Journal of Hazardous Materials Advances 10 (2023) 100294

Contents lists available at ScienceDirect

Journal of Hazardous Materials Advances

journal homepage: www.elsevier.com/locate/hazadv

On the effectiveness of tributyltin ban part II: Temporal and spatial trends of organotin pollution in intense sediment accumulation areas and dumping sites of the Baltic Sea

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ARTICLE INFO

Keywords:
Fresh tributyltin pollution
Baltic Sea
Klaipeda Port
Dumping sites
Bottom sediment contamination

ABSTRACT

Based on the knowledge gained from our previous study, our aim is to observe the current levels of butyltin (BTs) pollution, changes during different seasons, and the factors that affect these trends in the areas of highest concern. These areas include semi-enclosed bays in the Port that were previously affected by large tributyltin (TBT) inputs, as well as the dumping sites of dredged sediment in the Baltic Sea. Compared to previous studies, there has been a significant decrease in the levels of BTs in the Klaipeda Port. However, the sediment in the semi-enclosed bays still contained BTs, ranging from less than 0.5 ng Sn g^{-1} dw to as high as 728.5 ng Sn g^{-1} dw. Some BTs were also detected in the currently exploited dumping sites of the Baltic Sea. Moreover, butyltin degradation index (BDI) revealed occasional fresh TBT input or slow degradation both in the Port and in the Sea. Some trends in butyltin concentrations were indicative of the impact of climate change in Lithuania, which are consistent with global trends. We also found that variations in BTs concentrations were closely related to dredging and cleaning activities taking place in the Klaipeda Port. Correlation, principal component, and cluster analysis revealed close relationship between TBT and its degradation products, as well as between TBT and Zn, Pb, Cu. Ship cleaning/maintenance activities were identified as the main source of pollution in the study area. Despite the gradually decreasing BTs concentration in the Klaipeda Port, the problem is not yet completely solved.

1. Introduction

Tributyltin (TBT) is often referred to as one of the most hazardous anthropogenic chemicals that has been deliberately released to the environment (Beyer et al., 2022). Numerous studies on the fate and ecotoxicology of organotin compounds, especially TBT, have been published worldwide, and this topic still attracts significant attention. The most widely known biological effect of TBT is the development of imposex in female gastropods (Smith, 1971). Other confirmed TBT toxic effects on marine organisms include induced DNA damage (Gabbianelli et al., 2006), induced vitellogenin gene expression (Park et al., 2012), metabolic alterations in haemolymph proteins and heart glycogen of *Callinectes* sapidus crabs (Simões et al., 2022), distortion of locomotor activity in zebrafish (Guo et al., 2022), oxidative stress in the eyes and brains of juvenile medaka (Shi et al., 2021). Furthermore, TBT readily accumulates in aquatic organisms and could thus cause risks to human health through the consumption of contaminated seafood (Chung et al., 2020).

Historically, TBT was a common component of antifouling paints applied in the shipping industry, but the numerous reports on the acute toxicity of tributyltin lead to the international ban of this compound (Gipperth, 2009). For long, TBT has been considered as a historical pollutant and it was expected that its concentration in the environment would gradually decline over time. Despite the efforts to control TBT-related pollution, concerning TBT levels and fresh inputs of TBT continue to be reported worldwide (Batista-Andrade et al., 2018; Castro et al., 2018; Çetintürk and Ünlü, 2022; Gao et al., 2020; Jokšas et al., 2019; Kucharski et al., 2022; Mikac et al., 2022; Paz-Villarraga et al., 2015; Romanelli et al., 2019; Wang et al., 2019).

High TBT concentrations recorded in sediment might be related to the historical pollution since TBT has a high tendency to sorb onto sediments (Dowson et al., 1996; Fent, 1996) and is relatively stable (Furdek et al., 2016; Viglino et al., 2004). Fresh TBT might for the most part enter the environment with dust and paint chips formed during the cleaning of previously painted ships (Kucharski et al., 2022). In addition to that, TBT is widely applied in the manufacturing of

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https://doi.org/10.1016/j.hazadv.2023.100294
Received 30 January 2023; Received in revised form 7 April 2023; Accepted 11 April 2023

textile, silicone sealant, polyvinylchloride, polyurethane foams, and other synthetic materials (Çetintürk and Ünlü, 2022; Kowalska et al., 2011; Kucharski et al., 2022; Uc-Peraza et al., 2022). Moreover, recent study by Uc-Peraza et al. (2022) revealed that banned TBT-based antifouling products continue to be produced, exported, imported, and marketed in some countries. Hence, TBT pollution has been incorrectly considered to be eradicated, but regardless of the organotin compounds source, further research on TBT pollution is essential. Several recent papers have addressed temporal and seasonal variations of TBT in Mediterranean ecosystems, the southwestern Atlantic Ocean coast, and Cape Town harbor (Bancon-Montigny et al., 2019; Quintas et al., 2019). However, the most recent study on temporal changes in the distribution of organotin compounds in the Baltic Sea only reported data up to 2009 (Radke et al., 2012). In our previous research conducted in the Klaipeda Port, it was discovered that TBT and its by-products remained a problem in the area as late as 2013. It was revealed that even in a small port with rather moderate operation intensity, tributyltin is a relevant issue. Given the lack of knowledge on current BTs pollution and temporal variations in the region, potential effects of the climate change, unique characteristics of the Klaipeda port, and findings from our previous research, we conducted this study.

Our current study focuses on assessing the present state of butyltin (BTs) pollution, including temporal variations, and identifying factors that contribute to the observed trends in areas of utmost concern. Specifically, we investigated semi-enclosed bays of the Port that had previously experienced significant TBT inputs and the dumping sites of the dredged sediment in the Baltic Sea.

The Port of Klaipėda is located in the Klaipėda Strait, which connects the Curonian Lagoon and the Baltic Sea. The environment of the Klaipėda Port is significantly influenced by freshwater inflow from the Nemunas River and seawater inflow from the Baltic Sea (Jokšas et al., 2003) The port houses several industrial facilities, including large stevedoring, shipbuilding, and ship repair companies. Intense industrial activities in the port could potentially have a significant impact on the ecological condition of the Klaipėda Strait (Jokšas et al., 2019). The Klaipeda Port is a hub for international trade, serving as a gateway to Eastern Europe. As such, pollution in this port could have transboundary impacts on neighbouring countries and regions. Another object of our study were the dumping sites of the dredged sediment in the Baltic Sea. The Baltic Sea is a heavily trafficked and industrialized area, with numerous ports and shipping lanes. This makes it vulnerable to pollution from shipping activities, including the use of antifouling paints that contain butyltin compounds. Thus, understanding the sources and trends of butyltin pollution in this region can help inform policies and regulations to reduce pollution from shipping activities. It has been known for long that dumping of dredged sediment causes numerous negative effects on the marine environment and the organisms living in it. Not only it induces physical disturbances such as changes in the seabed topography and sediment's lithological alterations, but it might also increase the pollution level around the dumping sites as the sediment coming from the port area might contain various pollutants including TBT (Oliveira et al., 2020). Tracking butyltin pollution in the Klaipeda Port and dumping sites of the Baltic Sea over time is therefore important not only for local environmental and human health concerns but also for regional and global environmental protection efforts.

