nota GWAO-89.024

Impact of tributyltin in Dutch coastal waters
An environmental Problem

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datum: oktober 1989

SAMENVATTING
Uit chemische en biologische waarnemingen in het Deltagebied, Rijn en Schelde estuarium en in het kustgebied van de Noordzee, gekoppeld aan resultaten uit de literatuur, blijkt dat organotinverbindingen een ecologisch probleem veroorzaken in het milieu van de Nederlandse zoute wateren. Maatregelen worden voorgesteld.

Organotinverbindingen behoren tot een categorie stoffen die in Nederland weinig aandacht hebben gekregen. Zij vinden hun toepassing in: houtverduurzamingsmiddelen, aangroeiwerende middelen, conserveringsmiddelen in verf, schimmelbestrijdings-middelen, insectenbestrijdingsmiddelen, stabilisatoren in polyvinylchloride en katalysatoren.
Ruim 500 ton komt jaarlijks direct en diffuus in het nederlandse milieu. Hiervan komt per jaar 85 ton in het zoute water. Indicatoren voor organotin effecten in het zoute water zijn de japanse oester en de purperslak. Bij extreem lage concentraties organotin ($1*10^{-9}$gram per liter) treed al schelpverdikking op bij de japanse oester en de vrouwelijke purperslak krijgt mannelijke geslachtskenmerken, een verschijnsel aangeduid met de term imposex.
In 1988 is door de DGW in samenwerking met de universiteit van Bordeaux een onderzoek gedaan naar het voorkomen en de effecten van organotin in de Nederlandse zoute wateren.
In de onderzochte havens en bij Vlissingen werd opgelost tribu-tyltin gevonden: de concentratie lag tussen de 9.1 en 1650 nanogram per liter. Veldonderzoek heeft aangetoond dat alle japanse oesters schelpafwijkingen vertonen in de Delta, waarbij de sterkste verdikkingen rond de jachthavens gevonden worden. Alle purperslakken in de Delta vertonen imposex, zodat op het moment van een steriele populatie gesproken kan worden.
In aansluiting op internationale wetgevingen worden maatregelen ter voorkoming van een verdere aantasting van het ecosysteem voorgesteld zoals: het verbod op het gebruik van organotin houdende verven op schepen kleiner dan 25 meter en op alle permanente en semi-permanente opstellingen in het marine milieu. Het onderzoek naar vervangende aangroeiwerende verfsoorten moet aangemoedigd worden. Onderzoek naar de afbraak en de beschikbaarheid van tributyltin in de waterfase en in het sediment moet aangemoedigd worden.
In 1989 is het onderzoek naar het voorkomen van tributyltin voortgezet in een 40-tal nederlandse havens.

IMPACT OF TRIBUTYLTIN IN DUTCH COASTAL WATERS

An Environmental Problem

by

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INTRODUCTION

The fouling of ships is a problem of worldwide importance. Fouling slows down the vessel and leads to higher fuel consumption. In the last ten years anti-fouling paints containing organotin compounds have been increasingly used to treat hulls to prevent fouling. These organotin compounds (usually tributyltin) not only discourage a wide spectrum of marine organisms from settling on the hull, but also adversely affect many organisms in the surrounding seawater. Therefore, concern is growing about the environmental threat they pose. Figure 1 shows the sources of tributyltin in the aquatic environment and the fate of these compounds.

At the moment little is known about the relative contribution of these different sources of tributyltin compounds (TBT) to the concentration in the receiving water. Furthermore, the processes of their degradation and accumulation are also poorly understood (UNEP, 1988).

Yet, over 30 years ago, in the introduction to their three-volume work on research on organotin, van der Kerk and Luyten (1954) stated that "... among all organometallic compounds organotin compounds belong to the best studied in every aspect: chemistry, physical properties, applications and biological effects. There are no signs which would indicate the approach of a change in this position."

