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Butyltins in Marine and Freshwater Sediments of Poland

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Tri-*n*-butyltin (TBT) is an efficient antifouling and other purposes agent used from nineteen sixties mainly in paints on ships and boats. The first regulatory and legislative actions regarding use of this biocide were implamented in France in 1982 and later on other countries also banned use of TBT on vessels shorter than 25 m (82 ft) (Alzieu 1986). Other TBT appliances are used as disinfectans in polishes, waxes, sprays and in laundry washes, slimicide for textile and lumber treatment and in the paper industry, and in cooling water treatment (Fent 1996). TBT is actually a wide-spread very toxic contaminant in the marine environment and the Baltic Marine Environment Protection Commission has recommended that member countries should restrict pollution caused by antifouling paints containing organotin compounds (HELCOM, 1988). There are only limited data available on concentrations and effects of organotins in the Baltic Sea environment (HELCOM 1988 and 1990, Kamran and Falandysz 1995, Stuer-Lauridsen and Dahl, 1995), and on TBTs in sediment in Poland are lacking.

To understand the sources and concentrations of butyltins, species such as tri-, di- and monobutyltin were determined in the surface (0-10 cm) layer of sediments collected from the open Baltic Sea, and coastal marine and inland freshwater areas of Poland in 1993-1995.

MATERIALS AND METHODS

Surface sediment (0-10 cm) samples (~500 g wet weight) were collected using a grab sampler (open sea) and the Ekman-Brige sampler (other areas) in the Baltic Sea, and coastal and freshwater areas of Poland (Figure 1). Sediment was placed in clean polyethylene bags and a subsample (~100 g wet weight) was taken and air dried in the dark in room temperature, and then kept in dark until analysis.
The method for organotin analysis based on a long capillary column gas chromatographic (HRGC) separation and microwave-induced plasma atomic emission detection (AED), after microwave-assisted leaching/digestion of the sample matrix (Szpunar *et al.* 1996). In detail a sample of 0.1-0.2 g of

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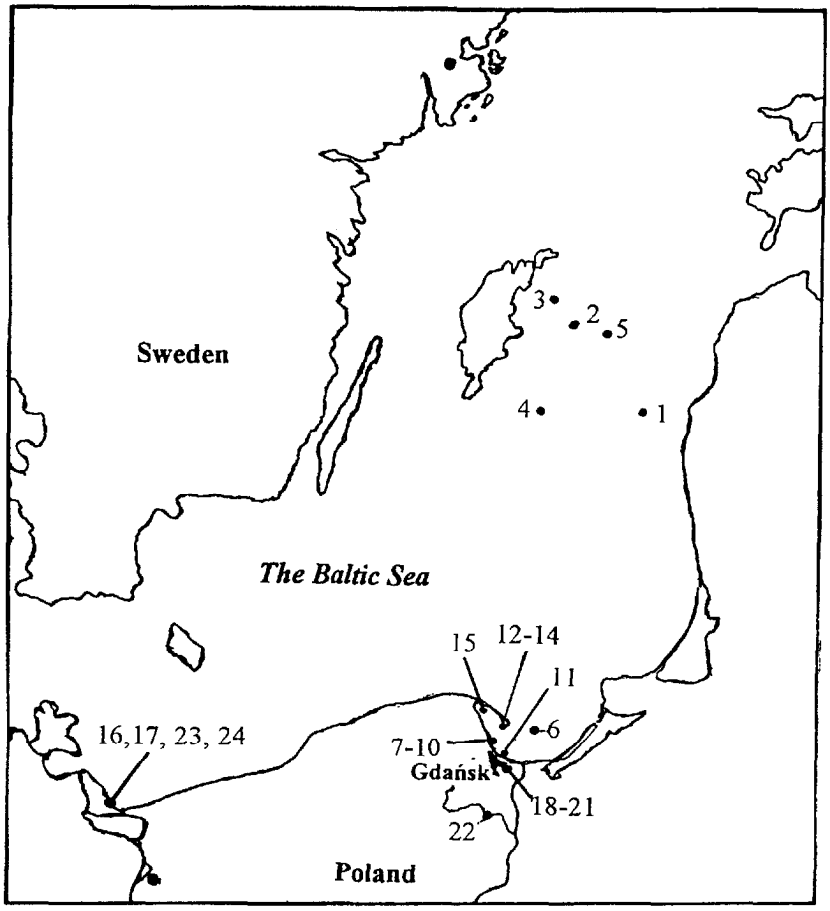