We aimed to analyze the changes in TBT and its degradation products (dibutyltin (DB) and monobutyltin (MB)) concentrations over a 2-year period and reveal the connection between organotin concentrations and different sediment parameters, such as relationship between the butyltin (BTs) loadings and physicochemical parameters of the sediment (total organic carbon (TOC), content of clay, silt, sand fraction), as well as relationship between the loadings of BTs, metals, and aliphatic hydrocarbons (AHs). The data obtained were analysed using various statistical methods in order to obtain co-occurrence network of different pollutants, identify potential pollution sources, and assess their significance.

2. Materials and methods

2.1. Study area and sampling

The Port of Klaipėda the northernmost ice-free port in the Eastern Baltic (Žilinskas et al., 2020). It occupies approximately 11.5 km long segment between the Strait mouth (Port gate) and Kiaulės Nugara Isle (Fig. 1), and its width ranges between 300 m at the port gates in the north and 1350 m in the southern part of the Strait. The average depth of the entrance channel is 15.2–15.5 m and the average depth of the navigation channel near most of the quays is 14.5 m (Žilinskas et al., 2020). Dissolved and suspended matter which might contain various pollutants collected from a broad catchment area (about 100,458 sqkm) of the Nemunas River is enters the Klaipėda Strait. In reverse, seawater inflow to the Port occasionally occurs (Jakimavičius et al., 2018). The inflow from the Baltic Sea dilutes the polluted harbor water, but the increased water salinity results in higher organic contaminants deposition rate in the Klaipėda Strait (Means, 1995).

The Port has numerous industrial objects, among them several large stevedoring, shipbuilding, and ship repair companies, the biggest among them are Klaipėda Shiprepair Yard and Western Shiprepair Yard (Fig. 1). Our study focused on the semi-enclosed bays of the Port (Fig. 1 and Table S1, P2-P6), which are typically surrounded by industrial facilities and have slow to very slow water circulation (Jokšas et al., 2003). Stations P1 and P7 (Fig. 1), located at the Port entrance gates and in the Curonian Lagoon, respectively, were expected to be free of butyltins based on previous studies (Jokšas et al., 2019).

Another object of our study were the dumping sites of the dredged sediment in the Baltic Sea (Fig. 1 and Table S1, stations S1–S3). Among them, station S1 is located in the most actively exploited dumping site in the Lithuanian territorial waters. Moreover, sediment that falls into II sediment assessment class according to the Lithuanian normative document for dredging and dumping (TBT concentration can reach MAC, LAND46A-2002) can be dumped into this dumping site.

Surface sediment samples (0–3 cm) were collected in May and November of 2019 and 2020. Sediment samples were collected with two replicates from 10 sites, resulting in a total of 40 samples (excluding subsamples) over a two-year period. A Van Veen grab sampler was used for sediment sampling. Sediment samples were stored at −20 °C in aluminum boxes before further processing.

2.2. Determination of butyltin compounds in sediments

An aliquot of each sample was used for total organic carbon (TOC) and grain size analyses. Sediment samples were freeze-dried, sieved through a 2 mm sieve, and homogenized with a MM 400 mill containing zirconium oxide grinding jars and grinding balls (Retsch GmbH, Germany).

The standard solutions of mono-, di-, and tri-butyltin chloride ($MBTCl_3$, 95.0%; $DBTCl_2$, 96.0%; and TBTCl, 98.2%, respectively) Tributyltin were purchased from Merck (Germany). The calibration standard solutions were prepared by derivatization and dilution of the standard solution right before the GC–MS analysis.

Sample preparation and analysis of MBT), DBT, and TBT content in sediment was performed as described in our previous paper (Jokšas et al., 2019). The procedure followed International Standard ISO 23161:2009 (soil quality-determination of selected organotin compounds-gas-chromatographic method) and Milivojevič Nemanič et al. (2009). In short, freeze-dried and homogenized sediment samples (10 g) were ultrasonicated with a mixture of acetic acid (puriss, Sigma-Aldrich, USA): methanol (HPLC grade, Sigma- Aldrich, USA): water (1:1:1) for 30 min. The procedure was repeated 3 times. Derivatization with $NaBEt_4$ (97%, Sigma-Aldrich, USA) and the following extraction with n-hexane (GC grade, Merck, Germany) were performed in a sodium acetate-acetic acid buffer solution under pH of 4.5. The resulting slurry was centrifuged (Eppendorf 5702, Germany). The

