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The evaluation of tributyltin concentrations in the sediments of the Port of Gdynia

Ocena stężeń tributylocyny w próbkach z Portu Gdynia

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Abstract: Tributyltin (TBT) may negatively affect various organisms. TBT has been used in antifouling paints for the protection of ship hulls and hence harbor sediments may contain high concentrations of TBT. This study shows TBT concentrations found in sediments from three basins (No. V, VI and VIII) of the Port of Gdynia. TBT concentrations ranged from 291 to 1,689 ngSn·g^{-1} d.w. and should be classified as highly contaminated and grossly contaminated [20]. These results indicate that TBT in harbor sediments is an environmental risk that may be emphasized by dredging operations in the region. However, the obtained results also confirm the global tendency for depreciating content of TBT in port sediments after the global ban on TBT in 2008.

Keywords: tributyltin, harbor sediments, degradation, dredged material

Streszczenie: Tributylocyna (TBT) może wpływać negatywnie na różne organizmy. TBT była stosowana jako komponent w farbach przeciwporostowych do ochrony kadłubów statków, dlatego też osady portowe mogą zawierać wysokie stężenia TBT. W pracy przedstawiono ocenę zawartości TBT w osadach z trzech basenów (nr V, VI i VIII) w Porcie Gdynia. Stężenia TBT zawierały się w zakresie od 291 do 1689 ngSn·g^{-1} s.m. i powinny być klasyfikowane jako wysoce zanieczyszczone i rażąco zanieczyszczone [20]. Wyniki te wskazują, że TBT w osadach portowych stanowi realne ryzyko środowiskowe, które może być zwiększone w wyniku prowadzenia prac pogłębiarskich w porcie. Jednakże, uzyskane wyniki potwierdzają również ogólną tendencję do zmniejszania zawartości TBT w osadach portowych w wyniku wprowadzenia zakazu stosowania TBT w 2008 roku.

Słowa kluczowe: tributylocyna, osady portowe, degradacja, urobek czerpalny

INTRODUCTION

Tributyltin (TBT) belongs to the group of dangerous chemical substances better recognized as organotin compounds (OTC). TBT may be removed from the aqueous phase, adsorbed onto suspended particulate matter and then settle to the bottom. There are evidences that TBT may affect various organisms [1-3]. Tributyltin was widely used in antifouling paints and algicides for the protection of ship hulls, and also as catalysts and plastic (PCV) stabilizers in the industry [4-7].

Since the first troubling signals concerning tributyltin appeared in specialist literature in 1980 [8], it has become clear that organotin compounds were one of the most dangerous substances ever introduced into the marine environment via human activities. To solve this situation, in 2008, the International Maritime Organization (IMO) banned the usage of organotin compounds in the antifouling systems [9]. Thanks to these regulations, the new input of organotins into the marine environment has been significantly limited.

Poland is one of the major countries located at the Baltic Sea, that is obliged to protect the marine environment. The Polish harbors are directly connected to the Gulf of Gdansk. This region is recognized as the one of most polluted areas in the Polish coastal zone. Additionally, it has received significant amounts of tributyltin over many years, mostly from maritime and tourist shipping (e.g., movement of vessels) as well as from port activities (e.g., Port of Gdansk, Port of Gdynia). Although the established ban has reduced fresh inputs of TBT to the ecosystem of the Baltic Sea, there is still a need for regular monitoring of TBT in the environmental samples. Sediment is

Tab. I. Tributyltin (ngSn·g⁻¹ d.w.) in sediment samples from selected marine harbors and shipyard area.

