1}. These values fall between LSV and HSV, pointing to low ecological toxicity according to USEPA sediment quality guidelines. The proposed Swedish Environmental Quality Standard (EQS) value for TBT in sediments (EQS_{sed} is 1.6 ng g^{-1}) is based on the normalization of the total TBT concentrations to 5 % C_{org} (Sahlin and Ågerstrand, 2018). However, the relatively lower contents of C_{org} in sediment of the Portuguese shelf makes this approach inadequate. The average C_{org} contents

Table 4
Action level values for total concentrations of TBT (ng g^{-1}) in European countries from the OSPAR and HELCOM regions (adapted from (MCWG, 2022; Warford et al., 2022)).

	Belgium	United Kingdom	France	Germany	Finland	Norway
AL1 (lower)	3	100	100	20	3	5
AL2 (upper)	7	500	400	300	200	20

is significantly lower than 5 % (the average C_{org} value is 1.6 % and 0.5 % in the Tagus region, and Sado and Sines region, respectively), the TBT concentrations normalized to 5 % C_{org} ranges from 40 to 243 ng g^{-1}. By using the Swedish approach, we may conclude that the sediments (where it was possible to quantify the TBT concentration) would be highly contaminated? Or the obtained results that greatly exceed the Swedish EQS value highlighting the importance of using normalization factors adjusted to their regional variability and the application of normalization criteria without critical sense?

4. Conclusions

This study demonstrates the occurrence of BTs in recent marine sediments of the Portuguese shelf. To our best knowledge, this is the first study reporting so extensively on the spatial and temporal distribution of BTs in Portuguese marine sediments. Although the use of TBT in antifouling paints has been forbidden for more than two decades, the current study found evidence of very localized contamination in the Portuguese shelf environment, particularly in the vicinities of disposal sites for materials derived from dredging in navigation channels, harbours, and shipyard facilities in the Tagus and Sado estuaries and in the offshore area of the Sines harbour.

This shows the need for monitoring the BT contamination in ports, marinas, shipyards, and shipping channels, and establishing adequate action levels of these compounds for environmentally responsible disposal of dredged material at sea. The absence of adequate regulation with regards to BTs in Portuguese legislation makes that several thousand tons of BT contaminated sediments on annual basis are still dredged and discharged at the disposal sites at sea, where they pose a potential threat to marine life. The resuspension of sediment particles enriched in TBT by storms and dredging and bottom trawling results in their further dispersion into the marine environment, which makes these disposal sites hotspots of continued risk of TBT contamination (Warford et al., 2022).

Despite that screening values for BTs are not included in the Portuguese legislation for the dredged materials (MAOTDR, 2007), application of guideline values implemented by other countries suggests that the sediments collected in the vicinities of the disposal sites may be contaminated to a degree to potentially cause adverse effects on marine fauna. The results of the present study suggest that despite the ban on the use of TBT, pollution by BTs remains a topic of concern. More research is required, contributing to adequate legislation to reduce the risk of dispersion of TBT through the disposal of dredged material. Monitoring and assessment of TBT (and other BTs) in sediments and organisms should be carried out in all Portuguese disposal sites for dredged material receiving Class 3 materials, to minimize the risk of BT contamination and to promote the Good Environmental Status of the Portuguese marine environment.

CRediT authorship contribution statement

Mário Mil-Homens: Conceptualization, Methodology, Investigation, Resources, Data curation, Writing original draft, Writing review and editing, Visualization, Project administration, Funding acquisition

C. Marisa R. Almeida: Investigation, methodology, Investigation, formal analysis, Data curation, Writing review and editing

Sofia Dias: Methodology, Formal analysis, data curation

Warley Soares: Methodology, Formal analysis, data curation

Piet van Gaever: Methodology, Formal analysis, data curation

Henko de Stigter: Methodology, Formal analysis, data curation, Investigation, Writing review and editing

Miguel M. Santos: Investigation, Writing review and editing

André Santana: Methodology, Formal analysis, data curation

Mafalda Freitas: Methodology, Formal analysis, data curation

Fátima Abrantes: Writing review and editing

Miguel Caetano: Conceptualization, Funding acquisition, Investigation, Writing - review & editing

All authors read and approved the final manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this manuscript.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.165872.

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