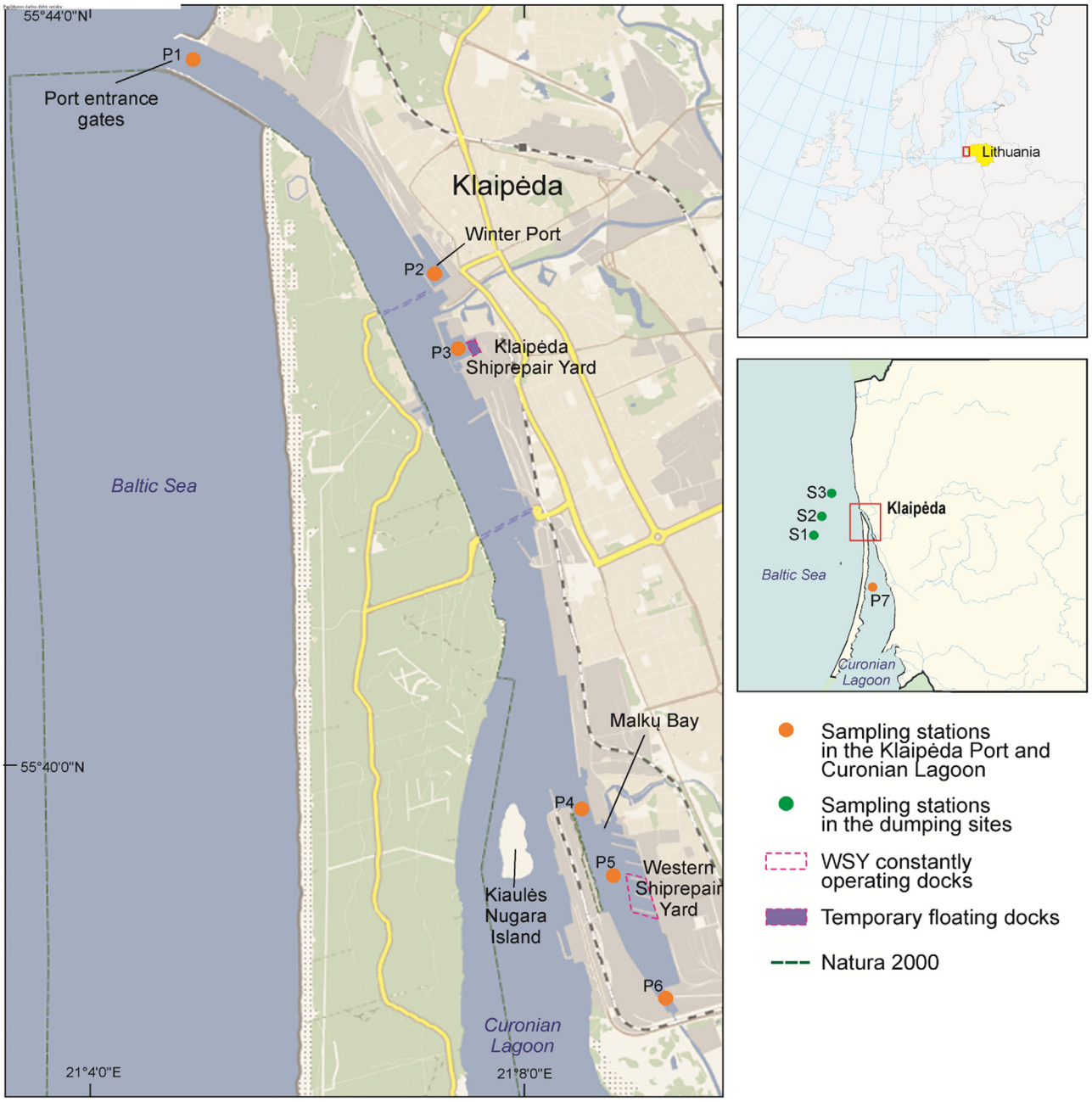

Fig. 1. Map of the study area and sediment sampling stations in the dumpsites of the Baltic Sea (S1-S3), in the Klaipeda Port (P1-P6), and in the Curonian Lagoon (P7).

hexane layer was collected over anhydrous sodium sulfate, and the sample was concentrated to 2 ml in a rotary evaporator (Heidolph Hei-Vap Value, Germany). CHROMABOND Florisil columns (6 ml/500 mg, Macherey-Nagel GmbH & Co, Germany) were used for purification of the extract. The sample was eluted with n-hexane (GC grade, Merck, Germany) and the volume of the sample was reduced to 1 ml under a gentle stream of nitrogen (99,999, Linde Group, Germany). The as-prepared extracts were analysed with a gas chromatographic system coupled with a mass spectrometer (MS) (Shimadzu GC-2010 plus, Japan). The GC was equipped with a Rxi-5sil MS capillary column (30 m × 0.25 mm I.D × 0.25 μm, coated with 5% phenylpolysiloxane). The injection mode was splitless. For a precise quantitative analysis, two separate calibration curves were prepared. One covered lower organotin concentration range (0.1–10 ng ml^{-1}), and the other – higher organotin concentration range (10 to 1000 ng ml^{-1}).

For the quality control, replicate samples (n = 3) and procedural blanks using sand samples (dried at 450 °C) were prepared. No traces of butyltins were detected in the chromatograms of the blank samples. For each compound, relative standard deviation (RSD) was lower than 14%. Every 10 samples, the procedural blanks were analyzed. Matrix (sandy and silty sediments dried at 450 °C) samples spiked with a precise volume of analytical standards: monobutyltin trichloride (97.0%, Dr. Ehrenstorfer, Germany), dibutyltin dichloride (96.0%, Sigma Aldrich, USA), and tributyltin chloride (96.0%, Sigma Aldrich, USA) were used to test the recovery efficiency. Recovery for TBT, DBT and MBT were 91%, 89% and 78%, respectively. The results were adjusted based on recovery.

To determine the limit of detection (LOD) and limit of quantification (LOQ) of the method, five sets of analytical blanks were analysed. Three multiples of the standard deviation of the mean signal to noise

ratio (S/N, $n = 10$) determined LOD, while ten multiples of the standard deviation of the mean signal to noise ratio (S/N, $n = 10$) corresponded to LOQ. LOD calculated for butyltin compounds was 0.15 ng Sn g^{-1}, LOQ for MBT, DBT, and TBT reached 0.5 ng Sn g^{-1} d w.

2.3. Determination of heavy metals in the sediments

To prevent contamination of the samples, the laboratory glassware was soaked in 2 M HNO_3 for 48 h and rinsed three times with deionized water prior to use. All the chemicals were of analytical reagent grade. Calibration standards were prepared by diluting stock solutions of 1000 ppm standards (Merck, Germany).

Sample preparation was done following a combined method by Hseu et al. (2002) and Oliver (1973). First, the sediment samples were dried and sieved through a 2 mm mesh. Prior to digestion, the samples were homogenized, and organic matter was destroyed by H_2O_2 (35%). Finally, 10 g of the sample was mineralized in hot block by aqua regia. The same procedure was followed to prepare blank samples. For the quality assurance, the quality control sample was run every ten samples. The necessary re-sloping and other corrections were made in the standard curve using freshly run standards. To provide a baseline correction, reagent blanks were analysed (1 blank for each batch of 10 samples). No traces of metals were detected in any of the blank samples.

The as-prepared sediment samples were analysed for Sn, Cu, Pb, Zn, Ni, Cr, and Cd. Analysis was done with an inductively coupled argon plasma spectrometer (DV ICP-OES) Perkin Elmer Optima 7000 (Palo Alto, CA, USA).

Determination of As, Hg and V was done in the Chemical Laboratory ALS Czech Republic which is accredited according to ISO 17025. For determination of As and V, sediment samples were mineralized in hot block by aqua regia, and the analysis was done by ICP-MS system (Agilent 7900, Agilent Technologies, USA).

For determination of Hg, US EPA 245.7 was applied. In short, the sample is oxidized by a potassium bromate/potassium bromide reagent. Subsequently, ionic Hg is reduced with $SnCl_2$, and Hg (II) is converted to volatile Hg (0) which is separated from solution by passing through a gas/liquid separator. While purging with high purity argon gas, Hg (0) is transferred into the inert gas and is carried into the cold-vapor atomic fluorescence spectrometer cell for detection with CVAF Mercury Analyzer (QuickTrace® M-8000 CVAF Mercury Analyzer, Teledyne Leemanlab, USA).

2.4. Determination of aliphatic hydrocarbons (AHs) in the sediments

The method used to analyze hydrocarbons relies on ISO 16703:2004. First, 20 g of a previously dried and homogenized sediment is mixed with a RTW-standard solution of n-decane and n-tetracontane. Next, the mixture is extracted by mechanical shaking (at a rate of 200 rpm) using n-hexane (GC grade, Merck, Germany) for 24 h. Afterwards, the samples were centrifuged at a speed of 2000 rpm for 30 min. The resulting extracts were then reduced to a volume of 2 mL using a rotary evaporator and cleaned with Chromabond Florisil cartridges (6 ml/500 mg). To elute the samples, 20 ml of n-hexane (GC grade, Merck, Germany) was used. The prepared samples were then concentrated further using a rotary evaporator until they reached a volume of 0.5 mL. Blank samples were also prepared using the same analytical method.

AHs were analyzed using a gas chromatograph GC-2010 Plus (Shimadzu, Japan) equipped with a flame ionization detector and using splitless injection mode. A fused silica capillary column Rxi1-ms (30 m × 0.25 mm i.d. × 0.25 μm) was utilized for organic compound separation.