COUNTRY	YEAR	CONCENTRATION	REFERENCES
		POLISH PORTS	
Poland, Port of Gdynia	1993-1995	470-3,500	[13]
Poland, Port of Gdynia	2008	8-1,910	[6]
Poland, Port of Gdynia	2009	72.0-2,200.8	[5]
Poland, Port of Gdynia	2010	290.98-1,688.52	This study
Poland, Hel port	1993-1995	<0.4-41	[13]
Poland, Port of Gdansk	1997	2600 – 40,000	[4]
Poland, Port of Gdansk	2003-2005	135.0-7,635.0	[14]
Poland, Port of Gdansk	2008	<0.3-15,780	[6]
		OTHER PORTS	
Indonesia harbors	2011	n.d.-4,250	[21]
Taiwan, Kaohsiung harbor	2009	1.2-111.2	[12]
Brazil, Santa Catarina harbor	2008	n.d. -1136.6	[11]
France, Port Camargue	2009	0.24 – 10,738	[8]
Taiwan, Fishing port	2001-2004	2.4-8458	[22]
Spain, Barcelona harbor	2002	98-4702	[18]
South Africa, Cape Town harbor	2012	10-829	[23]
South Korea, Harbor and shipyards	2010	Fishing port: 69-116 Harbors: 3-55,264	[3]
UK, Shoreham harbor and Brighton marina	2003-2004	<1-689	[24]
Argentina, Mar del Plata Port	2012	<2-150.4	[7]
Lithuania, Klaipėda port	2010-2012	1-5,200	[2]
South China, fishing port	2007	<0.7-86.0	[25]

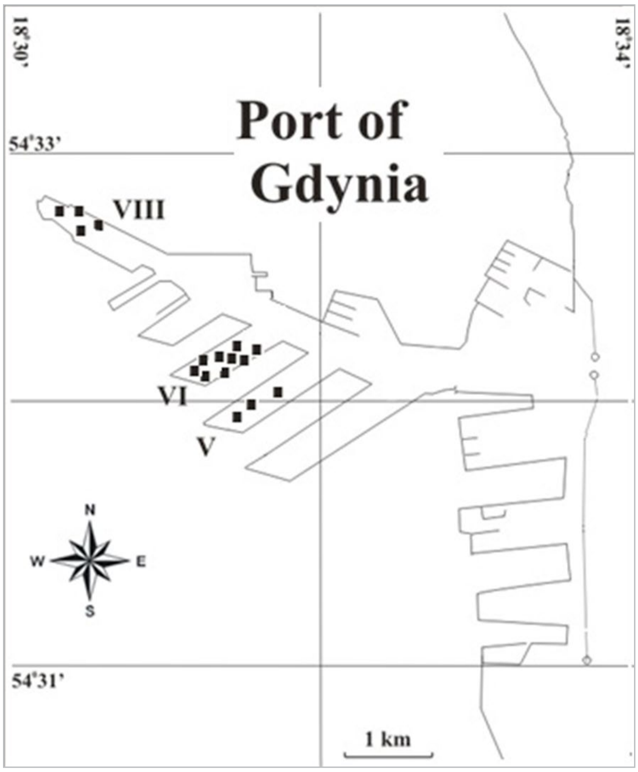

Fig. 1. Map of the Port of Gdynia with sampling sites, where: V, VI and VIII are individual basins.

a specific component of the aquatic environment in which the presence of anaerobic conditions may result in slow degradation processes of TBT (from 6 months to 8.7 years) [1, 10]. Additionally, the dredged material comprises a special case study of sediment, because its large deposit of TBT may considerably influence the state of the Baltic Sea [5-8, 11-12].

The aim of this study is to present the current concentration values of dredged material from the Port of Gdynia. Additionally, we compare the obtained results with previous works [4-6, 13-14] and with available literature data from other ports. This comparison can constitute a valuable point of reference for the assessment of progress in the reduction of the concentration level of TBT in sediments from the Polish ports. It is an important issue, considering the total ban on the use of TBT in antifouling paints, which has been implemented in January 2009. Therefore, the present study will constitute valuable material for future research.

MATERIALS AND METHODS

Study area

The port of Gdynia (Fig. 1) is located in the coastal zone of the Gulf of Gdansk in the region of the Baltic Sea. It is the third lar-

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Tab. II. Classification criteria for dredged material containing TBT (ngSn·g^{-1}) applicable in Baltic countries [19].