Worldwide organotin production and use started in 1940 and had increased to 35000 tonnes by 1982 (UNEP, 1988). During the 1960s organotins began to be used in anti-fouling paints. The yearly use of organotin compounds in the Netherlands has been estimated to be 850 tonnes of which 97 tonnes is used in anti-fouling paints (Olsthoorn,1987). Two factories in the Netherlands manufacture organotin compounds: Akzo Chemie b.v. in Amersfoort en M&T Chemicals in Vlissingen (Olsthoorn,1987)

Concern about the negative effects of tributyltin compounds in the aquatic environment first emerged in France in the early 1970s (Alzieu et al.,1980). The serious problems encountered in the commercial culture of the Pacific oyster (Crassostrea gigas) in France were soon followed by reports of simi-lair problems in England (Waldock & Miller, 1983). Although the concern about the effects of organotin compounds was initially highlighted by the problems experienced by commercial shell fish fisheries, considerable evidence of far more extensive effects in the aquatic environment was subsequently presented. Once released into the aquatic environment TriBultylTin (TBT) is involved in different processes. For instance, it adsorbs to particulate matter. It is degraded biologically and via photochemical processes, releasing a butyl group step by step . The resulting ionic tin and intermediates in the debuty-lation chain are then methylated by bacterial processes in the sediments, to become trimethyltin (TMT). The rates of degradation of TBT are poorly known, especially in sediments (Clark et al., 1988).

