PART E: SUBSTANCES AND NEW CRITERIA TO WATCH

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2 TBT Emissions inside the port of Rotterdam .....

2.1 Estimation of emissions .....

2.2 Application of the Mam-Pec model.....

2.3 Comparison with measured data.....

2.4 Forecasts for TBT and new antifoulants

2.5 Conclusions .....

References .....

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Full report and meeting reports form workshops within the project can be downloaded from:
http://w3g.gkss.de/i_a/dredged_material/index.html

General information on the POR-II project can be found at:
http://www.portmanagement.com/UK/Waterandweather/Waterquality/PORII/Index.asp

2 TBT emissions inside the port of Rotterdam

Shipping and cargo-handling related emissions in the Port of Rotterdam include mineral oil and the antifouling product TBT (tributyltin). TBT is used as an additive to marine paints, to prevent fouling by organisms, and leaches continuously from the paint applied below the waterline at typical leaching rates of 1– 5 μg/cm^2/day (Evers et al., 1995).

Due to the residence time (several days) of commercial ships in port, the affinity of TBT to particulate matter, and due to the increased settling of particulate matter in estuarine harbours, sediments in large commercial harbours usually have relatively high concentrations of TBT. Problems with TBT contamination of sediments and dredged material from ports and harbours have been documented widely in the international literature during the last two decades (Fent, 1996).

In the present chapter the computer model Mam-Pec Version 1.2, developed by Delft Hydraulics/WL and IVM (Van Hattum et al., 1999) was used to estimate emissions and concentrations of TBT in sediment, particulate matter and the water phase. This model was developed at the request of CEPE (European Paint Makers Association within CEFIC) and the EU-DG XI (CEPE-AWG, 1999). The dimensions and shipping statistics of the port of Rotterdam have been used for the prototype commercial harbour in this model.

In chapter 2.1 a description is given of the estimation of emissions of TBT in the Rotterdam port area. Predicted concentrations and descriptions of compound properties of TBT, port dimensions and environmental parameters assumed for the model estimations are presented in chapter 2.2. In chapter 2.3 a comparison is made with measured concentrations of TBT. Tentative forecasts of expected concentrations of compounds, suggested as alternative biocides for TBT, are discussed in chapter 2.4.

2.1 Estimation of emissions

Emissions of antifouling products form shipping cannot easily be estimated. Usually the emissions are quantified as the product of a *leaching rate* (μg/cm^2/day) and the *total antifouled underwater area* of the ships present. The leaching rate depends on the type of compound characteristics and age of paint matrix and velocity of the ship. The total antifouled underwater area depends on shipping intensities, dimensions of the various categories of ships, and many other factors such as cargo load and residence time of the various ships.

Leaching rate

Leaching rate estimates for different antifouling compounds, as reported in a selection of recent experimental or risk-assessment studies, have been summarised in table 2-1, adapted from the CEPE study (CEPE, 1999; Van Hattum et al., 1999). For many compounds broad ranges of leaching rate estimates have been observed. Copper leaching rates usually are higher than for other compounds. Leaching rates reported for TBT usually are below regulatory implied values of 4 μg/cm2/day in some countries (USA, Sweden).

Table 2-1: Summary of leaching rate estimates reported from various studies

Compound	Leaching rate µg/cm^2/day	Type of study	Author
TBT	4	North Sea	Stronkhorst *et al*. (1996)
	2.5	Marina	Johnson and Luttik (1996)
	0.1 – 5	Harbour	Willingham and Jacobson (1996)
	1.3 – 3.0	Ships > 25m	Lindgren *et al*. (1998)
Cu	6.2	Marina	Matthiesen and Reed (1997)
	1-20	Not specified	Hare (1993)
	8 – 25	Ships >12m	Lindgren et al. (1998)
	37 – 101	Ships > 25m	Lindgren *et al*. (1998)
	4 – 6 *	Exp. Studies	Berg (1995)
Irgarol	2 – 16	Marina	Ciba (1995)
	5	Marina	Scarlett *et al*. (1997)
	2.5 – 5	Exp. Studies	Thomas et al. (1999)
Sea-Nine 211	1 (0.1 – 5)	Harbour	Willingham and Jacobson (1996)
Zinc Omadine	3.3	Exp. Studies	Thomas et al. (1999)
Diuron	0.8 – 3.3	Exp. Studies	Thomas et al. (1999)
Dichlofluanid	0.6 – 1.7	Exp. Studies	Thomas et al. (1999)

* after 21 days. During the first 21 days leaching rates ranged between 7 – 61 µg/cm^2/day.

In co-operation with the CEPE Antifouling Working Group, the following values were proposed for the Mam-Pec model:

Copper	50	µg/cm^2/day
TBT	4	µg/cm^2/day
Other biocides	2.5	µg/cm^2/day

In the default scenarios of the Mam-Pec model the leaching rate for moving ships and ships at berth were taken similar because of the large uncertainties in the presently available data.

Estimation of antifouled underwater area

In the Mam-Pec model the total antifouled underwater area is derived from estimated average underwater areas for different length categories of ships, according to Willingham and Jacobson (1996) and the annual number of port arrivals of these length classes. In table 2-2 an overview is presented of the annual arrivals of sea going ships in Rotterdam and the total of ship movements in the period 1995 – 1998, as derived from the harbour information system of the port of Rotterdam.