COUNTRY	CRITICAL VALUE 1	CRITICAL VALUE 2
Denmark	7	200
Finland	3	200
Germany	20	60
Lithuania	3	30

Critical values are given in a different way. Critical value 1 and 2 correspond to the level value 1 and 2 in Demark, and to the limit value 1 and 2 in Germany and Lithuania.

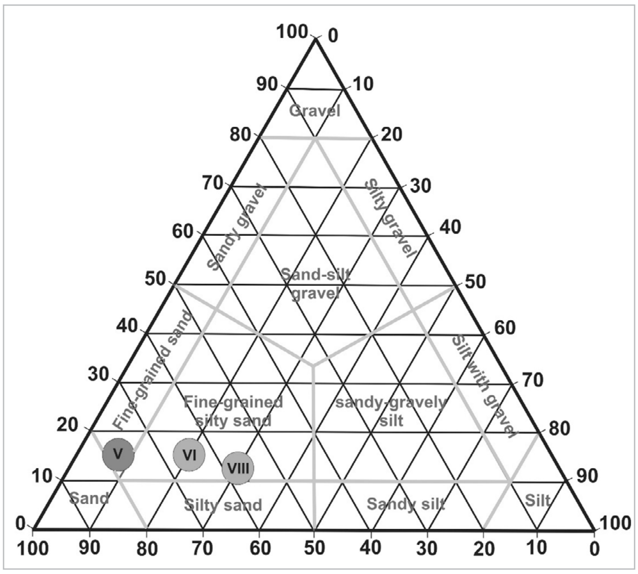

Fig. 2. Results of the granulometric analysis of sediment samples from the Port of Gdynia

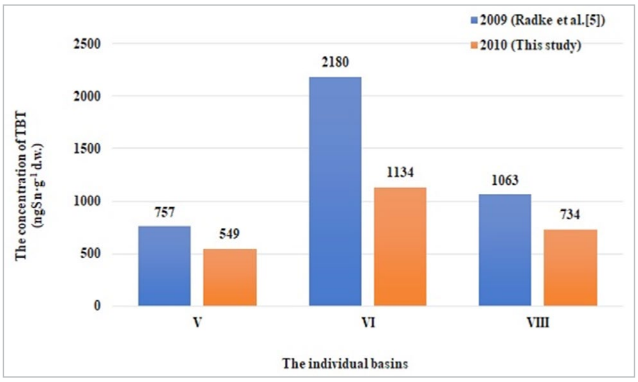

Fig. 3. A comparison of mean values of TBT (ng·Sn g^{-1} d.w.) in sediment samples from the Port of Gdynia, where: V, VI, VIII are individual basins of the port.

gest, universal seaport in Poland, with a total area of 973 hectares, including 621 hectares in land. The Port of Gdynia is naturally protected by the Hel Peninsula, although strong westerly winds may raise the level of water in the port by 60 cm [15].

Sampling and chemical analysis

Sediment samples were collected in 2010 with a vibrocorer on board of r/v IMOR owned by the Maritime Institute in Gdansk. Three basins of the Port of Gdynia were surveyed: V (3 stations), VI (9 stations) and VIII (4 stations) (Fig. 1). The collected samples were macroscopically examined, divided into segments and packaged in polyethylene bags and stored at -20°C prior to analysis. Prior to- chemical analysis, all sediment samples were lyophilized and then homogenized. Analyses of TBT in the samples were performed in accordance with the International Standard ISO 23161:2009. This method was later published as PN-EN 23161:2011. All validated conditions of this method were published by Wojtkiewicz et al. [16]. Quantitative measurements of TBT were performed in the sediment fraction with grain diameter <2.00 mm, which includes sand, silt, and clay. Gas chromatography with mass spectrometry (GC-MS) was used for the quantification of TBT.

