APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 8, 5–10 (1994)

Dissolved Butyltins in Marine Waters of the Netherlands Three Years After the Ban

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In 1990 the Dutch government banned the use of tributyltin-containing antifouling paint for ships up to 25 m long. Concentrations of dissolved (<0.45 μm) tributyltin and its degradation products di- and mono-butyltin were determined in six selected marinas during three consecutive years with a frequency of five times a year, starting in 1990. The highest butyltin concentrations were found in Scharendijke located in the salt-water lake Grevelingen: up to 2500 ng dm^{-3}. In tidal-water marinas butyltin concentrations were in the order of 50–300 ng dm^{-3}, depending on the boating and dredging activity. In some marinas higher butyltin concentrations were found during the summer period, probably indicating the illegal use of tributyltin-containing antifouling paints. No clear trend of decrease in dissolved tributyltin concentrations in the different marinas has been found. Due to the equilibrium between the butyltins dissolved in the water and the butyltins adsorbed onto the sediment, water concentrations will remain more or less constant.

Keywords: Butyltin compounds, tidal waters, marinas, monitoring, The Netherlands

INTRODUCTION

Tributyltin (TBT) has been used extensively for almost 30 years in marine paints to prevent fouling, e.g. on boat hulls. In the late 1980s the use of TBT-containing antifouling paints grew to an estimated 136 000 kg year^{-1}.[1] The major sources of TBT entry into the aquatic environment were shown to be linked directly to harbours, moored boats in marinas and facilities that service recreational and commercial vessels.[2-5]

Concern about the negative effects of butyltin compounds, especially TBT, in the aquatic environment first emerged in France in the early 1970s.[6] The serious problems encountered in the commercial culture of the Pacific oyster (*Crassostrea gigas*) in France were soon followed by reports of similar problems in England.[7] Although concern about the effects of organotin compounds was initially highlighted by the problems experienced by commercial shellfish fisheries, considerable evidence of far more extensive effects in the aquatic environment was subsequently presented. As a result the French government banned in 1982 the use of TBT-containing antifouling on boats less than 25 m long. The UK followed in 1987 with restrictions on the use of antifouling paints containing TBT. In the UK, the Environmental Quality Status for TBT in seawater was set at 2 ng dm^{-3}.

In Dutch coastal zones, specific effects of TBT such as thickening of the valve of the Pacific oyster and imposex of the dog whelk have been reported.[8] In 1988 the Tidal Waters Division of the Dutch Ministry of Transport and Public Works and the University of Bordeaux began a base-line study on the impact of butyltins in Dutch coastal waters. The concentrations of the different butyltin compounds were measured in the water phase (dissolved and particulate) and in the sediments in July and October 1988. Dissolved tributyltin (TBT) was found mainly in marinas and concentration ranged from 22 to 4000 ng dm^{-3}. Particulate TBT was ubiquitous in the Rhine and Scheldt estuaries; concentrations varied between 224 and 573 ng g^{-3} dry matter.[9, 10] In the coastal zone of the North Sea no TBT could be detected.[9] A survey in which the distribution of dissolved butyltins in Dutch marinas and harbours was studied was performed in 1989.[5] The range in concentration of TBT, dibutyltin (DBT) and monobutyltin (MBT) was between 0.1 and 7210 ng dm^{-3}, 0.1 and 1340 ng dm^{-3}, and 0.1 and 460 ng dm^{-3}, respectively.

In the harbours, average organotin concentra-

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CCC 0268–2605/94/010005–06

Received 21 June 1993
Accepted 15 October 1993

tions were relatively low (for TBT, <76 ng dm^{-3}), while the marina waters gave rise to higher average concentrations, for TBT between 71 and 3620 ng dm^{-3}. TBT concentrations in the tidal marinas were relatively low, 110 and 160 ng dm^{-3}, compared with the values found in fresh and brackish waters where concentrations of TBT reach values up to 930 ng dm^{-3}. Highest TBT concentrations (maximum 7210 ng dm^{-3}) were found in the enclosed Grevelingen salt-water marinas.