The temperature was raised from 60 °C to 315 °C at a rate of 10 °C/min, then held for 20 min at 315 °C. Helium was used as the carrier gas at a flow rate of 1.86 mL/min. Constant linear velocity of 40 cm/s) was set as a flow control mode. The standard mixture of n-alkanes (C10–40) in hexane (Restek, USA) was used to identify and quantify hydrocarbons. Quality control was assured by using replicate samples ($n = 3$) and procedural blanks. The RSD was less than 10%, and analyte signals were lower than the estimated LOD in blank samples. C10 and C40 were used as internal standards for n-alkane analysis, and the recoveries of all n-alkanes were in the range of 65–110%. The estimated LOD and LOQ were calculated as the average signal of the blanks plus three times and ten times the standard deviation of the signal of the blanks, respectively. The LOD ranged from 0.08 to 0.2 for individual n-alkanes, while the LOQ was between 0.15 and 0.4.

2.5. Grain size analysis and determination of total organic carbon

A fraction of the sediment samples was used for the grain size analysis. First, the samples were soaked in H_2O_2 (10%, puriss., Sigma-Aldrich) to remove organic matter. Classical sieve method was applied to determine the grain size of the sandy sediments and pipette analysis for silt and clay sediments (Folk, 1974). The percentage of clay (0.004 mm), silt (0.004–0.063 mm), and sand (>0.63 mm) sizes of sediments was determined.

A separate fraction of sediment was used for the determination of TOC. First, sediment was treated with hydrochloric acid to remove inorganic carbon. The analysis was done by high-temperature oxidation. The sediment sample was heated at 950 °C, and the combustion products were measured by an elemental analyser liquiTOC (Elementar analysensysteme GmbH, Germany) with a precision of ±1% (Hedges and Stern, 1984).

2.6. Statistical analysis

Relationships between the various parameters (BTs and metal concentrations in the sediment, sediment grain size, total organic carbon content) were analysed using Statistica 8.0 software (StatSoft, Inc., USA). Spearman correlation analysis (SCA) was conducted to reveal relationships between the variables, and a two-tailed test of significance was applied to estimate the statistical significance of the results. Before the Principal Component Analysis (PCA), raw data were mean-centered and scaled. PCA was performed using Varimax rotation as a preferable transformation technique, and three PCs with eigenvalues >1 were selected. Hierarchical cluster analysis (CA) was used to explore similarities between major variables. CA was performed with Ward's linkage algorithm in combination with Euclidean distances.

2.7. Calculation of butyltin degradation index (BDI)

A widely applied indicator of fresh TBT pollution is BDI, a ratio between the sum of concentrations of TBT degradation products (DBT and MBT) and the concentration of the parent compound (TBT) (Díez et al., 2002):

$$BDI = \frac{[DBT] + [MBT]}{[TBT]}$$

where [MBT], [DBT] and [TBT] refer to the concentrations of these compounds in sediment. BDI values below 1 indicate "fresh" TBT input or a poor TBT degradation (Díez et al., 2002; Furdek et al., 2016).

3. Results and discussion

3.1. Spatial changes in butyltin concentrations

Concentrations of BTs ranged between <0.5 and 728.5 ng Sn g^{-1} dw, concentrations of TBT were in the range of <0.5 and 333.3 ng Sn g^{-1} dw over the course of 2 years (Table S2, Fig. 2), with the highest content observed in spring 2020 and the lowest concentrations in all sampling stations in November 2019. The highest BTs concentration was recorded in the sampling station P3, but the title of the most contaminated sampling station varied from season to season. Among the most polluted

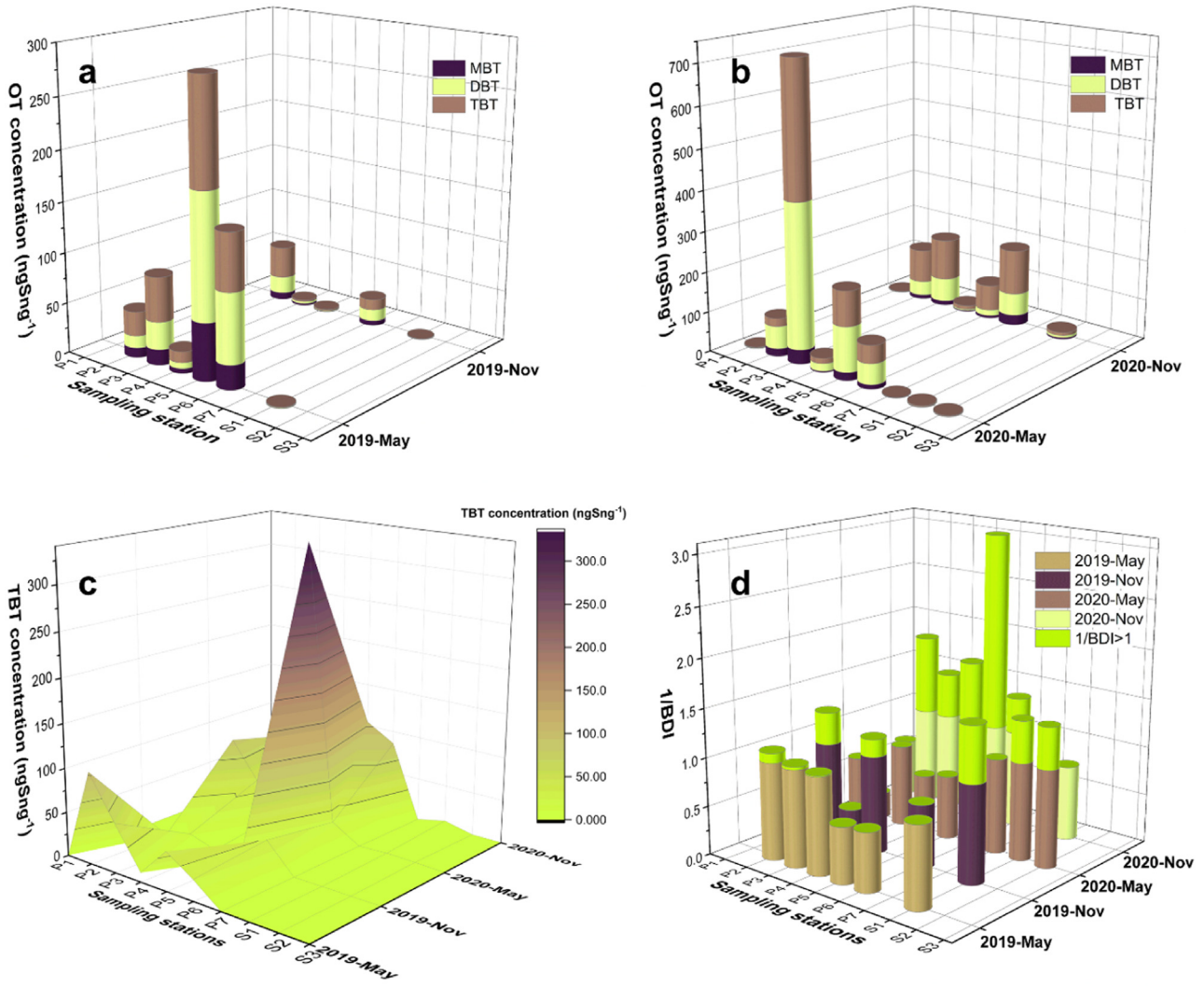

Fig. 2. BTs concentrations in the surface sediment samples collected in 2019 (a) and in 2020 (b); changes in TBT concentration in the surface sediment over a 2-year period (c); Butyltin degradation index ((d);1/BDI is used for a better visualization of the data. Bright green color indicates that the values 1/BDI are above 1, indicating low TBT degradation and fresh pollution).

sampling stations, P5, P6, and P3 could be distinguished. In general, stations of the semi-enclosed bays were found to be the most polluted with TBT. The condition of these sediments could be categorized as either poor (TBT concentrations ranging from 20 to 100 ng Sn g^{-1} dw) or extremely poor (TBT concentrations surpassing 100 ng Sn g^{-1} dw) in terms of TBT, according to Bakke et al. (2010).