Based on the figures of 1998 an estimation was made with the Mam-Pec model of the total emissions from ships moored or at berth (average period in port of 3 days) and from the total of ship movements in the harbour area (average manoeuvring time of 3 hrs). The relevant figures are presented in table 2-3. Details of the estimation procedure are described in Van Hattum et al. (1999). The Mam-Pec model predicts an average emission of approximately 35 kg/day or 13 tonnes/year in the Rotterdam port area, most of which stems from ships at berth (12.1 t/y). The contribution form moving ships is estimated at 8% (1.1 t/y).

Model predictions, derived from the Mam-Pec model, were in agreement with earlier (around 1990) estimates for the total amount of TBT emitted in Dutch waters of 11 – 28 t/y (Willemsen and Ferrari, 1992; Evers et al., 1995). Assuming that the number of ships in the Rotterdam harbour area account for 60% of the total of ships visiting Dutch ports, this implies a total emissions of TBT in the Port of Rotterdam of approximately 7 –17 t/y.

As demonstrated in figures 2-1 and 2-2 the majority of the TBT emissions originate from the larger ship classes (> 100 m). Although the small ship category (<100 m) constitutes almost 46 % (n = 13636) of the ships arriving in the Port of Rotterdam, their contribution to the total TBT emissions is relatively small: 6 % of the estimated TBT emissions (0.8 out of 13.2 t/y).

When a value of 1 μg/cm^2/day is used as minimum leaching rate for ships at berth, as mentioned by Willemsen and Ferrari (1992), and a value of 4 μg/cm^2/day is used for moving ships, the total emission is estimated at 4.0 t/y with 1.0 t/y from moving ships and 3.0 t/y from ships at berth.

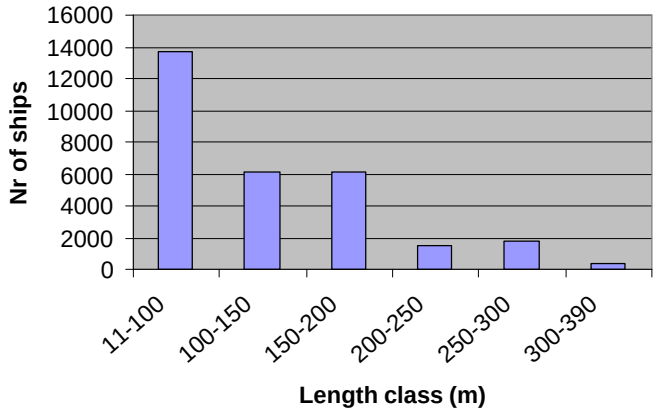

Figure 2-1: Port arrivals of sea going ships in Rotterdam (1998) according to length category

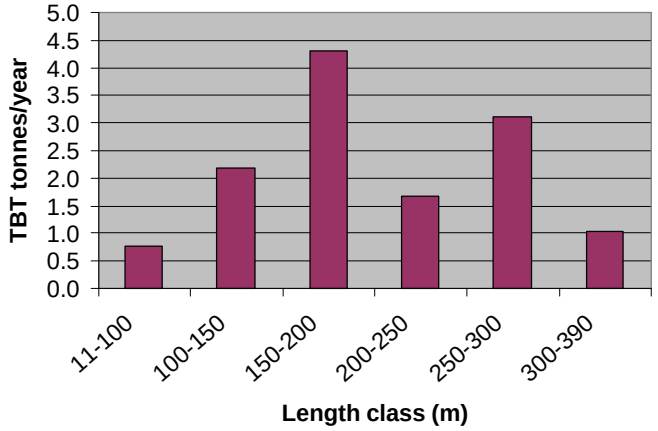

Figure 2-2: Total annual emissions of TBT in the Port of Rotterdam (1998) for different length categories of ships

Table 2.2: Ship arrivals of sea-going vessels at the port of Rotterdam by length class, 1995-1998.

	1998		1999		1996		1995
Class of length	Number	GRT/GT[a]	Number	GRT/GT[a]	Number	GRT/GT[a]	Number
11 – 100	13,636	27,808	13,930	27,050	14,305	27,426	-
101 – 150	6,126	46,269	6,220	47,652	6,179	47,114	-
151 – 200	6,157	121,691	5,932	119,092	5,593	114,239	-
201 – 250	1,450	53,333	1,394	52,406	1,378	53,171	-
251 – 300	1,790	108,088	1,782	106,468	1,666	98,525	-
301 – 380	392	49,712	349	45,481	295	40,187	-
							-
Total	29,551	406,901	29,607	398,149	29,416	380,662	29,319
ship movements sea-going vessels	83,535		82,912		82,313		87,348
Inland vessels	-		133,000		133,000		125,000

[a] Unit: GRT/GT x 1000 tons; source: Port of Rotterdam (1998). - = no data available or not included