In the Netherlands the results from the 1988 and 1989 studies initiated the ban of the use of organotin-containing antifouling paints for ships up to 25 m long. The Environmental Quality Objective for seawater, based on ecotoxicological data for TBT, were set at 10 ng dm^{-3}.[11] After it was clearly demonstrated that high levels of butyltins occurred in the Dutch marinas, a monitoring programme was started in 1990 in order to detect whether butyltin water concentrations would decrease. This paper describes the results from a three-year monitoring programme in six selected marinas, geographically spread along the Dutch coastal zone.

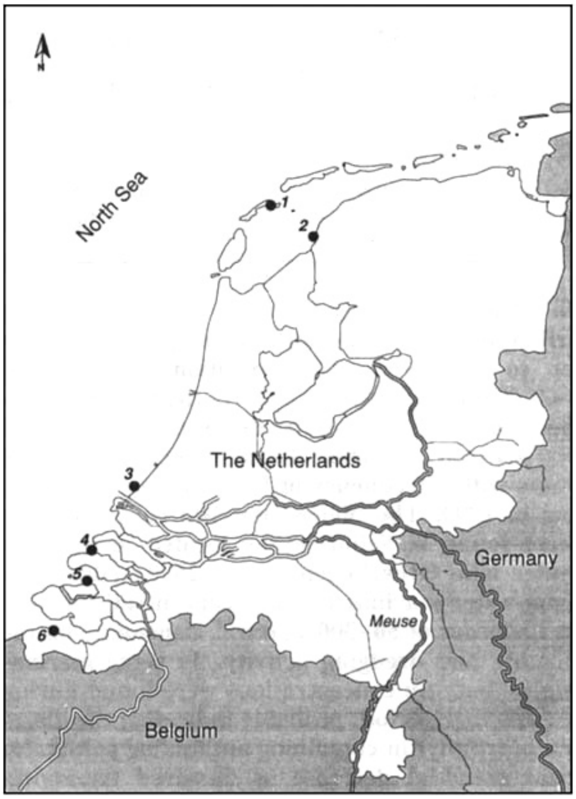


Figure 1 Sampling sites for the Dutch dissolved-butyltin monitoring programme.

MATERIALS AND METHODS

Sampling sites

The sampling sites are geographically spread along the Dutch coastal zone (Fig. 1). The selected sites for the Dutch programme monitoring TBT are given in Table 1.

Surface water samples from three different places in six different marinas were taken from the shore, 0.3 m below the water surface. Previous studies have indicated that TBT concentrations can vary from 2- to 20-fold over a tidal cycle, with the highest concentrations at low tide.[12-14] Therefore samples were always collected at the same tidal moment, in this case at low tide. Sampling was done five times a year, in March, May, July, September and December. The distance from the sampling location to the nearest boat was always more than 5 m. The first water sample was always taken in the mouth of the marina, and the last sample as far as possible inside the marina.

Table 1 Sampling sites for the TBT monitoring programme

Location	Marina	Boating activity[a]	Dredging activity	Tidal
1 Waddensea	Vlieland	Low	1/year	Yes
2 Waddensea	Harlingen	Low	None	Yes
3 Northsea	Scheveningen	High	None	Yes
4 Lake Grevelingen	Scharendijke	High	None	No
5 Eastern Scheldt	Colijnsplaat	High	3/year	Yes
6 Western Scheldt	Breskens	Medium	2/year	Yes

[a] Measures the number of boats and occupation during the whole year: low, average no. of boats <100; medium, average no. 100–350; high, average no. >350.

