Science of the Total Environment 441 (2012) 57–66

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Seasonal changes in organotin compounds in water and sediment samples from the semi-closed Port of Gdynia

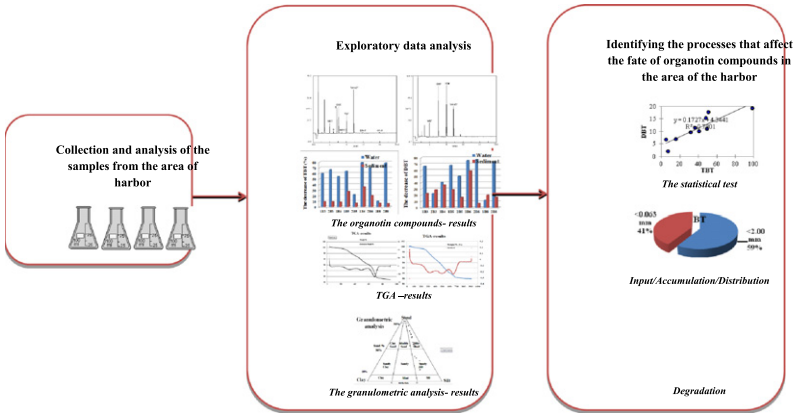
Barbara Radke [a,d,*,1], Andrzej Wasik [b,2], Linda L. Jewell [c,3], Stuart Piketh [d,1], Urszula Pączek [a,4], Agnieszka Gałuszka [e,5], Jacek Namieśnik [b,2]

[a] Department of Marine Geology, Institute of Oceanography, University of Gdańsk, Al. Marszałka Piłsudskiego 46, 81-378 Gdynia, Poland
[b] Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, 11/12 G. Narutowicza St., 80-952 Gdańsk, Poland
[c] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, Private Bag 3, Wits 2050, South Africa
[d] Climatology Research Group, University of the Witwatersrand, Johannesburg, Private Bag 3, Wits 2050, South Africa
[e] Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University, 15 G Świętokrzyska St., 25-406 Kielce, Poland

HIGHLIGHTS

- The seasonal changes of organotin compounds (OTC) in samples were investigated.
- The mechanisms of accumulation and degradation of OTC in the sediments were studied.
- We examine the influences of the biogenic substances on the changes of OTC.
- Higher concentrations of OTC for water and sediment samples were obtained for winter.
- The biogenic substances are not significant affecting the changes of OTC in area port.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 February 2012
Received in revised form 12 June 2012
Accepted 6 September 2012
Available online 4 November 2012

Keywords:
Sediments
Water

ABSTRACT

The effect of seasonal changes on the distribution of organotin compounds (OTC) in the sediments and seawater from the docks of the Port of Gdynia was investigated. Sediment and seawater samples were collected from four industrial docks in February (winter) and June (summer) in 2009. The samples were analyzed for butyltin, phenyltin, octyltin, and tricyclohexyltin (total of 9 OTC derivatives). The fine fraction (<0.063 mm) accumulated the highest concentration of OTC, although it was not the dominant fraction in the sediment samples from the Port of Gdynia. The average concentration of TBT, DBT and MBT in collected samples were as follows: 4400; 2188; 730 ng cation g^{-1} d.w. (February) 3638; 1590; 474 ng cation g^{-1} d.w. (June) in the fine sediment samples, 2805; 1266; 485 ng cation g^{-1} d.w. (February) in <2.00 mm sediment

* Corresponding author at: Department of Marine Geology, Institute of Oceanography, University of Gdańsk, Al. Marszałka Piłsudskiego 46, 81-378 Gdynia, Poland. Tel.: +48 58 523 66; fax: +48 58 523 68 18.
E-mail addresses: ocebr@ug.gda.pl (B. Radke), chemanal@pg.gda.pl (A. Wasik), linda.jewell@wits.ac.za (L.L. Jewell), stuart.piketh@wits.ac.za (S. Piketh), Agnieszka.Galuszka@ujk.edu.pl (A. Gałuszka), chemanal@pg.gda.pl (J. Namieśnik).
[1] Tel.: +27 11 717 6536; fax: +27 11 717 6535.
[2] Tel.: +48 58 347 21 10; fax: +48 58 347 26 94.
[3] Tel.: +27 11 717 7507; fax: +27 11 717 7591.
[4] Tel.: +48 58 523 66 81; fax: +48 58 523 68 18.
[5] Tel.: +48 41 349 70 26; fax: +48 41 349 70 62.

0048-9697/$ – see front matter
http://dx.doi.org/10.1016/j.scitotenv.2012.09.006

fractions and 118.6; 39.2; 25.3 ng cation L^{-1} (February) and 46.5; 12.6; 8.2 ng cation L^{-1} (June) in the water samples. Higher concentrations of butyltin derivatives (BT) were observed in samples collected in February than in those collected in June. Seasonal changes in BT correlate well with changes in the water pH and concentrations of organic matter and can be attributed to sorption/desorption to sediments, photodegradation and biodegradation. Although the Port of Gdynia does not represent the natural features of a marine environment, seasonal variations recorded in the pH values as well as BT, organic carbon and biogenic element concentrations seem to be influenced by temperature and microbial activity.

1. Introduction

Organotin compounds (OTC) are toxic to many organisms. Even at very low concentrations, OTC can cause several negative effects (e.g. shell deformation in oysters, imposex in gastropods, mussel larval mortality) (Blunden et al., 1984). Organotins have been introduced into the marine environment through human activities mainly by the application of antifouling paint with tributyltin (TBT) and triphenyltin (TPhT) for the protection of ship hulls. Such areas as shipyards, harbors and passenger ship terminals constitute a potential pollution source for the marine environment and potential risk for the marine living organisms. Due to the highest load of hazardous OTC species is deposited in the harbor sediment, the global prohibition on the application of OTC in anti-fouling systems on ships was implemented (IMO, 2008). Although a reduction of OTC contamination has been observed, TBT can still be detected in many areas of the world (Choi et al., 2009; De Oliveira et al., 2010).