Station P7, which is in the Curonian Lagoon, did not exhibit any BTs contamination except for May 2020 when it was found to contain small amounts of TBT and DBT. Sediment of the sampling stations in the Baltic Sea, Curonian Lagoon, and in the Port entrance channel could be attributed to the sediment quality class I (background level; TBT concentration was less than 1 ng Sn g^{-1} dw) or II (good sediment quality; TBT concentrations were between 1 and 5 ng Sn g^{-1} dw). Only in Nowember 2020 the sediment of the Baltic Sea sampling station S1 could be ascribed to sediment quality classification III which corresponds to moderate sediment quality (TBT concentrations were between 5 and 20 ng Sn g^{-1} dw; (Bakke et al., 2010)). It should be mentioned however that, unlike in the previous studies of the Klaipeda Port (Jokšas et al., 2019; Suzdalev et al., 2015), no sampling station was found to be grossly contaminated with TBT according to the old environmental quality classification system (TBT concentrations higher than 500 ng Sn g^{-1} dw; (Dowson et al., 1993). This implies that TBT pollution in the Klaipeda Port is gradually decreasing, albeit it does not refute the fact that the problem remains.

Sampling stations located in the regions of the dumping sites provided essential information on how the pollution of the Klaipeda Port might affect the Baltic Sea. The Lithuanian normative document for dredging and dumping (LAND46A-2002, 2019) defines TBT concentrations lower than 4 ng Sn g^{-1} dw as “expected no-effect” (target level). Slightly contaminated sediment contains up to 41 ng Sn g^{-1} dw which was an accepted maximum admissible concentration (MAC, LAND46A-2002, 2019) till 2021. Since January 2021, the Lithuanian MAC has been lowered to a value of 24 ng Sn g^{-1} dw. In the majority of the samples collected from the semi-enclosed bays in 2019 and 2020, the TBT concentration did not exceed the Lithuanian MAC at that time, which was 41 ng Sn g^{-1} dw. If such sediment were to be dredged, its disposal would not have required any actions such as cleaning prior to its dumping into the sea. This raises concerns considering that the great majority of the sediment treated as safe for dumping falls into the OSPAR assessment classes C and D, which pose extent risks to the environment and marine populations. Moreover, the highest TBT concentration recorded in the dumping sites has reached 7.5 ng Sn g^{-1} dw, corresponding to the OSPAR assessment class C (OSPAR, 2008). The effects of such TBT concentrations in the environment are rather uncertain.

Among the dumping sites, the highest BTs loadings were recorded in sediment from the sampling station S1. The dumping site around St. S1 is the most actively exploited dumping site within Lithuanian territorial waters. Moreover, sediment that falls into II sediment assessment class according to the Lithuanian normative document for dredging and dumping (TBT concentration can reach MAC, LAND46A-2002) can be dumped into this dumping site.

In a meanwhile, areas around S2 and S3 are designated as reserve dumping sites for dumping of the relatively clean sediment, which is classified as sediment assessment class I according to Lithuanian norms for dredging and dumping, where TBT concentration is lower than MAC (LAND46A-2002). If the primary dumping site is unavailable, the dumping site near St. S2 would be the preferred alternative. The dumping site near St. S3, on the other hand, is rarely used. In agreement with that, BTs loadings were recorded in the sediment of St. S2 in May 2020, indicating a recent dumping activity held in the area. Station S3, which is located farthest from the Port, did not show any BTs contamination during the sampling period.

Sediment characteristics can also provide some useful information on the dredging/cleaning and dumping activities. Fine sand is normally dominating in the sampling stations S2 and S3 at sea while silty sand is the prevailing sediment type in the Klaipeda Port area and station S1 in the sea (Fig. 1, Table S2). Whenever increased BTs concentrations were found in the dumping sites, changes in sediment composition were as a rule observed. This only confirms that dumping of the contaminated silty sediment from the Port is responsible for the increased pollution of the Baltic Sea sediment.

3.2. Temporal variations in butyltin levels and the factors that influence them

In the Port, higher BTs concentrations were recorded during the spring season. On the contrary, the Baltic Sea sampling station S1 demonstrated higher BTs loadings in autumn. A previous study investigating seasonal changes in TBT concentrations at the Baltic Sea Port (Port of Gdynia) found that the samples collected in February had higher BTs concentrations compared to those collected in June. The authors attributed this finding to the likelihood of more intense boating activities in autumn or the possibility of remnants remaining after the removal of antifouling paint containing TBT from the hulls (Radke et al., 2012). However, comparing these results with other ports might be inaccurate due to differences in hydrodynamic conditions and other characteristics.

The fluctuations in TBT levels may be linked to changes in the inflow from the Nemunas River basin. TBT pollution was previously recorded in the wastewater and sewage sludge samples across Lithuania (COHIBA, 2012), which suggests that some BTs might enter the Klaipeda Port with the Nemunas River runoff. Typically, an increase in water delivery from the Nemunas to the Curonian Lagoon and the Baltic Sea occurs during spring when winter snow and ice melt. However, recent studies indicate that Lithuanian climate has undergone significant changes, which is consistent with global trends (Čerkasova et al., 2021; Plunge et al., 2022). The warming climate has led to a reduction in snow formation throughout the Nemunas River watershed and an increase in water delivery to the Curonian Lagoon in winter (Čerkasova et al., 2021). These hydrometeorological changes related to climate shift have the potential to affect the water exchange mechanism between the Curonian Lagoon and the Baltic Sea. As a result of increased inflow from the Nemunas River in winter, there is a possibility of large pollutant concentrations entering the port environment along with suspended particulate matter during the colder months (Čerkasova et al., 2021). After entering the semi-enclosed bays of the Port, suspended matter may settle and accumulate in the sediment due to reduced hydrodynamic processes and low water exchange rates. Moreover, the fine-fractioned sediment that is rich in organic carbon (as shown in Table S2) acts as an excellent adsorbent for various pollutants, including BTs. Therefore, it is plausible that the increased TBT concentrations observed in spring could be linked to the elevated water delivery from the Nemunas River basin during the cold season.