Analysis

Water samples (0.5 dm^3) were immediately filtered at 0.45 µm with disposable sterile Nalgene filtration units. Filtrates, acidified with hydrochloric acid to pH 2, were stored in 500 cm^3 Pyrex bottles at 4 °C in the dark prior to analysis. The storage time of the samples was never longer than two weeks. Sample pre-treatment and storage conditions as described above were found suitable to achieve good stability of TBT and MBT, while DBT stability was found to be more doubtful.[4,16] Determination of the different dissolved butyltins was performed by means of on-line hydride generation (15 cm^3 of a 4% $NaBH_4$ solution), cryogenic trapping on a PTFE gas chromatographic column (100 mg Chromosorb GNAW 60/80 coated with 3% SP-2100) and atomic absorption detection at 224.6 nm (slit 0.2 nm) as described earlier in detail.[15] Dimethylbutyltin was used as an internal standard for correction of the efficiency of hydride generation, purge and atomization for DBT and TBT. Correction for these parameters was not necessary for MBT. The standard addition technique was used to quantify levels of TBT, DBT and MBT in the water samples.

Results are expresed in ng dm^{-3} of TBT, DBT and MBT ions. Detection limits, based on 3σ of the blank, for all three butyltin species were 0.1 ng dm^{-3} when analysing 0.500 dm^3 water. The recovery of the internal standard for the analysed seawater samples was always >90%. The standard deviation with the use of the internal standard at a 100 ng dm^{-3} level was 6% ($n = 7$) for each compound. During intercomparison exercises, coordinated by the Community Bureau of Reference (BCR), our laboratory achieved acceptable results (within 20% of the mean value) in analysing synthetic water samples.

RESULTS AND DISCUSSION

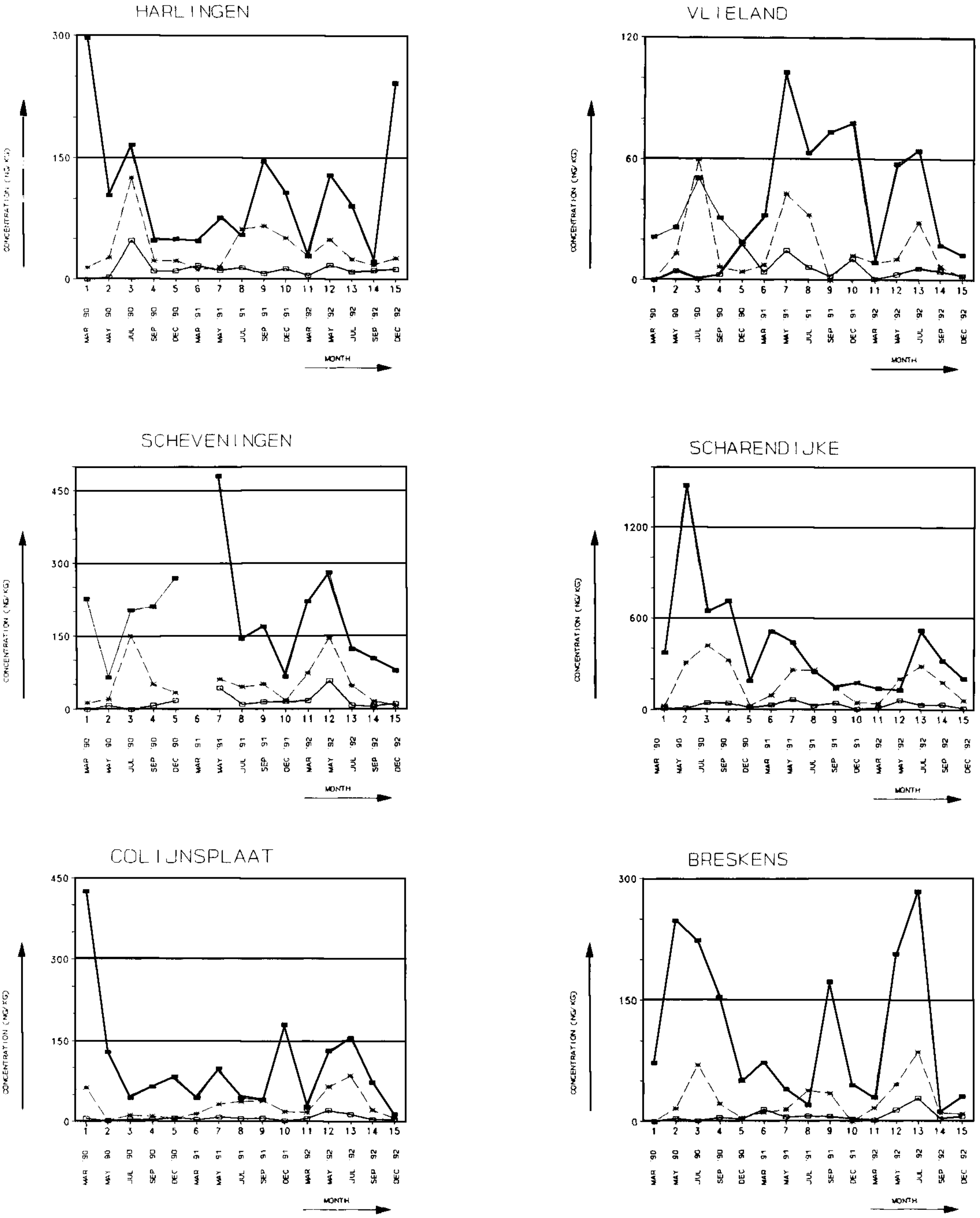
Concentrations of dissolved butyltin compounds varied considerably between the different marinas, as can be seen in Fig. 2. In this figure the mean concentrations of the three sample locations are given. In all marinas a gradient in concentration of TBT was found with lowest concentrations in the mouth of the marina and highest concentration at the land-side of the marina. The range in concentrations for TBT, DBT and MBT varied between 0.1 and 2500 ng dm^{-3}, 0.1 and 400 ng dm^{-3}, and 0.1 and 110 ng dm^{-3}, respectively. The highest TBT concentrations were found in Scharendijke (4) with a mean of 480 ng dm^{-3} for the last three years.

