Investigation of the Distribution of Tributyltin in the Sea Water from the Port of Piraeus, Greece[†]

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Résumé

La distribution du tributyl d'étain (TBT) provenant de peintures anti-pollution fut étudiée dans l'eau de mer du port de Pirée en Grèce, un port ayant une activité maritime intense. Des calculs théoriques ont été effectuées pour la région du port sous étude. Ces derniers étaient basés sur la quantité de TBT relâchée quotidiennement par les bateaux amarrés ainsi que sur la dégradation du TBT dans l'eau de mer. Ce modèle mathématique a été prouvé expérimentalement par le dosage de TBT dans des échantillons obtenus à différents endroits dans le port. Pour la préconcentration du TBT; les échantillons furent traités à l'aide d'un échangeur cationique, Dowex 50 W-x8, dans lequel le TBT fut passé à l'aide d'une solution méthanolique de HCL 3N. Après extraction de la phase liquide avec du dichlorométhane, le TBT fut dosé directement à l'aide la polarographie à courant alternatif (ACP). Les résultats et les calculs théoriques qui se basaient sur une dégradation cinétique de premier ordre n'ont montré qu'un faible relâchement de TBT des navires amarrés dans le secteur géographique étudié.

Abstract

The distribution of tributyltin (TBT), coming from antifouling paints, was investigated in the sea water from the port of Pireaus, Greece, which has intensive ship activity . For the investigated port area, theoretical calculations were made, based on the quantity of TBT leached daily from the moored ships and the degradation of TBT in sea water. This mathematical model was proved by experimental data obtained by the determination of TBT in sea water samples taken from different sites of the port. For the preconcentration of TBT, the samples were passed through a cation exchanger, Dowex 50 W-X8 , from which TBT was eluted with 3 N HCl in methanol. After extraction of the eluate with dichloromethane, TBT was directly determined in the organic phase by alternating current polarography (ACP). The theoretical calculations, based on a first order degradation kinetic, and the experimental results led to the conclusion of low daily leaching rates of TBT from the moored ships in the investigated area.

Introduction

The prediction of possible concentrations of toxic contaminants, such as tributyltin (TBT) in aquatic systems, is an important consideration in any effort to protect the marine environment. TBT is leached into the marine environment mainly from the antifouling paints used for the protection of ship's hulls (1). In ports and marinas, where a large number of ships and boats, respectively, are moored, the concentrations of TBT found in seawater exceed, in most cases, the concentrations currently considered adequate for the protection of marine species (2). As the non-observed-effect level (NOEL) for TBT in seawater is 20 ng/L (3) and in some countries, like the UK, the Environmental Quality Standard (EQS) has recently been limited to 2 ng/L (4), the analytical techniques used for the quantitative determination of TBT in such extremely low aqueous

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concentrations must be very sensitive, reliable and selective in order to differentiate the highly toxic TBT from its less toxic degradation products, mono-(MBT) and dibutyltins (DBT) (5). Most of the analytical techniques, which have been applied to the quantification of butyltins in seawater (6-9) need a preconcentration or derivatisation step prior to analysis to reach these low concentrations of TBT. It is therefore essential to be able to estimate first, the expected concentration range of TBT in a closed marine area and then to prove these calculated data by experimental observations. For the estimation, the leaching rate of TBT from moored ships' hulls is needed, which depends in a closed marine environment on the sea water temperature, the pH, the salinity and the TBT content of the paints (10, 11).

The aim of this investigation is, based on the experimental results, to estimate leaching rates and inputs of TBT from moored ships in the main port of Greece, the port of Piraeus, taking into consideration the degradation of TBT.

The TBT concentration in the investigated area was experimentally determined with an electrochemical technique developed earlier for sea water samples (9,12,13). By using a preconcentration step with a cation exchanger, followed by elution , extraction and analysis of TBT by alternating current polarography (ACP) in the organic phase, it was possible to determine TBT in the ng/L level in the sea water samples of the port.