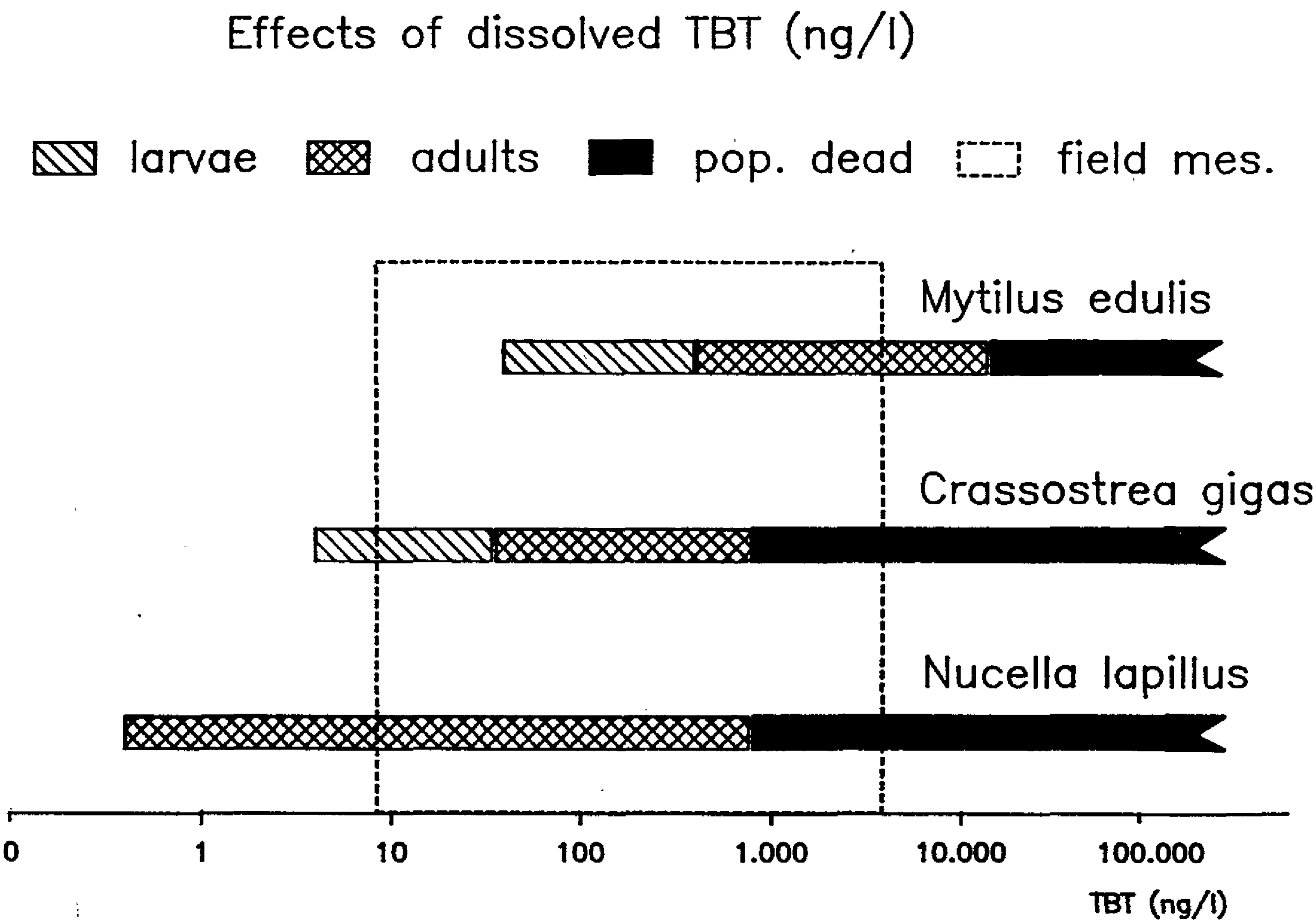

Figure 2. Summary of the available data on the toxicity (sublethal and lethal) of TBT to spat and adults of the dogwhelk (Nucella lapillus), the Pacific oyster (Crassostrea gigas) and the mussel (Mytilus edulis) (UNEP, 1988). larvae, adults, population dead, range of TBT concentrations found in Dutch coastal waters.

TOXICITY.

Whereas inorganic tin compounds are relatively innocuous, organotin compounds are very toxic. However, their effects differ strongly, depending on the compound and the species of organism. In general, trialkyl tin compounds are more toxic than dialkyltin and monoalkyltin compounds; for mammals and insects the trimethyltin and triethyltin compounds are most toxic. The longer the hydrocarbon chain in the organotin compounds, the lower the toxicity for mammals, but the higher the toxicity for fungi, algae and bivalves (Hall & Pinkney, 1985; Maguire, 1987; Snoey et al., 1987). In general, tributyltin is very toxic to many aquatic organisms (UNEP, 1988).

Specific indicators for the toxicity for tributyltin compounds in the marine environment are the Pacific oyster (Crassostrea gigas) and the dog whelk (Nucella lapillus) (Bryan et al.,1988; Gibbs et al, 1988).

The data available on the toxicity (sublethal and lethal) of TBT to spat and adults of the oyster, dog whelk and mussel are summarized in Figure 2 (UNEP, 1988).

At concentrations of 30 ng.TBT per litre the growth of shellfish is retarted and abnormal thickening of the shell valve can already be observed in the Pacific oyster. The thickening of the valve is expressed by the ratio between the length and thickness (L/T). The gradient is from 4 to 11: values of 4-5 indicate that the oysters are severely deformed, 6-8 is an intermediate zone with shell thickening, 9-10 a subnormal population and above 10 a normal population (Heral, et al, 1981). The spat of the oysters is already affected at concentrations below 30 ng. TBT per litre (Lawler & Aldrich, 1987).

The most sensitive of the organisms in Figure 2 are the juvenils of the dog whelk, Nucella lapillus. They are already affected at extremely low concentrations of 0.4 ng. TBT per litre (Maguire, 1987). In the females of this species a penis is induced. As a result of this phenomenon (called imposex) they become sterile. Failure in recruitment causes the population to age until local extinction. The degree of penis induction is expressed in percentage RPS (relative penis size index) (Gibbs et al., 1988).