In Table 2 the mean concentrations for each year for the different marinas are given. For all locations, except for Scharendijke (4) and Colijnsplaat (5), there is no significant decrease in TBT concentration during the past three years. For Scharendijke (4) and Colijnsplaat (5) there is a decrease in the mean TBT concentration in the last two years. This decrease in the mean TBT concentration is a factor of 2–3 compared to the mean concentration observed in 1990.

All TBT concentrations determined are well above the Environmental Quality Target (EQT) value of 10 ng dm^{-3} for Dutch waters. The EQT, set by the Dutch Government, is exceeded by a factor of 2–250. The relatively high TBT concentrations found in Scharendijke (4) are caused by the fact that there is no tidal movement in Lake Grevelingen, this is in agreement with earlier observed published data.[5] All the other locations do have a tidal movement, so most of the dissolved butyltins are transported to the open waters.

Despite the fact that the half-life for TBT is very short in water, approximately 6 days,[17] water concentrations are still in the range of 30–2500 ng dm^{-3}. These high TBT water concentrations are most probably due to desorption of the sediments. In sediments TBT has a half-life of almost two years under anaerobic conditions, so TBT sorbed to the sediment at depth will act as a source for the TBT water concentrations during many years.[18]

In Fig. 2 the seasonal influence is clearly demonstrated for the marinas Scharendijke (4) and Breskens (6): in the summer period there is an increase in the TBT concentration. An explanation for this increase is most probably that the ban on TBT-containing antifouling paint is not followed by the owners of the yachts, so that there is a new TBT input during the summer period from freshly painted yachts. This significant increase in TBT concentrations during the summer period at Scharendijke (4) and Breskens (6) was not observed at the other four locations despite the similar conditions such as tidal movement, harbour size and boating activity, so probably the increase in TBT concentrations at locations 4 and 6 is not related to any geochemical process and the implication that these increases are due to new inputs is justified.


HARLINGEN

VLIELAND

SCHEVENINGEN

SCHARENDIJKE

COLIJNSPLAAT

BRESKENS

Figure 2 Butyltin concentrations in the six selected marinas. The concentrations in ng dm^{-3} correspond to the mean value, from the three sampling points, in the marina. ■, TBT; *, DBT; □, MBT.