The operating range was from 4 to 2,660 ngSn·g^{-1} d.w., while the limit of quantification (LOQ) of the applied analytical method was 4.00 ngSn·g^{-1} d.w. The obtained results of recovery for the certified reference material PACS-3 from NRC, Canada, was 86%. Calculations were based on peak areas. All reagents used for analysis were of high purity (Suprapur® and Ultrapur®) and came from Merck.

RESULTS AND DISCUSSION

Characteristic of the sediment samples

The analysis of grain size of sediments collected from individual basins indicates sand as the dominant fraction, in particular fine-grained silty sand as well as fine-grained sand (Fig. 2). Similar results were reported by [5-6, 13]. Fine-grained silty sand was found in samples from basins VI and VIII. However, basin VI was more abundant in silty sand than basin VIII. Basins VI and VIII are located in the inner parts of the port, where conditions are better for the deposition of fine particles. In basin V, fine fractions are removed to the sea. This distribution of grain size is consistent with the results obtained in previous studies [5-6]. Organic matter was not investigated in this study.

Concentration of TBT in sediment samples

The results obtained in 2010 showed total TBT concentrations ranging from 290.98 to 1,688.52 ngSn·g^{-1} d.w. with a mean value of 924.44 ngSn·g^{-1} d.w., median 938.53 ngSn·g^{-1} d.w.

Additionally, an increasing trend of TBT content (ngSn·g^{-1} d.w.) has been observed in samples collected from individual basins. This can be presented as follows:

- basin V: 290.98 - 918.03 (mean: 549.18, median: 438.52),
- basin VIII: 385.25 - 1040.98 (mean: 733.61, median: 754.10),
- basin VI: 438.52–1688.52 (mean: 1134.34, median: 1016.39).

The highest level of TBT was found in sediment samples from basin VI, which -has been used in the past by the large Shipyard of Gdynia for the construction and renovation of various vessels, such as large passenger ships, ferries, semi-container vessels, tankers. Currently, the load of contamination is mostly associated with activities of other shipyards, such as Nauta S.A. Shiprepair Yard Gdynia, the Crist Shipyard and manufacturing companies. The high load of TBT in sediments from basin VIII could be associated with the proximity of the biggest shipping terminal and its intense ship traffic. Additionally, the abundance of fine particles in VI and VIII may facilitate the retention of TBT, as well as other contaminants at the bottom [2, 6, 12]. The lowest concentrations of TBT were measured in sediment samples from – basin V, whose activity is mainly related to the Baltic General Cargo Terminal. Sediments contained less clay and silt and more sand [5], which decreases the sorptive capacity of sediments for TBT [17].

Comparison of the obtained results with previous works and literature data

In this study, there was no value of tributyltin below the limit of quantification. However, this finding confirms the presence of TBT in the area of the port [7, 11]. It is difficult to indicate the recent input of TBT, as the remaining derivatives of OTC (i.e., monobutyltin (MBT) and dibutyltin (DBT)) were not investigated in this study. Therefore, the Butyltin Degradation Index (BDI) [18] seems to be useless in this particular case. However, taking into account the previous measurements of TBT in surface sediments collected from the Port of Gdynia (Tab. I.), we can make a short summary of literature data.

The highest TBT concentration (namely 3,500 ngSn·g^{-1} d.w.) in sediment samples was found by Szpunar et al. [13] between 1993 and 1995. Later, in 2008 Filipkowska et al. [6] reported up to 1,910 ngSn·g^{-1} d.w., whereas in 2009 Radke et al. [5] measured up to 2,200.8 ngSn·g^{-1} d.w. In 2010, the Department of Environmental Protection found the maximum concentration of 1,688.52 ngSn·g^{-1} d.w. (present study). This comparison presents a decreasing trend of TBT concentrations in dredged material during the last 13 years. It is worth mentioning, that Filipkowska et al. [6] have mainly examined samples from the outer part of - the harbor (i.e., - near the mouth of the sea). There was no determination of TBT in samples from the investigated basins (i.e., V, VI and VII). In order to detect the decreasing trend of TBT in material dredged from these basins, it is better to refer results to the literature data published by Radke et al. [5]. Fig. 3 presents the obtained data in 2009 and 2010. These results also confirm a worldwide tendency for the depreciating concentration level of TBT in port sediments after the global ban on TBT-based antifouling paints in 2008 [2, 7, 12].