Table 2.3: Estimation of emissions of TBT in Mam-Pec model

Length class	Average surface area antifouled	Port arrivals 1998	Total ship move-ments	Application factor [b]	Emission of TBT from moored ships [c]	Emission of TBT from moving ships [b]	Emission of TBT from moored ships	Emission of TBT from moving ships
M	m^2			%	kg/day	kg/day	t/year	t/year
11-100	450	13636	51705 [a]	90	1.82	0.29	0.7	0.1
101-150	3061	6126	12252	90	5.55	0.46	2.0	0.2
151-200	5999	6157	12314	90	10.93	0.91	4.0	0.3
201-250	9917	1450	2900	90	4.25	0.35	1.6	0.1
251-300	14814	1790	3580	90	7.85	0.65	2.9	0.2
301-380	22645	392	784	90	2.63	0.22	1.0	0.1
Total		29551	83535		33.0	2.9	12.1	1.1

[a] total of manoeuvring at arrival and departure; transit traffic added to the 11-100 m category. [b] fraction of ships with TBT containing antifouling; for all ships a leaching rate of 4 μg/cm^2/day was used. [c] average residence time: 3 days. [d] average manoeuvring time: 3 hrs

It should be mentioned at this stage that large uncertainties are implied in the emission estimation, related to variations in the leaching rate (age and type of paint matrix, velocity of the ship), large variations in the estimated exposed antifouled surface area (due to differences in design of underwater area, loading of ship), and variations in assumed exposure time (time in port, manoeuvring time). No quantitative estimations of the uncertainty have yet been made; it is expected that this may well range for individual ships from less than 100% to several 100%.

2.2 Application of the Mam-Pec model

In the Mam-Pec model several prototype environmental scenarios can be chosen (commercial harbour, estuarine harbour, marina, shipping lane and open sea). These generic environments can be edited to a limited extent to match user defined dimensions. An example of the editing screen is given in figure 2-3.

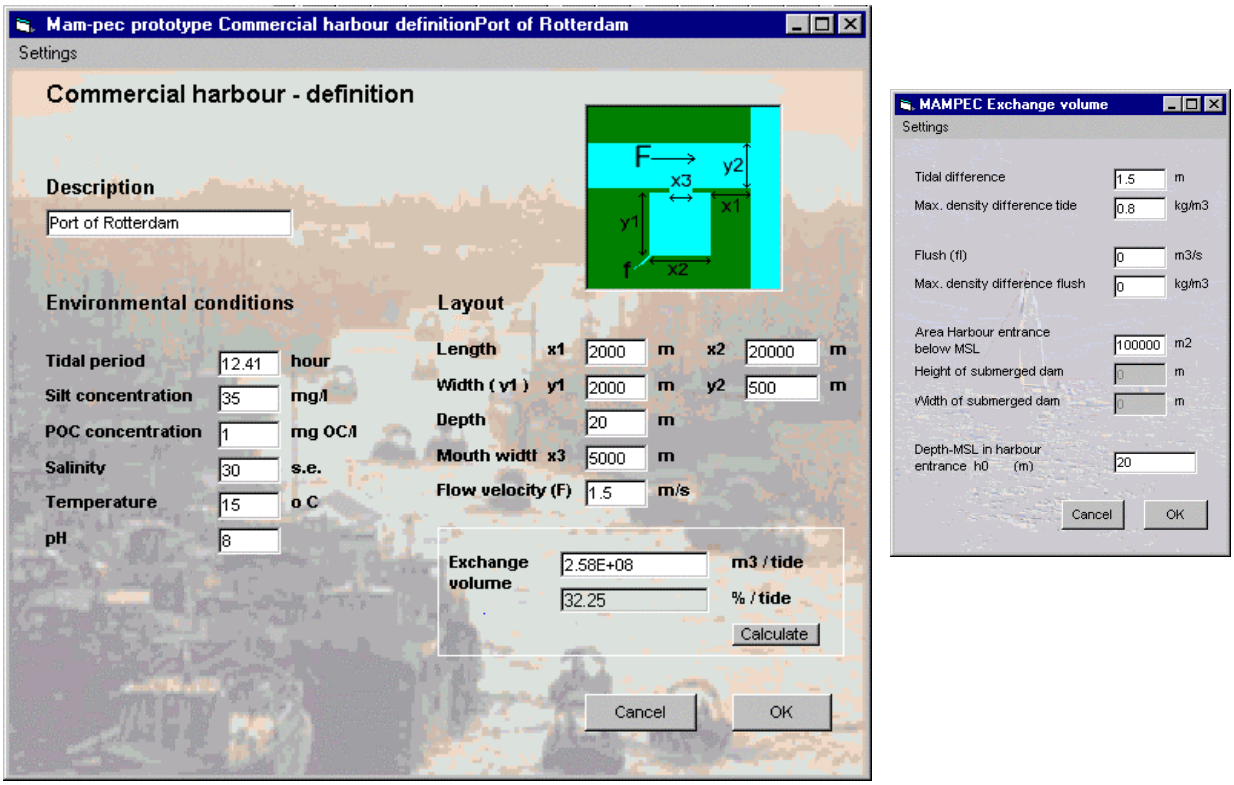

Figure 2-.3: Editing screen of port dimensions and environmental parameters in Mam-Pec 1.2

The complex geometry and hydrography of the port of Rotterdam was approached in the Mam-Pec model with two different scenarios. In the first scenario the geometry of the Rotterdam port area was conceptualised as a rectangular area (2 x 20 km; 4000 ha; depth 20 m), with a 5 km wide open front to the river in order to mimic a harbour segment with an average water exchange of 32% per tidal period. A second scenario, with a 10 km wide open front to the river was chosen to represent harbour segments with a water exchange of 65% per tidal period. The dimensions assumed are indicated in appendix 2.2a.