The level of boating activity is not linearly related to the observed TBT levels in the different tidal-water marinas. The dredging activity seems to be more important for the level of TBT contamination in a marina. Comparing the marinas with low boating activity, namely Vlieland (1), which has been dredged each year in the past three years, and Harlingen (2), which was not dredged in the past three years, it is clear that the TBT contamination is higher in the Harlingen marina (2) by a factor of 3. The same is true for the marinas with a high boating activity. Only the marina of Colijnsplaat (5) was frequently dredged. TBT contamination in Scheveningen (3) and Scharendijke (4) is higher than in Colijnsplaat (5) by a factor of 4 and 11, respectively.

Generally, TBT contamination in marinas that were frequently dredged is lower by a factor of 3–10 compared with marinas which were not dredged for the past three years. Dredging the marina removes TBT-contaminated sediments and, because of the sediment–water partitioning, finally results in lower TBT concentrations in the water phase.

CONCLUSIONS

The more or less constant TBT concentrations in the water originate from the sediments. The increased TBT levels in summertime are most probably due to the fact that there is still an illegal use of TBT-containing antifoulings. Contamination of the marine environment with TBT has been shown to occur in many countries. The levels of TBT in Dutch marinas were generally between 30 and 250 ng dm^{-3} and were similar to those reported for marinas in the UK,[19] France,[20,21] Spain,[22] the USA[23] and New Zealand.[24] Significant reductions in TBT water concentrations as reported for the UK[14,15,17-19] and France[25] have not been found for marinas in the Netherlands. The impression exists that the use of TBT-containing antifouling paint was already reduced and replaced by the use of other types of antifouling paint in the late 1980s, thus not resulting in a significant decrease of TBT water concentrations. (R. Ritsema, personal communications with several marina masters in the Netherlands, 1989).

Table 2 Mean butyltin concentrations for six sites of the Dutch butyltin monitoring programme

Marina	Year	TBT	DBT	MBT
1 Vlieland	1990	23 ± 24	18 ± 16	5 ± 10
	1991	73 ± 46	18 ± 20	7 ± 4
	1992	32 ± 39	12 ± 12	3 ± 3
2 Harlingen	1990	130 ± 100	44 ± 44	13 ± 19
	1991	85 ± 44	42 ± 24	12 ± 6
	1992	100 ± 90	30 ± 18	10 ± 6
3 Scheveningen	1990	195 ± 150	53 ± 70	6 ± 9
	1991	171 ± 180	44 ± 32	20 ± 18
	1992	160 ± 130	57 ± 73	20 ± 28
4 Scharendijke	1990	880 ± 1100	210 ± 200	24 ± 18
	1991	290 ± 220	160 ± 100	34 ± 25
	1992	270 ± 190	150 ± 100	29 ± 20
5 Colijnsplaat	1990	61 ± 170	20 ± 26	4 ± 4
	1991	33 ± 65	28 ± 12	4 ± 3
	1992	32 ± 65	38 ± 34	9 ± 6
6 Breskens	1990	61 ± 93	22 ± 28	3 ± 3
	1991	31 ± 78	22 ± 16	7 ± 6
	1992	53 ± 140	40 ± 32	12 ± 10

Reduction of TBT water concentrations in marinas to as low as the EQT value of 10 ng dm^{-3} will take a long time: first all the TBT sorbed to the sediments must be desorbed or all TBT-contaminated sediments must be dredged and dumped at a suitable location.

To obtain an impression of the extent of illegal usage of TBT-containing antifouling paints, the monitoring of the water phase is suitable. For the long-term decrease of the TBT load in a marina it is useful to monitor both phases: water and sediment. Therefore in 1993 the Tidal Waters Division of Rijkswaterstaat started, as well as the TBT monitoring programme for water, a TBT monitoring programme for sediments. At the same locations and with the same frequency as for the water-phase monitoring programme, organotin determinations will be carried out in order to get an impression of the reduction of TBT concentrations in the sediments.

Acknowledgements The author would like to thank Alfred de Jong and Petra Aarnoutse for butyltin water analysis. Thanks also go to Piet de Rijke, Ton van Schie and Jaap Nijdam for collecting the samples.

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