Figure 1. The sampling sites (l-24) of sediment.

dry sediment 100 µl of the Pr_3SnCl internal standard solution (TPrT; Aldrich, St. Quentin Fallavier, France) and 10 ml of acetic acid solution (l+l), were placed in an extraction tube and exposed to microwaves at a power of 60 W (Microdigest Model A301 microwave digestor; Prolabo, Briare, France) for 3 min. The supematant solution was transfered by means of a Pasteur pipette into a narrow-neck 20 ml extraction tube. Acetate buffer (10 ml), ammonia (5 ml), 1% m/v solution of sodium tetraethylborate ($NaBEt_4$ 1 ml) and isooctane (1 ml) containing 20 ng ml^{-1} of tetrabutyltin were added to the supernatant. The mixture was shaken for 5 min. After separation of the phases (several seconds), sufficient water (de-ionized and further purified in a Milli-Q system) was added to force the organic phase into the narrow neck to faciliate its recovery. Chromatographic separation of ethylated tin species was performed on a Hewlett-Packard Model 5890 Series II gas chromatograph with a 30 m x 0.32 mm (i.d.) capillary column coated with DB-210 (J&W) at 0.25 µm film thickness. The chromatograph was

equipped with a split/splitless injection port. Detection was achieved with an HP Model 5921A atomic emission detector. A multi-compound working standard solution of butyltin trichloride, dibutyltin dichloride and tributyltin chlorine each 0.25 µg ml^{-1} were prepared in methanol and diluted with methanol as required. The samples were analysed in duplicate. The method was validated, with two sediments having certified contents of butyltin species (PACS-1 from the National Research Council of Canada and CRM 462 from the Community Bureau of Reference), were reference materials used.

RESULTS AND DISCUSSION

We did not find any historical records as regards to kind, pattern or volume of organotin compounds used as antifouling agents in marine paints, and for other purposes in Poland. Since recommendation by the Helsinki Commission (HELCOM, 1988) the Baltic States should restrict sources of organotins from antifouling paints and so ban use of such agents on a small (<25 m. long) boats.

The analytical data gained within this study clearly indicated noticeably high concentrations of TBTs found in a specific sediment samples (Table 1). In the general speaking the butyltins were found in relatively elevated concentration in some sediment taken from the coastal waters - lower in the sites of relatively low ship traffic, such as the port of Hel and the area of the Bay of Puck, and much higher in the sites of high traffic, such as the port of the city of Gdynia and port of Gdansk.

The butyltins (ΣBTs) concentration recorded in sediment sample taken from marina of the city of Gdynia was 8,100 ng/g on a dry weight basis, and for TBT alone it was 3,500 ng Sn/g. Such high concentration of ΣBTs in sediment seems to be evident of a fresh input of TBT due to its use in antifouling paints. Another sediment sample with relatively high content of butyltins (5520 ng Sn/g dry weight) was taken from one of the canals of the seaport of the city of Gdynia at site 7 (Figure l), which is relatively close to the shipyards and navy, and for sampling sites more distant from the shipyards, at the points 8 and 9, a much lower concentrations (1300-1500 ng Sn/g dry weight) were recorded.
The sediment sample collected from the canal of high ship traffic in port of Gdansk (Figure 1; site 11) contained the butyltins in concentration 1300 ng Sn/g dry weight, which is comparable to that found for the area of similar ship activity in port of Gdynia.
The sediment samples collected from the open Baltic Sea (Figure 1; sites 1-5) as well as those from the central area of the Gulf of Gdansk (site 6) were in low contamination or were free (<0.4 ng Sn/g dry wt) of butyltins.