The hydrodynamic exchange in the Mam-Pec model is derived from the following parameters: density differences (between marine and freshwater), tidal period and height, river flux and the dimensions of the rectangular port area. For the calculations for TBT physico-chemical and environmental data (appendix 2.2b) were taken as presented in Van Hattum et al. (1999), which were used in recent Dutch risk assessment studies (Evers et al., 1995; Stronkhorst, 1996). Combined with the emission scenarios for TBT presented in the previous chapter (table 2-3) steady state calculations were executed.

Predicted concentrations are indicated in table 2-4 and 2-5. Predicted average sediment concentrations (mg/kg dry wt; sediment with 5% Org-C) for the two scenarios (with 65% and 32% exchange per tidal period) ranged from minimum values of 0.01 mg/kg (near the river

entrance) to average values of 0.7 – 1.6 mg/kg in the harbour segments. In the poorly flushed harbour sections (rear end of harbour) maximum predicted concentrations ranged from 2.2 to 2.8 mg/kg.

Table 2-4: Predicted concentrations of TBT for the Port of Rotterdam for segments with an average water exchange of 32% per tidal period

	Dissolved µg/L	Total* µg/L	Sediment mg/kg Org-C	Sediment** mg/kg dry weight
Average	0.82	0.85	33	1.6
Median	0.95	0.99	38	1.9
Minimum	0.006	0.007	28	0.01
P_{95}	1.40	1.45	56	2.8
Maximum	1.40	1.46	56	2.8

* based on concentration of suspended matter of 35 mg/L with 3% Org-C; ** sediment with 5% Org-C

Table 2-5: Predicted concentrations of TBT for the Port of Rotterdam for segments with an average water exchange of 65% per tidal period

	Dissolved µg/L	Total* µg/L	Sediment mg/kg Org-C	Sediment** mg/kg dry weight
Average	0.39	0.41	16	0.7
Median	0.04	0.04	1.4	0.07
Minimum	0.007	0.007	0.3	0.01
P_{95}	1.2	1.2	46	2.3
Maximum	1.2	1.2	46	2.2

* based on concentration of suspended matter of 35 mg/L with 3% Org-C; ** sediment with 5% Org-C

Due to differences in the spatial distribution patterns of predicted concentrations in both scenarios, the differences between median and average values do not coincide and differ between both scenarios.

Other calculations for more shallow (10 m) poorly flushed harbour segments (not presented here) yielded TBT concentrations up to 20 mg/kg.

2.3 Comparison with measured data

A compilation of measured TBT concentrations form various national and international monitoring studies is presented in table 2-6 (water) and 2-7 (sediment). In table 2-8 sediment concentrations measured in the annual monitoring programmes of the Rotterdam Municipal Port Management and Rijkswaterstaat have been summarised. The available data confirm that the highest concentrations usually are found in harbours and marinas and that decreasing gradients towards open sea locations can be observed. The predicted minimum water concentrations of 0.006 – 0.007 µg/L are in the order of the concentrations measured in coastal areas and the concentrations measured in the mouth of the Nieuwe Waterweg in the early '90s (Länge, 1996). The median total water concentrations predicted with the Mam-Pec model for the harbour segments (0.04 – 0.9 µg/L) are well above the range of values reported by Länge (1996) measured in the upstream part of the Nieuwe Waterweg (0.03 – 0.04 µg/L) and similar or above values measured in other international harbours, such as e.g. Bremerhaven and Genoa (table 2-6).

In the study reported by Stronkhorst (1996), sediment TBT concentrations in the Rotterdam area ranged from 0.01 – 0.1 mg/kg (dry weight) at the entrance of the Nieuwe Waterweg to maximum values of 2.1 mg/kg in the Rotterdam area (figure 2-4).