On the other hand, variations in BTs concentrations are closely related to the dredging and cleaning activities held in the Klaipeda Port. Based on the data of the Klaipeda State Seaport, an intense deepening and cleaning of the Port channel took place in 2019 with more than 3,000,000 m^3 of the sediment being removed. The Port channel was deepened near sampling stations P2, P4, P5, and P6, while cleaning was carried out near stations P1 and P2. Hence, most of the study area was affected by cleaning and dredging activities. This could be a reason for the significant decrease in BTs loadings in the Klaipeda Port sampling stations in November 2019. It should be noted that the effects of port deepening may not be limited to the sampling stations directly impacted by dredging activities, as sediment from nearby areas could be transported to the newly formed deeper area due to hydrodynamic processes. This might result in decreased loadings of the contaminants in these supposedly undisturbed sites. In our case, this could be said about P3: significant decrease in BTs loadings is observed in the sediment of this sampling station in November 2019 even though no maintenance works were held in the semi-enclosed bay of P3. However, dredging and cleaning activities were held in the Klaipeda Strait close to this semi-enclosed bay which might cause migration of the polluted sediment to the nearby locations.

In 2020, Port maintenance works were conducted on a smaller scale, with only 1,480,000 m^3 of dredged sediment removed, which is half the amount removed in 2019. The channel was deepened around sampling stations P1, P5, and P6, while cleaning took place near P2 and P4. However, despite these processes, there was a significant increase in BTs concentrations observed in 2020. This could be due to the smaller scale of the dredging and cleaning activities, but it is also possible that a recent influx of BTs contributed to the increase.

It is obvious that, compared to the previous data on BTs contamination in the Klaipeda Port area, the TBT contamination has gradually and significantly decreased. However, higher BTs concentrations were recorded in 2020 than in 2019 which show that fresh TBT input still occurs. Subsequently, BDI was calculated to estimate recent TBT input. It should be noted that sediments with higher content of TOC tend to exhibit stronger adsorption of TBT and weaker degradation of TBT, resulting in a higher persistence of toxic TBT in the sediments (Furdek et al., 2016). Hence, the BDI values <1 might either indicate recent TBT input or simply a slow degradation of the previously released pollutant.

In Fig. 2(d), we presented 1/BDI values for a better visualization of the results: in this case we can clearly see when the values of 1/BDI are above 1. In spring 2019, 1/BDI values slightly exceeded 1 in the sampling stations P4, P3, and P2. In November 2019, TBT prevailed over its degradation products in the sampling stations P4, P2, and in the dumping site S1. In May 2020, only the dumping sites S1 and S2, located in the Baltic Sea, were affected by a fresh TBT input. On the contrary, in November 2020, 1/BDI values slightly exceeded 1 in the Klaipeda Port stations (P2-P6).

As it was already mentioned, the area surrounding sampling station S1 is the most heavily utilized dumping site within Lithuanian territorial waters while the remaining dumping sites (S2 and S3) are only sporadically used for sediment displacement. As a result, higher concentrations of BTs and a recent TBT input were observed at sampling station S1. Although the concentrations of BTs detected in the Baltic Sea stations were relatively low, the presence of TBT not only in the Port but also in the Baltic Sea environment is concerning.

Compared to a sparse data on butyltins in the Baltic Sea and around it, BTs concentrations measured in the sediment from the dumping sites where similar to those observed at the dumping sites in Gdynia and Gdansk (Table 1, Filipowska and Kowlewska, 2019). TBT concentrations in the Klaipėda Port are comparable to the ones recorded in Odra River estuary in 2019 or in Swedish ports in 2010 (Table 1, Eklund et al., 2010) while significantly higher values were measured in the sediment from the Gulf of Gdansk (Table 1, Zaborska et al., 2019), shipyards in

Table 1
Concentrations of MBT, DBT, and TBT (ng g^{-1} Sn d.w.) measured in sediment sampled in this study and reported in studies from other dumping sites (blue), coastal sites (white), harbours (gray) and estuaries (green) around the Baltic Sea.
headlines, description of the sampling points, sources/reference must be added.
At the table some marks (*) present in the Sweden Baltic Sea Eklund et al. (2010) line; it should be described.

Country	Location	Year	MBT	DBT	TBT	References
Lithuania	Semi-enclosed bays of the Klaipeda Port	2020	<0.5-35.2	<0.5-360.0	<0.5-333.3	This study
	Dumping sites in the Baltic Sea	2020	<0.5-3.8	<0.5-6.0	<0.5-7.5	This study
	Semi-enclosed bays of the Klaipeda Port	2019	<0.5-56.9	<0.5-123.9	<0.5-104.3	This study
	Dumping sites in the Baltic Sea	2019	<0.5	<0.5	<0.5-0.6	This study
	Semi-enclosed bays of the Klaipeda Port	2013	4.3-30.4	8.7-107	41-737	(Jokšas et al., 2019)
	Semi-enclosed bays of the Klaipeda Port	2010	11-62	14-210	140-840	(Jokšas et al., 2019)
	Semi-enclosed bays of the Klaipeda Port	2006	7.4-88	18-97	107-1228	(Jokšas et al., 2019)
	Semi-enclosed bays of the Klaipeda Port	2005	11-35	35-490	80-3000	(Jokšas et al., 2019)
	Klaipeda strait	2010-2012	-	-	1.0-5200	(Suzdalev et al., 2015)
Poland	Odra river estuary	2019	-	-	4.5-249	(Kucharski et al., 2022)
	Gulf of Gdańsk	2019			610- 28500	(Zaborska et al., 2019)
	Shipyards in Gdansk and Gdynia	2018	20.9-490	32.2-889	111-1942	(Filipkowska and Kowalewska, 2019)
	Dumping sites in Gdynia and Gdansk	2018	1-2.9	1-5.3	3.7-9.9	(Filipkowska and Kowalewska, 2019)
	Port of Gdynia	2009	12.0-884	50.0-1944	72.0-2761	(Radke et al., 2013; Radke et al., 2012)
Germany	German coastal site	2015	n.d.-328	n.d.-484	n.d.-155	(Abraham et al., 2017)
	Central Baltic Sea	2015	n.d.-4.1	n.d.-10.0	n.d.-1.2	(Abraham et al., 2017)
	Elbe Estuary	2012	<1.0-21.0	<1.0-10.0	<1.0-41.0	(Wetzel et al., 2013)
Sweden	Swedish west coast: natural harbours, marinas, waterways	2014	-	-	n.d.-123	(Egardt et al., 2017)
	Baltic Sea, Sweden: ports (e.g. Stockholm)	2006-2007	24-673	19-714	27-533	(Eklund et al., 2010)
Finland	Baltic Sea, Archipelago Sea	2010	-	-	17.2-591	(Lilley et al., 2012)

Gdansk and Gdynia (Table 1, Filipowska and Kowlewska, 2019), or the Port of Gdynia (Table 1, Radke et al., 2013,2012). These locations have also reported recent or "fresh" TBT input in certain sampling locations. However, while comparing, one should consider not only the spatial, but also temporal changes that might have occurred.