MEASURES AND LEGISLATION

The first restriction to the use of TBT in anti-fouling paints was made in France. In 1982 the French government banned the use of TBT paints on ships less than 25 long. Other countries subsequently took measures to reduce the TBT input to the environment. For instance, an initial measure in the United Kingdom was to prohibit anti-fouling paints containing more then 7.5% tin. Later, the use of organotin-containing paints on boats less than 25 metres long was also prohibited. In most countries the water quality target level for TBT has been set at 1 ng per litre. After the legislation in France and the United Kingdom, cultivated oysters improved considerably and further deterioration of the dog whelk population was halted (UNEP, 1988).

In the USA the EPA announced that only two tributyltin hull paints would be allowed to be sold in 1989. The 1988 organotin Anti-fouling Paint Control Act (December, 1988) established that only paints releasing less than 4 ug/cm2/day could be certified for sale and use in the USA (Anonymous, 1989). The Act established this release rate as an interim measure until further study

had delivered a more scientifically based standard. The Act also prohibits the use of TBT paints on all vessels less than 25 m in length that have non-aluminium hulls.

Shipowners in both the USA and Europe have responded positively to the introduction of new TBT-free anti-fouling paints. It has been reported that in the USA nearly 100 merchant vessels and over 60 naval ships have been treated with the TBT-free products. After the TBT ban in the United Kingdom it was found that the ecosystem had recovered after a few years (Waldock et al., 1988).

International European cooperation (EEC legislation) is under way.