It has been frequently reported that the distribution of OTC in sediments and the water column may undergo some changes including seasonal changes (Harino et al., 1998; Choi et al., 2009; Meena et al., 2009). Sediment and water monitoring should be performed in harbors according to the International Maritime Organization guidelines (IMO, 2008). However, in the Port of Gdynia neither detailed data on the content of OTC in the water and sediments nor the percentage of fine fraction in the total sediment fraction is available. To fill this gap in our knowledge, we designed a study which aimed at the determination of nine tin derivatives according to ISO 17353 (2004) in water and sediment samples collected in the Port of Gdynia during two sampling campaigns. The main objectives of the study were: (i) to find and discuss the seasonal variations in OTC concentrations, (ii) to compare the percentage of fine (<0.063 mm) and coarse (<2.00 mm) fractions in the sediment samples and (iii) to characterize factors contributing to OTC accumulation in sediments. To accomplish these goals, granulometric analyses of sediments and thermogravimetric analysis accompanied by chemical analyses of water and sediments were performed (determination of OTC, carbon, nitrogen and sulfur, pH, salinity).

It is well documented that organotin compounds tend to accumulate in the fine fraction of sediments (<0.063 mm) thus this fraction is important for environmental quality assessment (Langston and Pope, 1995; Stronkhorst and van Hattum, 2003). However, the high OTC concentrations in fine fraction of sediments will not create a risk for the environment if the percentage of this fraction is very small (Radke et al., 2008). Thus the knowledge on the granulometric composition of sediments is important. It should be mentioned that butyltin and phenyltin derivatives were determined in the sediment samples collected at the Port of Gdynia (Szpunar et al., 1997; Filipkowska et al., 2011), but no granulometric analysis has been performed in these samples.

Since ISO 17353 (2004) requires results for the nine tin derivatives (tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT); triphenyltin (TPhT), diphenyltin (DPhT), monophenyltin (MPhT); monooctyltin (MOT), dioctyltin (DOT) and tricyclohexyltin (TCHT)) in the water samples, and there is no data about the concentrations of OTC in water samples from the Polish coastal zone, we try to provide the pertinent information. Additionally, we performed analysis of inorganic and organic carbon (C_{inorg}, C_{org}), organic matter (OM), total nitrogen (N_{tot}), total sulfur (S_{tot}), granulometric analysis and thermogravimetric analysis (TGA), which may characterize the contribution of some factors to the fate of organotin compounds in the sediments from the semi-closed harbors, such as the Port of Gdynia.

2. Materials and methods

2.1. Study area

The Port of Gdynia (Fig. 1) is the 3rd biggest merchant port of Poland occupying an area of 755.4 ha including 492.6 ha of land. It is one of the largest and most modern universal ports on the Baltic Sea. The port is located in the coastal zone of the Gulf of Gdańsk and it is protected year-round by a 2.5 km breakwater. The port is characterized by very favorable conditions for navigation, and never freezes over during winter. The Chylonka stream (3.2 km long) begins at the Kashubian valley and has its mouth in the area of the port channel west of the Port of Gdynia (docks: IV, V, VI, VIII).

2.2. Sample collection

The water and sediment samples were collected in February and June 2009 from the most contaminated quays: IV, V, VI and VIII of the port of Gdynia. Two locations for each of the docks were

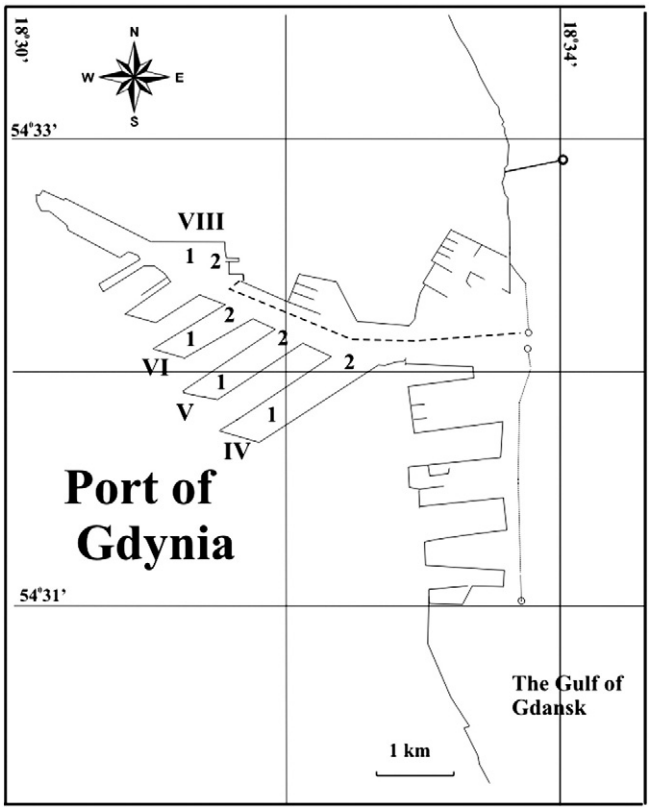


Fig. 1. A map of the Port of Gdynia, where IV, V, VI and VIII are individual docks with two sampling sites each, designated 1 and 2. - - - The dashed line marks the perimeter of the Port of Gdynia, where the samples were collected.