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The content of butyl- and phenyltin derivatives in the sediment from the Port of Gdansk

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ABSTRACT

Harbor sediments containing large deposits of organotin compounds constitute a potential threat to the marine environment.

Samples of harbor sediments were collected twice in the years 2003 and 2005 from the following locations: Ziółkowskiego, Siarkowe, Wiślane, Węglowe, Chemików and Paliw Płynnych Quays. The cores of 25 cm length sliced into 2- and 5-cm segments were analyzed. After drying and homogenization, samples were split into two granulometric fractions, i.e. <2.00 and <0.063 mm. The dominant fraction in whole sediment, i.e. fraction grain diameter <2.00 mm, was sand (grain diameter 2.00–0.063 mm). However, the highest concentrations of butyltin (BT) and phenyltin (PT) compounds were found in the fine sediment fraction. The mean values of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in the analyzed samples in the <2.00 mm fraction were 2144.9, 434.7 and 148.1 ngSn g^{-1} d.w., respectively, while the corresponding mean values in the <0.063 mm fraction were 6556.4, 1593.7 and 450.0 ngSn g^{-1} d.w. The mean concentrations of monophenyltin (MPhT) have been estimated at 29.0 and 49.9 ngSn g^{-1} d.w. for the <2.00 and <0.063 mm fraction sizes, respectively. The estimated content levels of diphenyltin (DPhT) and triphenyltin (TPhT) were in most cases below the detection limit of the applied method. The sediment cores collected from the locations characterized by high industrialization and intense exploitation (Wiślane, Węglowe Quays) contained the highest concentrations of BT and PT.

1. Introduction

Tin is one of the most important metals necessary for humans and animals to maintain life functions. Its toxicity towards live organisms is low however the organic compounds of tin are poisonous (Hoch, 2001). Organotin compounds (OTC) are widely used as biocides in agriculture and as catalysts and plastic (PCV) stabilizers in industry. However the main input of butyl- and phenyltin derivatives to the sea originates from antifouling paints (Morcillo and Porte, 2000) that are used to protect ship hulls from fouling organisms. The application of antifouling systems based on organotins allowed the shipping industry to reduce the maintenance cost of fuel and to protect the hull effectively.

The first troubling signals in regard to toxicity of these compounds appeared in 1975 in the reports from the Arcachon Bay (Alzieu, 2000). Further results from toxicity testing have proven that organotins are responsible, among others, for imposex in snails (Shim et al., 2000), shell delamination in bivalves (Gomez-Ariza et al., 1999), fry mortality (Fent and Looser, 1995), hampering of catalytic activity of cytochrome P450 aromatase in marine mammals (Kim et al., 1997).

In light of the above, since 1980 many industrialized countries have introduced internal regulations dealing with bans on the use of TBT-containing antifouling paints on vessels up to 25 m long (Albanis et al., 2002). The Helsinki Convention published on April 9, 1992 also introduced such ban over the Baltic Sea area. The resolution A.895 (21) adopted by the International Maritime Organization on November 25, 1999 forbids the use of TBT in new antifouling system from 1 January 2003 and requires that the old system be disabled until January 1, 2008.

Thanks to the introduced legal sanctions the input of new organotins into the environment, including benthic sediments, has been significantly limited. However, the risk of remobilization of pollutants from sediments into the water column is still present. This is particularly so in the case of harbor sediments that are removed from port canals for navigational safety reasons, and then dumped at sea under specific conditions or stored on land. The load of hazardous substances deposited with dredged material,

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including toxic organotins, may pose a potential threat to the marine ecosystem.

In the regulation on the type and concentrations of substances causing the contamination of dredged material that has been adopted by the Polish Minister of the Environment (Dz. U. No 55, pos. 498, 2002), there are no indicator values for organotins. Considering that the amount of sediments to be removed annually from the basins of the Port of Gdansk ranges from 50 to 60 thousand ton, it is necessary to elaborate such indicators and, in addition, to constantly monitor and analyze the samples of dredged material.

The determinations of organotin compounds in the organisms (mussels and fish) from the Gulf of Gdansk and in sediments from the Polish harbors (the Port of Gdynia, Hel Harbor and the Port of Gdansk) were performed by Kannan and Falandysz (1997), Szpunar et al. (1997), Senthilkumar et al. (1999), Falandysz et al. (2002) and Albalat et al. (2002). The study in the Port of Gdansk area was conducted in Szczecińskie Quay only (Senthilkumar et al., 1999) (Fig. 1). Moreover, two surface samples from Siarkowe Quay were analyzed by Mędrzycka et al. (2006). In all cases (i.e. including the literature data from the Gdynia, Hel and Gdansk harbors), only the butyltin derivatives were analyzed. The phenyltin derivatives, which are also toxic, have not been determined. Moreover, the determinations were made in whole sediment, i.e. sediment grain size <2.00 mm. Fine fraction, i.e. <0.063 mm which is recommended for assessing the content of organotin derivatives in benthic sediment samples (Quevauviller and Donard, 1990) has not been analyzed.

The presented work is the first complete and detailed study, including the physical properties of sediment, that deals with the contents of butyltin (BT) and phenyltin (PT) derivatives in sediment samples from the Port of Gdansk area, fractioned into two grain sizes of <2.00 and <0.063 mm.