3.3. Relationship between parameters and source determination

Pollutants found in the marine environment might originate from multiple sources. This is especially true in the case of highly anthropogenised zones as well as in the river estuaries/deltas where pollutants from a broad catchment area tend to accumulate. The Klaipeda Port fits both descriptions. Determination of co-occurrence relationship between pollutants and identification of pollution sources is especially important in this case. To this end, different statistical methods could be applied. To obtain information on co-occurrence of various pollutants, identify pollution sources and locate pollution hot spots, concentrations of various heavy metals and aliphatic hydrocarbons in the bottom sediment were measured. The concentrations together with sediment characteristics (content of clay, silt, and sand, total organic carbon content (TOC)) are presented in the Supplementary information (Table S2). First, the correlation between butyltins,

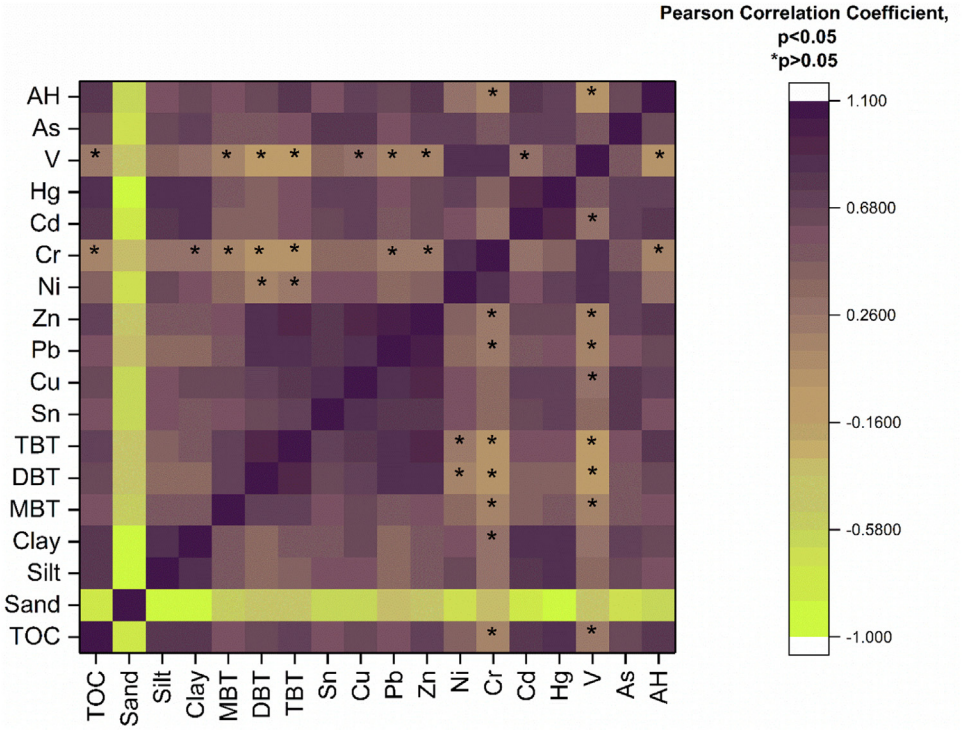

Fig. 3. Heatmap representing Spearman correlation coefficients between determined components of the sediment.

different heavy metals, aliphatic hydrocarbons and sediment characteristics (TOC, clay, silt, sand content) was estimated. The calculated correlation coefficients between the investigated variables are presented in Fig. 3. TBT showed the highest positive correlation with DBT ($r = 0.95$, $p < 0.05$) and Zn ($r = 0.91$, $p < 0.05$). Strong positive correlation ($r > 0.70$, $p < 0.05$) was also observed between TBT and MBT, Pb, Cu, AHs, Sn, and TOC. Significant positive correlation ($r > 0.50$, $p < 0.05$) was demonstrated by TBT and Cd, Hg, As.V demonstrated insignificant negative correlation with both TBT and DBT ($r < -0.3$, $p > 0.05$), whereas significant to moderate negative correlation ($0.99 \geq r > 0.3$, $p > 0.05$) was found between sand and the remaining variables. Clay and silt content in sediment did not show significant correlation with BTs.

Correlation (bivariate) analysis provides some useful data on the co-occurrence of the pollutants and relationships between different variables. However, due to the complexity of environmental data, it cannot be used for a precise identification of pollution sources. Multivariate statistical analysis revealing how more than two operationalised concepts are interrelated is better suited for this purpose. In this study, principal component (PCA) and hierarchical clustering analyses were applied to better understand the interrelations between TBT and different variables.

In this study, three major principal components (PC1, PC2, and PC3) with initial eigenvalues >1.0 were extracted using PCA. The first three components contributed to 86.68% of the overall data variance, and the total variances of PC1, PC2, PC3 were 64.2%, 16.08%, and 9.39%, respectively. The plot loadings of different variables in three components are shown in Fig. 4(a), the PCA biplot for PC1 and PC2 is given in Fig. 4(b). Each parameter is represented by a vector, its direction and length determine relationships between the main components. PC1 was loaded with organotins (TBT, DBT, and MBT), Zn, Cu, Sn, TOC, AHs, As. The closest relationship was observed between BTs and Zn, Cu, and Sn. PC1 had the highest impact on the most polluted sampling stations P2, P3, P5.

PC2 was found to be loaded with Ni, Cr, V, while PC3 was loaded with sand content. Notably, there were significant positive loadings of Cr and V on PC3, but they were attributed to PC2 due to their higher loadings onto this component. PC2 had the highest impact on the sampling stations P6 and P4, while PC3 was associated with sampling stations in the Baltic Sea (S1–S3), as well as those located in the Klaipėda strait and Curonian lagoon (P1 and P7) that had a sediment dominated by sand.

For the hierarchical clustering (connectivity-based clustering), the data were first rescaled before running the analysis. Similar data were grouped into three distinct clusters, as seen in Fig. 4(c). Slightly different data patterns were observed in this analysis compared to the PCA. The first cluster contained most of the pollutants, including BTs, Cu, Pb, Zn, AHs, Sn, As. It was divided into several sub-clusters, revealing that TBT had the highest similarity to DBT, Cu, Pb, and Zn. This cluster could be associated with pollution originating from the long-term ship standing, ship-repairing, and cleaning activities. The second cluster consisted of Ni, V, Cr, while sand content in sediment showed no relationship to other parameters and was assigned a separate cluster.

Strong relationship between TBT and other organotin compounds is to be expected as DBT and MBT are the main TBT degradation products (Norén et al., 2022; Raudonyte-Svirbutaviciene et al., 2018). However, MBT has a significant, but weaker correlation with other TBTs compared to DBT. Additionally, the results obtained from PCA and cluster analysis suggest that MBT is related to the other TBTs, but it has some distinctive properties that distinguish it from the others. This finding is not surprising, as MBT, DBT, and TBT might originate from different sources. As such, it is possible that they may exhibit non-identhical variation patterns using different statistical techniques. It is possible that some MBT might have originated from sources other than TBT. For instance, from industrial and manufacturing processes, such as the production of PVC plastics and stabilizers. This could have led to a lower correlation between MBT and TBT concentrations in sediment.

Cu- and Zn- containing antifouling paints have been widely used not only prior to the discovery of antifouling properties of TBT, but also after the tributyltin ban as more benign antifouling agents (Lagerström and Ytreberg, 2021; Lagerström et al., 2018). Hence, just like TBT, these metals might enter the port environment from the same ship-maintenance and cleaning activities, even if they do not necessarily originate from the same vessels. This might explain well the co-occurrence of TBT, Zn, and Cu.