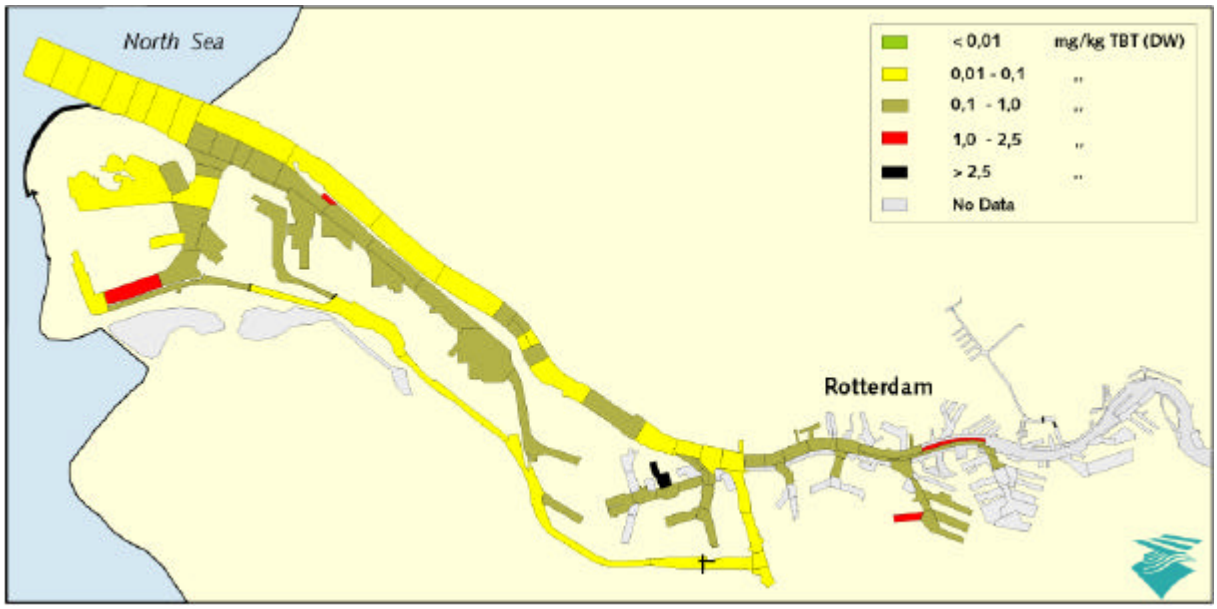

Figure 2-4: Spatial distribution of TBT in the port of Rotterdam, 1995 (Stronkhorst, 1996). Reproduced with permission of the RIKZ.

Similar spatial trends have been observed in the Port of Rotterdam for other years (table 2-8). The mean and maximum TBT concentration, measured in the period 1997 – 1999 seem to be lower than values encountered in the period 1994 – 1996.

A similar range (0.03 – 2 mg/kg dry weight) has been reported for the Noordzeekanaal and the Amsterdam Port area (Van Hattum et al., 1996) and other harbours in the Netherlands (Evers et al., 1995). Increased values for TBT in harbour areas also show up in the database of the ICPR. Average annual tributyltin concentrations in 1996 of suspended matter increased from 0.01 mg/kg in Lobith (German/Netherlands border) to 0.104 mg/kg in Maassluis, situated a few kilometers downstream of Rotterdam (ICPR, 1998).

Table 2-6: Measured TBT in water (in ng/L) in European harbours, estuaries and open sea

Harbour, period	Coastal area	Mouth	Estuary	Harbour	Open Sea
Bremerhaven (1990-1993)	5 – 10	15 - 30	20 - 35	200 – 350	
Genoa (1990-1992)	<5 – 10			80 – 150	
Rotterdam (1990-1993)	5 – 10	10 - 15	20 - 25	35 – 40	
Milford Haven (1990-1993)	3 – 3	4 - 6		4 – 9	
North Sea, German Bight					1
North Sea, central area					0.01
British Channel					0.5
France, Toulon 1997	< 0.6 – 3			4 – 237	

Sources: Länge (1996); Michel and Averty (1998).

Table 2-7: Measured TBT in sediment (in mg/kg dry weight) in harbours, estuaries and open sea

Harbour, period	Coastal area	Mouth	Estuary	Harbour	Open Sea
Rotterdam (1994-1995)		0.01–0.1		0.1 – 2.5	
Rotterdam (1994-1999)*			0.08 –0.28		
Noordzee (1996)	0.01 – 0.05				0.001-0.03
Central North Sea (1999)					<0.001 – 0.003
Waddensea (1996)	0.01 – 0.02				
Hong Kong (1989)				0.01-0.4	
Poole Harbour (UK, 1992)				0.01 – 1.3	
Amsterdam Harbour (1994)		0.03 – 0.1		0.1 – 2.0	
Bremerhaven (1999)				0.05 – 48	
Hamburg (1999)				0.02 – 42	
Wilhelmshaven (1999)				0.004 – 0.3	
Sweden, Göteborg (1997)			0.02 – 0.6	0.1 - 11	

Source: Länge (1996); Stronkhorst (1996); Van Hattum et al. (1996); Fent (1996); Laane and Groeneveld (2000); Ten Hallers-Tjabbes et al. (1999); Greenpeace (1999); Dela Cruz and Molander (1998). * Dredings disposed at sea, Yland et al. (2000).

Table 2-8: Summary of TBT concentrations measured in the Port of Rotterdam

Year	Mean concentration mg/kg (dry weight)	Minimum	maximum	Number of measurements
1993	0.08	0.01	0.24	6
1994	0.24	0.005	3.7	55
1995	0.16	< 0.002	3.3	107
1996	0.12	< 0.002	2.1	62
1997	0.10	< 0.005	0.85	89
1998	0.10	0.004	0.58	72
1999	0.07	<0.01	1.0	70

Source: data provided by the Rotterdam Municipal Port Management

In a recent report by Greenpeace (1999) extremely high values were encountered in some harbour segments in Bremerhaven and Hamburg (42 - 48 mg/kg). It is not clear to what extent these locations have been affected by additional TBT emissions from painting and docking operations.