2. Samples and methods

2.1. Sample collection

The Port of Gdansk is located in the costal zone of the Gulf of Gdansk by the river mouth of Martwa Wisła in the Baltic Sea. The total length of Martwa Wisła between Przegalina and Nowy Port equals 27 km (plus 2.5 km of Śmiała Wisła), while its surface area is about 9 km^2. The river bed of Martwa Wisła remains under the strong influence of the marine water masses (Majewski, 1977).

The Port of Gdansk consists of an inner and outer harbor, the latter being called the North Port. The inner harbor is located on both sides of the ship channel through which Martwa Wisła flows, and on the eastern side of Kaszubski Kanał. In this part of the port the loading quays for, among others, sulphur, phosphate minerals, coal and citrus fruits, and passenger ferry terminals are found. The outer harbor is the newest area of the Port of Gdansk situated about 2.5 km from the old shoreline. Loading and unloading, among others, of crude and heating oil, diesel fuel, coal and liquid petroleum gas (LPG) take place within the North Port.

Sediment samples were collected in the Port of Gdansk from the underwater area of the following quays with a Niemistö gravitational corer on board the hydrographic vessel Oceanograf 2 (University of Gdansk) (Fig. 1):

- Ziółkowskiego, Wiślane and Węglowe Quays (in 2003).
- Siarkowe, Chemików and Paliw Płynnych Quays (in 2005).

Two cores ranging in length from 15 to 25 cm (one for granulometric and the other for chemical analysis) were collected from each station. The cores were macroscopically evaluated (i.e. color, the condition of sediment, reaction with 20% HCl, water content, smell and admixtures such as, shells and anthropogenic materials) and sliced with the help of measuring rings and knives into the following segments: 0–2 cm, 2–5 cm, 5–10 cm, 10–15 cm, 15–20 cm and 20–25 cm. The sliced cores were packaged in labeled polyethylene bags and stored at −20 °C prior to analysis.

For each separate sediment layer to be granulometrically analyzed, the water content (i.e. sediment sample was weighted on an analytical balance and dried at 105 °C until reaching constant weight), loss on ignition (LOI) (dried benthic sediment samples after reaching constant weight were burnt in a muffle oven at 550 °C, and weighted again after cooling down) and the bulk density (obtained with the cutting ring method) were measured in the laboratory.

Samples to be analyzed for the content of organotins were lyophilized (Christ, Alpha 2–4) and then homogenized by means of mortar and pestle. The separation of specific sediment fraction was achieved with a set of calibrated metal sieves (Fritsch). For the granulometric analysis, the sieves of 8.0; 4.0; 2.0; 1.0; 0.5; 0.25; 0.125; and 0.0625 mm mesh diameter were used, while chemical analyses were performed on the samples fractioned through the 2.00 and 0.063 mm mesh size sieves. According to the HELCOM Recommendation 13/1 (1992), each sediment sample destined for chemical analysis was cleaned of coarse fractions (i.e. grain diameter >2.00 mm; for example, boulders, pebbles, stones, etc.). The obtained whole sediment samples (grain diameter <2.00 mm, i.e. sand, silt and clay) were split into two subsamples. One was analyzed without any further changes. The second subsample was analyzed only after removing, via sieving, the fine fraction (<0.063 mm, i.e. clay and silt). The sediment fractions (<0.063 and <2.00 mm) were stored in the dark at −20 °C prior to analysis.

2.2. Chemical analysis

The procedure originally developed by Wasik et al. (2007) (Fig. 2) was used for determining butyltin and phenyltin compounds in sediment samples.

An ASE 200 device (Dionex, Sunnyvale, CA) equipped with the 22 ml cells was used for sample extraction. The following extraction parameters were used: temperature 50 °C, pressure 13790 kPa (2000 psi), preheat time 5 min, heat time 5 min, static extraction time 9 min, flush volume 150%, purge time 100 s, static extraction cycles 4, solvent volume: 43 ml, solvent composition: 750 ml of methanol, 250 ml of water, 1 mol of acetic acid, 1 mol of sodium acetate, 0.6 g of tropolone.

The butyltin and phenyltin compounds were measured by a gas chromatograph (GC 8000 series, Carlo Erba) equipped with an flame-photometric detector fitted with 610 nm interference filter (Pörschke, Germany) and capillary column (DB-1, 30 m × 0.32 mm, i.d. × 0.25 μm, J&W). The following chromatographic conditions were applied: carrier gas H_2, 100 kPa (constant pressure mode), temperature program 90 °C (2 min), 10° min^{-1}, 270 °C (0 min), injection volume 1 μl, injection mode Splitless (purge valve open after 1 min), injector temperature 250 °C, detector temperatures base: 280 °C, body: 200 °C, detector gases H_2 (170 ml min^{-1}), air (160 ml min^{-1}).

For calibration purposes, sediment was chosen from the samples collected in the relatively unpolluted region of the Gulf of Gdansk. For method validation, PACS-2, BCR-646 reference material (purchased from LGC Promochem), certified for butyl- and phenyltin concentrations, was used (Table 1).

2.2.1. Reagents

Monobutyltintrichloride (MBT, 96%), tributyltinchloride (TBT, 97%), triphenyltinchloride (TPhT, 98%) and tetrabutyltin (TetraBT, 95%), Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1one) were purchased from Merck. Dibutyltindichloride (DBT, 96%), monophe-