Pb is not a common ingredient in antifouling paint. However, various lead compounds might be used in paint as pigments, corrosion inhibitors

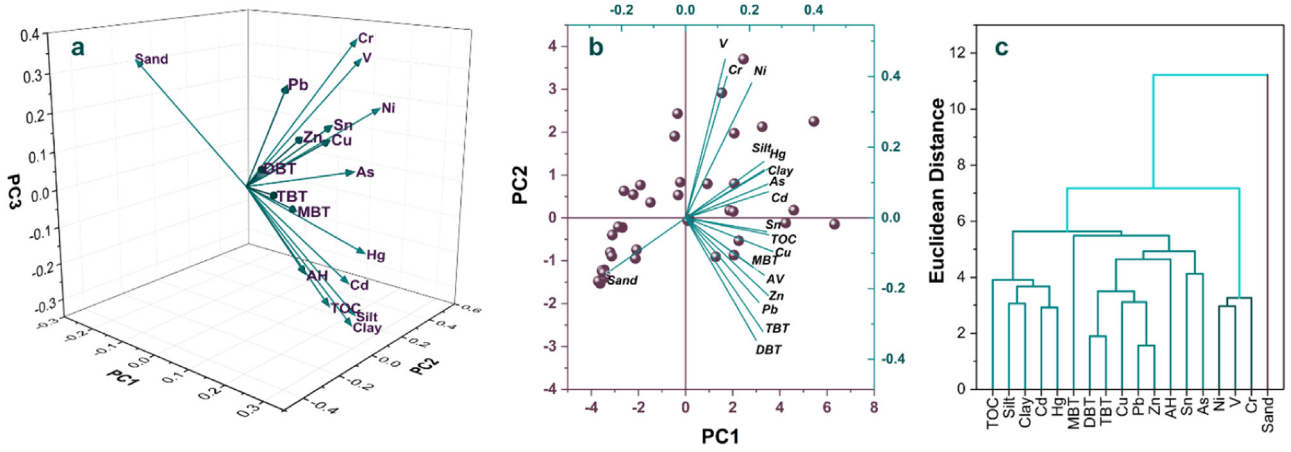

Fig. 4. Three-dimensional plot loadings (PC1, PC2, and PC3) of the active variables (standardized properties such as concentration of tributyltin (TBT), metals, total organic carbon (TOC), alyphatic hydrocarbons (AHs), and sediment characteristics) used to construct the PCA (a); the PCA biplot for PC1 and PC2 of all the sediment samples analyzed in this study (b); hierarchical cluster analysis of the variables (c).

or drying catalysts (Ranjbar Jafarabadi et al., 2021; Turner, 2021). Relatively high concentrations of this metal were indeed found to be associated with the discarded antifouling paint particles by Turner (2021). In addition to that, both Pb and TBT are common additives used in the production of plastics (Levin et al., 2021). The study carried out in the Odra River estuary has already found a significant correlation and co-occurrence between TBT, Cu, and Pb, and identified shipyards, ship maintenance, ports, and marines as the main sources of pollution in the area (Kucharski et al., 2022). Sediment characteristics are often reported as the main factors determining pollution of the sediment. In our study, a high positive correlation was observed between TBT and TOC. This is due to the fact that sediment rich in organic carbon has a higher surface-to-volume ratio and has a high affinity to hydrophilic compounds (Abraham et al., 2017; Jokšas et al., 2019). A high positive correlation between TOC and AHs was also observed. Furthermore, TOC showed a strong positive correlation with most of the metals analysed. In this case, both the increased surface-to-volume ratio and the potentially forming complexes between organic carbon and metals play an important role (Li et al., 2020; Ranjbar Jafarabadi et al., 2020). Moderate positive correlations were observed between TBT and silt content in sediment, as well as between TBT and clay content in sediment. Similar correlation patterns were observed for DBT, while MBT showed slightly higher correlation coefficients (0.53 and 0.50, $p < 0.05$ for silt and clay fractions, respectively). The sorption efficiency of BTs onto silt and clay particles can be influenced by various factors such as the organic matter content in sediment, salinity and pH of the ambient water, fresh TBT input, and the presence of positively charged background ions such as Ca^{2+} and Mg^{2+} in the environment (Fang et al., 2017). Moreover, the presence of ship traffic or inflows from the lagoon and the sea can cause water movement that may remove BTs from the port sediment. The complexity of the adsorption/desorption processes can also explain the moderate correlations observed between BTs concentrations and the fine sediment fraction.

The significant positive correlation found between BTs and AHs is somewhat unexpected, as these pollutants are generally accepted to originate from different sources. High loadings of AHs are usually associated with the use of crude oil and its products (Hasani Moghaddam et al., 2021). However, in this case, the high correlation between BTs and AHs may be attributed to the characteristics of specific sampling locations, such as the level of technogenisation, sediment properties, and hydrodynamic processes. The study mainly focused on the semi-enclosed aquatories which are characterised by a slow water exchange rate and intense technogenic activity (Stakėnienė et al., 2016). Moreover, the bottom sediment of these semi-enclosed bays consists of fine particles rich in organic carbon. Long-term ship standing and ship-repairing activities around these semi-enclosed aquatories result in accumulation of different types of pollutants in the ambient sediment. Several previous studies have already reported increased concentrations of various organic and inorganic pollutants in these locations (Jokšas et al., 2019; Stakėnienė et al., 2016). Such localised pollution sources may accumulate and release different types of pollutants originating from various sources, which could explain the co-occurrence of BTs and AHs in this study.

4. Conclusions

The present study has revealed that tributyltin is still an issue in the Klaipėda Port area. Despite gradually decreasing butyltin levels if compared to previous studies, TBT prevalence over its metabolites, owing to either slow degradation or a fresh input, raises concern. Moreover, this study has uncovered the extent of TBT pollution in the Baltic Sea. Recent TBT input was observed in the dumping sites with the highest BTs levels recorded in the most actively exploited dumping site. Dredging/cleaning activities of the port and the subsequent dumping of the sediment are responsible for the Baltic Sea pollution with BTs. Also concerning is the fact that sediment meeting the Lithuanian requirements for dumping is not always considered to be safe at international level, and disposal of such sediment might pose extent risks for the environment.

Dredging and cleaning of the Port channel played a major role in butyltins variations, while temporal changes were of lower importance. However, increased BTs concentrations recorded in spring season could be related to the increase in water delivery from the Nemunas River during winter. Such a trend is an indirect indicator of the climate change impact to the water exchange mechanism between the Curonian Lagoon and the Baltic Sea and is in agreement with other studies which have already reported a higher exchange rate between the lagoon and the sea in the winter than in the warm season.

Correlation, principal component, and cluster analysis confirmed close connection between TBT and DBT. Rather significant relationships between TBT and MBT, Zn, Pb, Cu was also observed. TBT must originate from previously applied antifouling paints, while DBT and MBT are its degradation products, although some MBT may have originated from different sources. In the meantime, Zn, Pb, and Cu could enter the environment from currently used antifouling paints. Like TBT, these metals could be introduced to the port environment through ship-maintenance and cleaning activities, even if they do not necessarily originate from the same vessels. Additionally, areas with intense anthropogenic activity and limited water circulation could be classified as intense sediment accumulation areas. They act as localised sources of pollution for different

types of pollutants, even though the primary sources of these pollutants may differ.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2023.100294.

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