The range of sediment TBT concentrations predicted by the Mam-Pec model (0.01 – 2.8 mg/kg) coincides with gradients reported from monitoring studies in the Nieuwe Waterweg, as well as ranges reported for other harbours. The median values (0.07 – 1.9 mg/kg) and average values (0.7 – 1.6 mg/kg) predicted for the harbour segments are comparable to concentrations

measured in harbours in the eastern section of the Rotterdam port area and in some harbours in the western section of the port of Rotterdam, not exchanging directly with the Nieuwe Waterweg.

2.4 Forecasts for TBT and new antifoulants

A prediction of the chemical fate of TBT accumulated in the sediment is difficult. Available data on biodegradation summarised by Evers et al. (1995) indicate that for TBT in the water column photolysis and aerobic degradation are the most important processes, with reported half lifes (DT_{50}) ranging from 6 to 17 days in the summer season and 37 – 335 days in the winter season. In sediments the biodegradation is slow, with reported half lifes ranging from 120 – 673 days. For anaerobic sediments half life values of 475 – 1606 days have been reported form sediment core studies (deMora et al., 1995). It is not known what degradation rate should be applied for the Port of Rotterdam, but the poor biodegradation in anaerobic sediments suggests that in a situation, when emissions of TBT have stopped, the TBT accumulated in the sediments probably will act as a source for many years.

The problem of contamination of suspended particulate matter with tributyltin will carry on as long as TBT is used in antifouling paints for ship hulls. A draft resolution which includes a proposed deadline of 2008 for the complete prohibition of organotin compounds acting as biocides in anti-fouling systems on ships is currently under debate within the forum of the IMO (International Maritime Organization) (IMO, 1999). It is expected that a whole range of new products for biocide-based paints (CEPPE-AWG, 1998) or biocide–free coating systems will be applied in the future. This may result in emissions of new compounds in the area.

At this moment various products are allowed and used in different European countries as substitutes for TBT, especially for the small boating sector. In most European countries TBT is not allowed on small pleasure boats (< 25 m). CEPE has published a list of available and proposed products (CEPE-AWG, 1999). With respect to the regulatory status, there are large differences between countries in products allowed.

For two compounds (Irgarol 1051, Sea-Nine-211), currently available on the market in various European countries, simulations were executed with the Mam-Pec model. Basic compound property data were derived from CIBA (1995) and Willingham and Jacobsen (1996) and are indicated in appendix 2.2b. Both products are more degradable than TBT and have a lower affinity toward particulate matter or sediment

For the emission-scenario similar conditions were chosen as for TBT; it was assumed that each product would be applied on 90% of the ships, with a leaching rate of 4 $\mu g/cm^2$/day resulting in a net emission of 36 kg/day (13 t/y). The environmental scenario with 32% exchange per tidal period was used. Predicted concentrations are indicated in table 2-9.

The predicted sediment concentrations (mg /kg dry wt; 5% Org-C) for both Irgarol (median 0.08; min-max range 0.0005 – 0.13) and Sea-Nine (median 0.002; min-max range 0.0007 – 0.005) are much lower than values for similar scenarios for TBT (median 1.9; min-max range 0.01 – 2.8).

Table 2.9: Predicted concentrations for Irgarol-1051 and Seanine-211 for the port of Rotterdam (harbour segments with 32 % exchange per tidal period)

	Dissolved µg/L	Total* µg/L	Sediment mg/kg Org-C	Sediment** mg/kg dry weight
Irgarol				
Average	1.1	1.1	1.4	0.07
Median	1.3	1.3	1.6	0.08
Minimum	0.007	0.007	0.009	0.0005
P95	2.0	2.0	2.5	0.13
Maximum	2.0	2.0	2.5	0.13
Sea-Nine				
average	0.003	0.003	0.05	0.003
median	0.003	0.003	0.04	0.002
minimum	0.001	0.001	0.01	0.0007
P95	0.007	0.007	0.1	0.005
maximum	0.007	0.007	0.1	0.005

* based on the concentration of suspended matter of 35 mg/L with 3 % Org-C, ** sediment with 5 % org-C

2.5 Conclusions

From the previous chapters the following conclusions can be drawn:

- Current emissions of TBT in the Port of Rotterdam were estimated at 4 - 13 t/y and rank among the highest in the world. The majority of the TBT emissions are caused by the larger ship classes (> 100 m); the relatively large number (46%; n = 13636 in 1998) of small ships contributes to only 6 % of the total TBT emissions. The uncertainty of the estimation of emissions of antifoulants is high.
- The range of sediment TBT concentrations predicted with the Mam-Pec model (0.01 – 2.8 mg/kg) for harbour segments with different rate of water exchange per tidal period (32% and 65%) coincides with gradients reported from monitoring studies in the Nieuwe Waterweg, as well as ranges reported for other international harbours. Median and average values (0.07 – 1.9) are comparable to harbours in eastern section of the Rotterdam port area and to some harbours in the western section of the port of Rotterdam, not exchanging directly with the Nieuwe Waterweg.
- The pending IMO ban on TBT is expected to have a serious impact on TBT emissions between 2003 and 2008. Many of the newly proposed alternative biocides are more degradable or have a lower affinity to sediment compared to TBT. Predicted sediment concentrations for 2 potential alternative products (Irgarol 1051 and Sea-Nine-211) are more than an order of magnitude lower than sediment concentrations predicted for TBT.