Classification of TBT in sediment samples

Poland has no environmental quality levels of TBT concentration in dredged material. However, there are other classifications proposed by countries located at the Baltic Sea (Tab. II.). According to these criteria, the concentration level of TBT in dredging sediments from the Port of Gdynia exceeds the limit values at certain points (i.e., sediments suitable for disposal at sea). Another classification proposed by Dowson et al. [20] characterizes the concentration levels (ngSn·g^{-1} d.w.) of TBT--contaminated sediments as follows: <3 uncontaminated sediments; 3-20 lightly contaminated; 20-100 moderately contaminated; 100-500 highly contaminated; and >500 grossly contaminated. Using this scale, the sediments in this study (concentrations ranged from 290.98 to 1,688.52 ngSn·g^{-1} d.w.) should be classified as highly contaminated and grossly contaminated. In general, the obtained concentrations of TBT were comparable to those determined globally in the samples from different ports (Tab. I.). These results indicate that TBT in harbor sediments presents - -an environmental risk that may be emphasized by dredging operations in the region.

CONCLUSION

The distribution of TBT in sediment samples was determined at three basins of the Gdynia Port. All collected samples were abundant in sand fraction. There was no concentration below the limit of quantification of the applied analytical method. These results confirm the global tendency for depreciating content of TBT in port sediments after the global ban on TBT in 2008. The concentrations of TBT in the Port of Gdynia were comparable to those determined globally in the samples from other ports.

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References:

[1] Sternberg R.M., Gooding M.O., Hotchkiss A.K., LeBlanc G.A., 2010. Environmental-endocrine control of reproductive maturation in gastropods: implications for the mechanisms of tributyltin-induced imposex in prosobranchs. Ecotoxicology 9, 4-23.

[2] Suzdalev S., Gulbinskas S., Blažauskas N., 2015. Distribution of tributyltin in surface sediments from transitional marine-lagoon system of the south-eastern Baltic Sea, Lithuania. Environ. Sci. Pollut. Res., 22, 2634–2642.

[3] Kim N.S., Hong S.H., An J.G., Shin K.H., Shim W.J., 2015. Distribution of butyltins and alternative antifouling biocides in sediments from shipping and shipbuilding areas in South Korea. Mar. Pollut. Bull., 95, 484-490.

[4] Senthilkumar, K., Duda, C. A., Villeneuve, D. D. L, Kannan, K., Falandysz, J., Giesy, J. P. 1999. Butyltin Compounds in Sediment and Fish from the Polish Coast of the Baltic Sea. Environ.Sci. and Pollut.Res. 6, 200-206.

[5] Radke B., Wasik A., Jewell L., Pączek U., Namieśnik J., 2013. The speciation of organotin compounds in sediment and water samples from the Port of Gdynia. Soil Sediment Contam. 22, 614-630.

[6] Filipkowska F., Kowalewska G., Pavoni B., Łęczyński L., 2011. Organotin compounds in surface sediments from seaports on the Gulf of Gdańsk (southern Baltic coast). Environ. Monit. Assess., 182, 455-466.

[7] Laitano M.V., Castro I.B., Costa P.G., Fillmann G., Cledon M., 2015. Butyltin and PAH contamination of Mar del Plata Port (Argentina) sediments and their influence on adjacent coastal region. Bull Environ. Contam. Toxicol., 95, 513-520.

[8] Briant N., Bancon-Montigny R., Elbaz-Poulichet F., Freydier R., Delpoux S., Cossa D., 2013. Trace elements in the sediments of a large Mediterranean marina (Port Camrgue, France): Level and contamination history. Mar. Pollut. Bull. 73, 78-85.