CONCENTRATION AND EFFECTS OF TRIBUTYLTIN IN DUTCH COASTAL WATERS

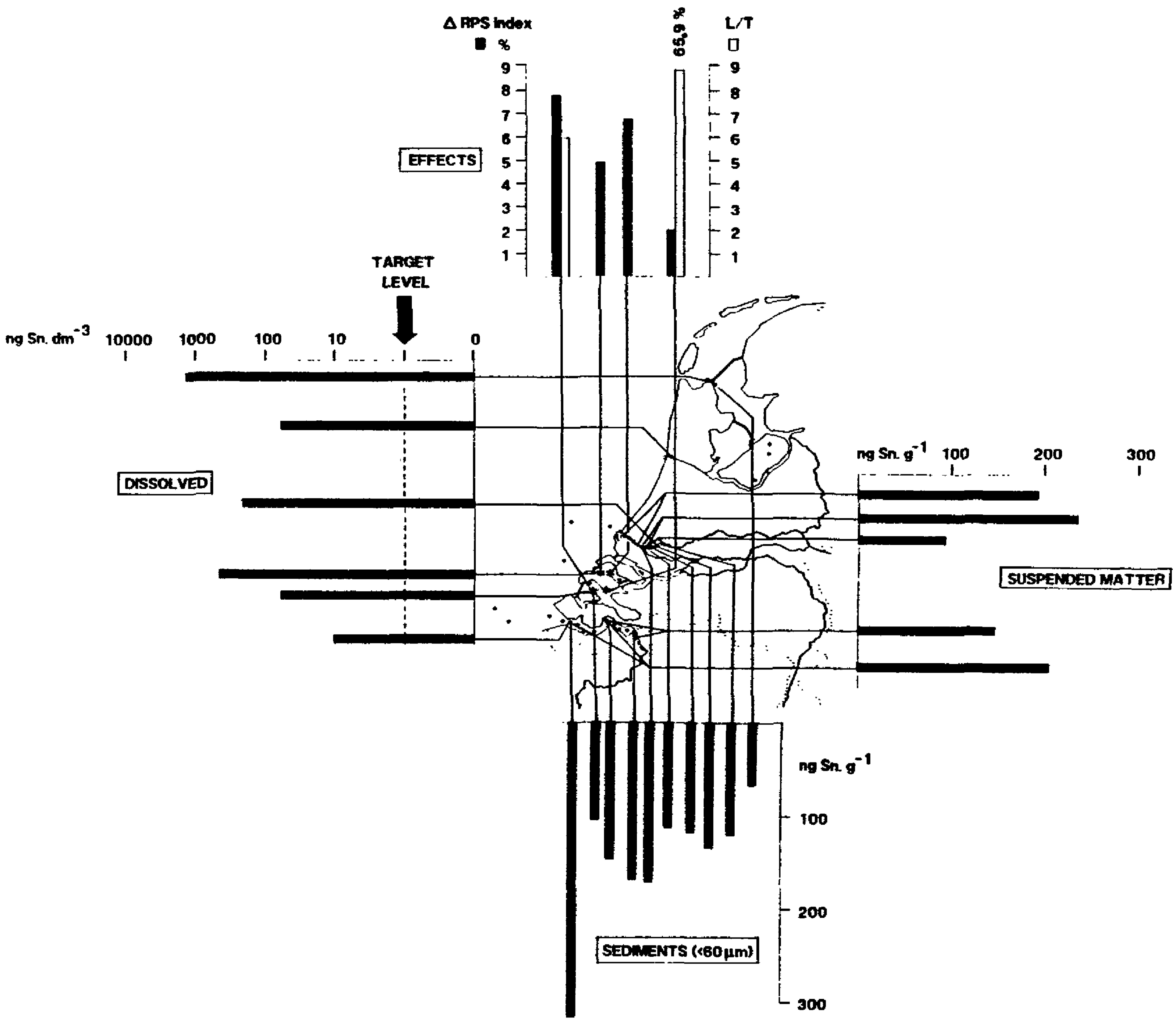

Figure 3. Concentration of tributyltin (TBT) in filtered water (dissolved, ng $Sn.dm^{-3}$), in suspended matter and in the sediment fraction <63um (ng $Sn.g^{-1}$) at different locations in the Dutch coastal zone in 1988. The effects (RPS index and L/T ratio) are also indicated.
A natural population of dog whelks with a RPS (relative penis size) index of 65.9% was found in the Eastern Scheldt. The increase in RPS index (ΔRPS) of the exposed dog whelks at four marinas is given. At two location the ratio of the thickening of the valve (L/T) of the Pacific oyster is given (Sampling locations, ● and *).

IMPACT OF TBT IN DUTCH COASTAL WATERS.

In 1988 the Tidal Waters Division of the Dutch Ministry of Transport and Public Works and the University of Bordeaux began a joint investigation on the impact of TBT in Dutch coastal waters. The concentrations of the different butyltin compounds were measured in the water phase (dissolved and particulate) and in the sediments, at different locations (Fig. 3) in July and October.

The specific effects of TBT on the Pacific oyster and the dog whelk were studied in four locations (Fig. 3 marked with *). Since all local dog whelk populations were seriously affected (RPS=65.9%, Fig.3), it was necessary to transfer relatively clean dog whelks from England (RPS=0.8%) to the Netherlands. They were exposed to ambient concentrations of TBT for 6-7 weeks at different locations (see Figure 3, locations marked with an *).

The concentrations of dissolved and particulate TBT and TBT in the sediments and the effects on the dog whelks (increase in RPS, ▲RPS) and on the local oyster population (valve thickening, L/T) are summarized in Figure 3.

The concentration of dissolved TBT ranged from 9.1 to 1650 ng per litre: the 4 marinas in the southwest of the Netherlands, 1 marina in the Wadden Sea and at 1 location in the main channel of the Scheldt estuary near the M&T organotin-producing factory. Dissolved TBT was also detected in the Wilton Feyenoord harbour of Rotterdam (150 ng per litre).

Particulate TBT was measured in all the particulate matter collected at all locations in the Rhine and Scheldt estuaries, (also at places where the concentration of dissolved TBT was below detection limit (<1.8 ng per litre). The concentration of particulate TBT varied between 92-235 ng per g dry matter. Near the organotin factory in the Scheldt estuary TBT was also found in the sediments, in concentrations ranging from 67 to 311 ng per g sediment.