References

Berg, E.A. (1995). Measuring copper release from antifouling paints. EJC 7-8/95, p. 534-538.

CEPE-AWG (1998). Classes of biocidal antifouling paint commercially available in the European Union. CEPE, Brussels.

CEPE-AWG (1999). Utilisation of more 'environmentally friendly' antifouling products. EC project No 96/559/3040/DEB/E2. Phase 1 - final report. CEPE Antifouling Working Group, Brussels. July 1999

Ciba (1995). Summary on ecological and health effects of Irgarol 1051. Information Brochure Ciba Geigy 5/1/1995.

Dela Cruz, M.A.T. and S. Molander (1998). Butyltins in marine sediments form the Swedish West coast – Report to the Swedish National Chemicals Inspectorate (KEMI). Report nr. 1998:1. Dept. of Technical Environmental Planning – Chalmers University of technology, Göterborg, Sweden.

DeMora, S., C. Stewart, and D.Philips (1995). Sources and rate of degradation of Tri(n-butyl)tin in marine sediments near Auckland, New Zealand. Marine Pollution Bulletin 30, 50-57

Evers, E.H.G., J.H. van meerendonk, R. Ritsema, J. Pijnenburg en J.M. Lourens (1995). Watersysteemverkenningen 1996. Butyltinverbindingen - een analyse van de problematiek in aquatisch milieu. Rapport RIKS-95.007. Rijksinstituut voor Kust en Zee, Den Haag.

Fent, K. (1996). Ecotoxicology of organotin compounds. Crit. Rev. Toxicol. 26, 1-117.

Greenpeace (1999). TBT-Belastung deutscher Nordseehäfen. Greenpeace Germany, Hamburg.

Hare, C.H. (1993). Anatomy of paint - antifouling coatings. J. Protective coatings and linings, Vol. 10, 83-90.

ICPR (1998) Zahlentafeln der physikalisch-chemischen Untersuchungen des Rheinwassers und des Schwebstoffes 1996; International Commission for the Protection of the Rhine.

IMO (1999). International Maritime Organization News No. 2, 1999

Johnson, A., R. Luttik (1994). Risk assessment of antifoulants - position paper. Paper nr. 1994-05-03. Paper presented at the 7th meeting of the Ad Hoc Group of Experts of Non-Agricultural Pesticides, 16-18 May 1994. National Chemicals Inspectorate, Sweden; National Institute for Public Health and the Environment, Netherlands.

Laane, R. and G. Groeneveld (2000). Butyltin-verbindingen in sediment van de Noordzee Delta en Waddenzee (1996). Report nr. RIKZ/2000.019. Rijkswaterstaat, RIKZ, Den Haag.

Länge, R. (1996). Monitoring current levels of TBT in the US and European seawater and evaluation of the risk in the context of recent ecotoxicity data. In: Stewen, U. (Ed.). The present status of TBT-copolyment antifouling paints. Proceeding of International One Day Sympoisum on antifouling paints for ocean-going vessels, 21st Febr. 1996, The Hague, . Ministry of Transport, Public Works and Water Management, Rijkswaterstaat, DGSM; ORTEP, Association, The Hague, Netherlands.

Länge, R. (1997). Use of Tributyltin compounds in antifouling apints – update on the results of monitoring programme in different parts of the word. In: Stewen, U.(Ed.). Harmfull effects of the use of antifouling paints on ships – Tributyltin (TBT) antifouling paints. CEFIC / ORTPE, Brussels.

Lindgren, P., B. Olsson, and C. Unger (1998). Antifoulingsprodukter FARTYG. PM-beslut 1998-10-20. KEMI, Stockholm (Sweden).

Matthiessen P. & J. Reed (1997). Evaluation of copper and zinc concentrations in Suffolk and Essex estuaries. CEFAS report C967E280.

Michel, P. and B. Averty (1998). Contamination of French Coastal waters by organotin compounds: 1997 update. Marine Pollution Bulletin 37, 1 – 8.

Port of Rotterdam (1998). Annual Report 1997. Rotterdam (NL).

Scarlett, A., M.E. Donkin,T.W. Fileman and P.Donkin (1997). Occurrence of the marine antifouling agent Irgarol 1051 within the Plymouth Sound locality: implications for the green macroalga Enteromorpha intestinalis. Mar. Pollut.Bull 34, p. 645-651.

Stronkhorst, J. (1996). TBT Contamination and toxicity of sediments: a persistent problem. In: Stewen, U. (ed.). The present status of TBT-copolyment antifouling paints. Proceeding of International One Day Sympoisum on antifouling paints for ocean-going vessels, 21st Febr. 1996, The Hague. Ministry of Transport, Public Works and Water Management, Rijkswaterstaat, DGSM; ORTEP, Association, The Hague, Netherlands.

Ten Hallers-Tjabbes, CC., B. van Hattum, J.F. Kemp & Jan P. Boon (1999). New evidence of impact of TBT in the north sea, Neptunea Antiqua. NIOZ, Texel (NL).