[9] IMO, 2008. International Convention on the Control of Harmful Anti-fouling Systems on Ships. International Maritime Organization. Derived from: http://www.imo.org/en/about/conventions/listofconventions/pages/international-convention-on-the-control-of-harmful-anti-fouling-systems-on-ships-(afs).aspx

[10] Stewart C., Thompson J.A.J., 1997. Vertical distribution of butyltin residues in sediments of British Columbia harbours. Environ. Technol., 18, 1195 – 1202.

[11] De Oliveira C.R., Dos Santos D., Madureira L.A., de Marchi M.R., 2010. Speciation of butyltin derivatives in surface sediments of three southern Brazilian harbors. J Hazard Mater., 181:851-856.

[12] Dong C.D., Chen C.F., Chen C.W., 2015. Composition and source of butyltin in sediments of Kaohsiung harbor, Taiwan. Estuar. Coast. Shelf. Sci., 156, 134-143.

[13] Szpunar J., Falandysz J., Schmitt O., Obrebska E., 1997. Butyltin in marine freshwater and sediments of Poland. Bull Environ. Contam. Toxicol., 58:859-864.

[14] Radke B., Łęczyński L., Wasik A., Namieśnik J., Bolałek J., 2008. The content of butyl- and phenyltin derivatives in the sediment from the Port of Gdansk. Chemosphere 73, 407-414.

[15] Rosińska S., 2016. Port Gdynia. The official website of the Gdynia Port. Derived from: www.port.gdynia.pl

[16] Wojtkiewicz M., Stasiek K., Galer-Tatrowicz K., Pazikowska-Sapota G., Dembska G., 2015. Validation of analytical methods for determination of tributyltin (TBT) in soils and bottom sediments. BMI 20, 189-194.

[17] Hoch M., Schwesig D., 2004. Parameters controlling the partitioning of tributyltin (TBT) in aquatic systems. Appl. Geochem. 19, 323–334.

[18] Díez S., Jover E., Albaigés J., Bayona J. M., 2006. Occurrence and degradation of butyltins and waster marker compounds in sediments from Barcelona harbor, Spain. Environ. Int. 32, 858-865.

[19] SMOCS, 2012. Contamination in sediments from the Baltic Sea region. Situation and Methods. Derived from: https://www.researchgate.net/publication/301481508_Contamination_in_sediments_from_the_Baltic_Sea_region_Situation_and_Methods_wwwsmocseu

[20] Dowson P. H., Bubband J. M., Lester J. N., 1989. Temporal Distribution of Organotins in the Aquatic Environment: Five Years after the 1989 UK Retail Ban on TBT Based Antifouling Paints. Mar. Pollut. Bull., 26, 487-494.

[21] Undap S.L., Nirmala K., Miki S., Inoue S., Qiu X., Honda M., Shimasaki Y., Oshima Y., 2013. High tributyltin contamination in sediments from ports in Indonesia and Northern Kyushu, Japan. J. Fac. Agric. Kyushu. Univ., 58, 131–135.

[22] Lee C.C., Hsieh C.Y., Tien C.Y., 2006. Factors influencing organotin distribution in different marine environmental compartments, and their potential health risk. Chemosphere 65, 547-59.

[23] Okoro H.K., Fatoki O.S., Adekola F.A., Ximba B.J., Snyman R.G., 2013. Spatiotemporal variation of organotin compounds in seawater and sediments from Cape Town harbour, South Africa using gas chromatography with flame photometric detector (GC-FPD). Arab. J. Chem., 9, 95-104.

[24] Cassi R., Tolosa I., de Mora S., 2008. A survey of antifoulants in sediments from ports and marinas along the French Mediterranean coast. Mar. Pollut. Bull. 56, 1943–1948.

[25] Zhang K.G., Shi J.B., He B., Xu W.H., Li X.D., Jinag G.B., 2013. Organotin compounds in surface sediments from selected fishing ports along the Chinese coast. Chin. Sci.Bull., 58, 231-237.

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