At all locations in the estuaries the concentrations of dibutyltin (DBT) and monobutyltin (MBT) were above detection limit (>0.4 ng per litre).

Only at the 4 locations in the coastal zone of the North Sea were no TBT or DBT detected and only dissolved and particulate MBT was found.

A natural population of dog whelks with an RPS index of 65.9% was found in the Eastern Scheldt. The RPS index of the exposed dog whelks increased from 0.8% to values around 1.9% and up to 7.7% within 7 weeks at four marinas marinas (▲RPS in Figure 3). At two of these marinas there was an appreciable valve thickening of the Pacific oyster (L/T ratio between 5.8 and 8.7).

TBT concentrations in mussels ranged from 46-945 ng per g dry weight at the four different locations marked with an * in Figure 3.

DISCUSSION

It is difficult to compare the concentrations of dissolved TBT measured in this study with those already published, because in most studies the total TBT (dissolved plus particulate) was measured (UNEP,1988).

At 6 different locations (the 5 marinas and a site in the Western Scheldt near an organotin-producing factory) the concentrations of TBT considerably exceeded 1 ng TBT per litre, which is the level at which TBT is thought to have no effect on organisms. At these locations, the specific effects of TBT (i.e. imposex of the dog whelk and shell thickening of the oysters) were found. The field populations of dog whelk in these locations are completely sterile (RPS=65.9%).

TBT was found in all sediments and suspended matter sampled at the estuarine locations, at concentrations higher then those published in the literature for polluted areas (UNEP,1988).

The distribution of TBT over the water phase and suspended matter, expressed in the distribution coefficient Kp was on average, $24*10^3$ kg per litre, which is in agreement with the published data ($0.11-55.4*10^3$ kg/l, UNEP,1988). This indicates that nearly all dissolved TBT adsorbs on particles and will accumulate in the sediments.

The effects on the dog whelk (severe imposex) and on the Pacific oyster (shell thickening) in the southwestern part of the Netherlands indicate that here the ecosystem is strongly affected by these organotin compounds. The natural population of dog whelks is dying out.

All the shellfish sampled were founds to contain TBT (46-945 ng/g for mussels and 109-126 ng/g for oysters). The bioconcentration factor (BCF) for TBT in the mussels was 11,000, which is in agreement with values published in the literature (UNEP,1988).

The acceptable daily intake (ADI) for humans ranges between 1.6 and 3.2 μg per kg bodyweight (UNEP,1988). This means that a person weighing 60 kg is permitted to eat about 650 g mussels per day.

CONCLUSIONS AND PROPOSED MEASURES

Various conclusions about the use of organotin compounds can be drawn from this research and from research done elsewhere, and on the basis of this, measures to alleviate the problem can be proposed.

1. The increasing use of organotin as anti-foulant has introduced an environmental problem in the Netherlands too.

2. Rising levels of organotin compounds form a threat to all creatures using marine waters.

3. To minimize the problem in the shortrun, only anti-fouling paints with low triorganotin release rates should be permitted.

4. The use of anti-fouling TBT paints on all vessels less than 25 metres long must be prohibited in the Netherlands, in line with the measures already taken in the United Kingdom, France and the USA (1990)

5. Research on alternatives to replace organotin anti-fouling paints must be encouraged.

6. The use of anti-fouling paints containing organotin compounds on boats must be banned once alternatives are commercially available (i.e.circa 1995).

7. The use of anti-fouling paints containing organotin compounds on all structures used in the aquatic environment must be banned.

8. The use of new anti-foulants that do not contain TBT or copper must be encouraged.

9. The lack of knowledge on the availability and the degradation rate of TBT in sediments is cause for concern. Studies of the availability studies of the degradation products of TBT (e.g. trimethyltin) and their effects on organisms must be encouraged.

REFERENCES.