Thomas, K.V., J. Chadwick, K. Raymond, and M. Waldock (1999). The effects of changes of environmental parameters on the release of organic booster biocides from antifouling coatings. Proceedings of the 10th International Congres on Marine Corrosion and Fouling, Melbourne, Australia.

paint booster biocides: the current status of inputs and impacts in the UK coastal environment. Poster presented at the S

Van Hattum, B., A. Baart, J. Boon, F. Aries and R. Steen (1999). Computer model to generate predicted environmental concentrations (PECs) for antifouling products in the marine environment. Report E-99/15.Institute for Environmental Studies, Vrije Universiteit, Amsterdam

Van Hattum, B., F. Ariese, J. van Kesteren, I. Freriks (1996). Organotinverbindingen in sediment uit het Noordzeekanaal. IVM-R96/10, VU Boekhandel/Uitgeverij, Amsterdam, 28 p.

Willemsen and Ferrari (1992). Emissions of organotin to Dutch surface waters. TNO-Coatings, Den Helder (in Dutch).

Willingham, G.L. and A.H. Jacobson (1996). Designing an environmentally safe marine antifoulant. In: De Vito, S.C and R.L. Garrett (eds). Designing safer chemicals - Green chemistry for pollutant prevention. American Chemical Society, Washington DC. ACS Symposium Series 640, p. 225-233.

Yland, E.M.L., H. Sonneveldt and J. Stronkhorst (2000). Evaluatie chemische toetsing zoute baggerspecie: gegevensanalyse periode 1986 – 1997. Rapportnr. RIKZ/2000.005, Rijkswaterstaat, RIKZ, Den Haag.

APPENDIX PART E: SUBSTANCES AND NEW CRITERIA TO WATCH

Chapter 2: TBT emissions inside the port of Rotterdam

2.2a Port of Rotterdam: Definition of environmental variables, harbour layout and hydrological parameters

Parameter	Symbol	Unit	Port of Rotterdam (1)	Port of Rotterdam (2)
Water quality				
Silt concentration	C_{pm}	mg/L	35	35
Temperature	T	^{o}C	15	15
Salinity	S	$^{o}/_{oo}$	30	30
Part. Matt. Org-C	POC	mg/L	1	1
pH	pH		8.0	8.0
Background concentration	C	mg/L	0	0
Hydrology				
Tidal period		hour	12.41	12.41
Tidal height		m	1.5	1.5
Tidal current	F	m/s		
River flow velocity	F_{riv}	m/s	1.5	1.5
River width	y_2	m	500	500
Depth of river		m	20	20
Density difference		kg/m^3	0.8	0.8
Flush in harbour	F	m/s	0	0
Density difference of flush		kg/m^3	0	0
Harbour lay-out				
Distance from mouth	X1	m	2000	2000
Length	X2	m	20000	20000
Width	Y1	m	2000	2000
Depth of harbour		m	20	20
Harbour entrance width	X3	m	5000	10000
Harbour entrance depth		m	20	20
Height dam harbour entr.		m	0	0
Width dam harbour entr.		m	0	0
Calculated water exchange per tidal period		%	32	65

2.2b Compound property input data [1]

Compound			Irgarol-1051 [2]	Seanine-211[3]	Copper	TBT[4]	Zinc-pyrithione
Parameter	Symbol	Unit					
Compound class	CmpIsType		3	3	2	3	3
Molecular mass	CmpMolmass	g/mol	253.37	282	63.5	290.04	317.7
Vapour pressure [5]	CmpVappress	Pa	8.8E-05	4.5E-06	0	8.5E-05	1E-06
Solubility [5]	CmpSol	g/m^3	7	4.7	0.001	1.9	6
Octanol-water partitioning coefficient	CmpKow	-	2.8	2.85	0	3.8	0.93
Sediment-water distribution coefficient	CmpKd	m^3/kg	-	-	30	-	-
Organic carbon adsorption coefficient	CmpKoc	L/kg oc	3.1	2	0	4.6	3.0
Henry's constant [5]	CmpH	$Pa.m^3/mol$	0.00319	6E-09	0	0.02	5E-05
Melting point	CmpTmelt	^oC	130	41	0	0	260
Acid dissociation constant pKa	CmppKa	-	5.16	14	0	0	14
Biotic degradation rate constant (water)[5]	CmpDegr Biowater	day^{-1}	0.028	16.5	0	0.041	2.08
Hydrolysis rate contant (water)[5]	CmpDegr Hydwater	day^{-1}	0	0.05	0	0	0.054
Photolysis rate constant (water)[5]	CmpDegrPhot	day^{-1}	0	0	0	0	8.3 [6]
Sediment biotic degradation [5]	CmpDegrBioSed	day^{-1}	0.028	16.5	0	0.0014	7.9
Sediment abiotic degradation rate constant [5]	CmpDegrHydSed	day^{-1}	0	0	0	0	0

[1] values provided by participants of CEPE-AWG (Van Hattum et al, 1999)

[2] derived form CIBA (1995)

[3] based on Willingham and Jacobsen (1996)

[4] according to Evers et al., (1995) and Stronkhorst *et al.* (1996).

[5] at 20 ^oC

[6] average over 3 meter water column (154 W/m^2; attn. 1.74).