An earlier study (Kannan and Falandysz, 1995) reported the presence of relatively high concentrations of butyltins (between 14 and 455 ng g^{-1} on a wet weight basis) in various species of fish collected from the Gulf of Gdansk in 1990. Despite the recommendation in 1987 by the Helsinki Commission to reduce by the contract

Table 1. Concentrations of mono- (MBT), di- (DBT), tri- (TBT) and butyltins (SBTs) in surface sediments (in ng Sn/g dry weight)

Site	Date of collection	No	MBT	DBT	TBT	ΣB Ts
Baltic Sea, Open Sea						
56°43.5'N/20°33'E (1)*	4 VI 1994	1	<0.4	<0.4	<0.4	<0.4
57°27'N/19°01'E (2)	2 VI 1994	1	<0.4	<0.4	<0.4	<0.4
57°33.5'N/19°01'E (3)	30 V 1994	1	<0.4	<0.4	<0.4	<0.4
56°48'N/20°16'E (4)	4 VI 1994	1	23	4.2	3.2	30
57°20'N/20°03'E (5)	2 VI 1994	1	17	8.0	16	41
Gulfs, Bays and Coastal Areas						
Gulf of Gdańsk						
Open area, 54°35'N/18°58,5'E (6)	30 V 1994	1	17	2.2	<0.4	19
Gdynia, seaport (7)	22 IX 1993	1	320	2200	3000	5520
Gdynia, seaport (8)	22 IX 1993	1	590	310	470	1300
Gdynia, seaport, Kościuszko Square (9)	22 IX 1993	1	630	320	560	1500
Gdynia, marina (10)	22 IX 1993	1	2000	2600	3500	8100
Gdańsk, Wisłoujście, ferry (11)	19 IX 1993	1	460	370	470	1300
Hel, port - eastern part (12)	22 IX 1993	1	110	2.8	<0.4	113
Hel, port - western part (13)	22 IX 1993	1	110	53	41	200

Table 1, continued

Site	Date of collection	No	MBT	DBT	T B T	Σ BTs
Hel, port - outside area (14)	22 IX 1993	1	18	<0.4	9.8	28
Puck Bay (15)	7 VII 1995	11	13±2 (9.7-16)	5.4±6.8 (<0.4-22)	28±13 (9.4-45)	47±12 (28-66)
Szczecin Lagoon, Karnocice (16)	7 VII 1994	1	2.4	<0.4	6.2	8.8
Szczecin Lagoon, Stepnica, port (17)	5 VII 1994	1	7.0	4.9	11	23
Inland Freshwater Areas						
Dead Vistula River Canal (18)	21 IX 1993	1	11	<0.4	48	59
Gdańsk, Olszynka, canal (19)	21 IX 1993	1	7.9	3.1	51	62
Gdańsk, Czarna Łacha River (20)	21 IX 1993	1	32	12	21	65
Gdańsk, drainage canal (21)	21 IX 1993	1	1.4	<0.4	<0.4	1.8
Wieżyca River, Starogard Gd. (22)	16 VII1994	1	3.3	<0.4	<0.4	3.7
Świna River, Płachcin (23)	8 VII 1994	1	2.2	5.2	9.6	17
Mieliński Canal (24)**	8 VII 1994	1	5.5	12	17	35

*Sampling site (Figure 1)

**Former Soviet military base

parties the pollution of the Baltic Sea with organotins by antifouling paints, the data gained for a limited number of sediment samples analysed in this study seems to indicate that such measures, if taken, remain not effective in the area of the Gulf of Gdansk.

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