Alzieu, Cl., Y. Thibaud, M. Heral & B. Boutier. 1980. Evaluation des risques des á l'emploi des peintures antisalissures dans les zones conchylicolis. Rev. Trav. Inst. Pêch. marit. 44:301-348.

Anonymous. 1989. Few TBT Paints on Market. Marine Pollution Bulletin 4:157.

Brady, R.F. & J.R. Griffith. 1987. Nontoxic Alternatives to anti-fouling paints. Journal of Coating Technology, 59:113-119.

Bryan, G.W., P.E. Gibbs & G.R. Burt.. 1988. A comparison of the effectiveness of tri-n-butyltin chloride and five other organotin compounds in promoting the development of imposex in the dog-whelk, Nucella Lapillus. Journal Marine Biological Association UK 68:733-744.

Clark, E.A., R.M. Sterritt, J.N. Lester. 1988. The fate of Tributyltin in the aquatic environment. Envir. Sci. & Techn. 22:

Gibbs, P.E., P.L. Pascoe & G.R. Burt. 1988. Sex change in the female dog-whelk, Nucella Lapillus, induced by tributyltin from anti-fouling paints. Journal Marine Biological Association UK 68:715-731.

Hall, L.W. Jr. & A.E. Pinkney. 1985. Acute and sublethal effects of organotin compounds on aquatic biota: an interpretative literature evaluation. CRC Critical Reviews in Toxicology. 14:159-209.

Heral, M., J.P. Berthome, E. Polanco Torres, Cl. Alzieu, J.M. Deslous-Paoli, D. Razet & J. Garnier. 1981. Anomalies de croissance de la coquille de Crassostrea gigas dans le bassin de Marennes-Oleron. Bilan de trois annees d'observation. ICES paper CM 1981/K:31.

Kerk, G.J.M. van der & J.G.A. Luijten. 1954. Investigations on organotin compounds. 3 volumes, Greenfort.

Lawler, I.F. & J.C. Aldrich. 1987. Sublethal Effects of bis(tr-n-butyltin)oxide on Crassostrea gigas Spat. Marine Pollution Bulletin 6:274-278.

Maguire, R.J. (1987). Environmental aspects of Tributyltin. Applied Organometallic Chemistry 1:475-498.

Mertens, O. 1988. Mosselen en organotin. Een onderzoek naar effecten in de Nederlandse getijdewateren. Rijkswaterstaat report GWAO-88.026, 28pp (in dutch).

Mertens, O. & C. van Zwol. 1988. Purperslakken en organotin. Een onderzoek naar effecten in de Oosterschelde en de Grevelingen. Rijkswaterstaat report GWAO-88.029, 26pp (in dutch).

Oltshoorn, C.S.M. 1987. Organotinverbindingen in Nederland 1985. CBS publication, Staatsuitgeverij, Den Haag, 54pp.

Snoey, N.J., A.H. Penninks & W. Seinen. 1987. Biological activity of organotin compounds-an overview. Environmental Research 44:335-353.

UNEP. 1988. Assessment of organotin compounds as marine pollutants and proposed measures for the Mediterranean. UNEP(OCA)/MED WG.1/7, 62pp.

Waldock, M.J. & D. Miller. 1983. The determination of total and tributyl tin in seawater and oysters in areas of high pleasure craft activity. ICES paper 1983/E:12.

Waldock, M.J., M.E. Waite & J.E. Thain. 1988. Inputs of TBT to marine environment from shipping activity in the UK. Environmental Technology Letters 9:999-1010.

Zwol, C. van & O. Mertens. 1988. Oesters en organotin. Een onderzoek naar effecten in de Oosterschelde. Rijkswaterstaat report GWAO-88.027, 29pp (in Dutch).

Quevauviller, Ph., M. Ewald & O.F.X. Donard. 1989. Organotin compounds distribution in estuarine and coastal waters of the Netherlands. Internal Report, 85 pp.