Estimated Quantities of TBT Leached from Ship's Hulls Case Study

Piraeus is a naturally protected port (Fig.1) with one entrance of only 200 m width in the west, a water volume of $13 \times 10^6 m^3$ (14) and a flood of a few centimeters, reaching to a maximum of 30 cm, without any ingoing or outgoing currents. It is a commercial port, where passenger and dry-cargo ships are moored. Let us assume that there is practically no exchange of water in the port and that the antifouling paints leached from the hulls of the vessels within the port are the main source of TBT in this area. Also the assumption is made, that all the ships in the investigated area are coated with relatively low-release selfpolishing copolymer paints (SPC), where the biocide (TBT) is chemically bound to the polymer matrix and the attack by seawater on the paint film causes hydrolysis of the organotin-ester linkage (15). These paints also contain cuprous oxide as a biocide. When ships are moving, the leaching rate of TBT from SPC antifouling paints does not exceed the amount of 4 $\mu g/cm^2$/day (16), while for moored vessels the critical leaching rate of TBT (expressed as Tributyltin-oxide, TBTO) is less than 0.4 $\mu g/cm^2$/day (15, 17) The leaching rates of the biocides TBTF (Tributyltin-fluoride) or TBT-methylmethacrylate used in the SPC- paints in the investigated area are expected to be much lower than those of TBTO (15). The UK Royal Navy and the United States Navy stated that, if they introduced TBT antifoulants, they would have leaching rates less than 0.1 $\mu g/cm^2$/day (11). Due to this low TBT leaching rate from moored ships, paint manufacturers do not guarantee that vessels staying at the port for more than 15-20 days will not be fouled.

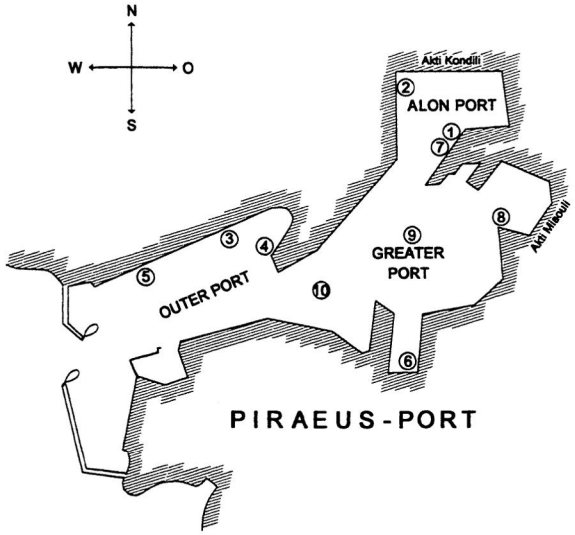

Figure 1. Sampling sites in the port of Pireaus.

Table. I. Calculation of the effective total underwater area of all ships moored daily in Piraeus Port.

Category of ships	Mean number of ships calling port daily	Mean underwater area of ships [$m^2 \times 10^3$]	Total ship's underwater area [$m^2 \times 10^3$]	Percentage of time spent daily by moored ships [%]	Effective underwater area of ships moored in port daily [$m^2 \times 10^3$]
1.Passenger ships of domestic lines	34	2.6	88.4	70	61.9
2.Pass.ships of Argo-Saronic Bay	15	0.5	7.5	75	5.6
3.Cruise ships	12	4.4	52.8	73	38.5
4.Dry-cargo	11	8.3	91.3	70	63.9
5.Ships under repair	8	2.3	18.4	65	12.0
6.Motor ships	10	1.0	10.0	75	7.5
7.Other ships	28	1.2	33.6	75	25.2
Total	118	20.3	302.0	72	214.6

For the port of Piraeus, the estimated mean release of TBT from all ship's hulls moored within has been calculated for the time period of one year (1993). First, the effective total underwater area of all these ships was calculated (Table 1). According to the Piraeus Port Authorities (18), the ships were classified in seven categories. This classification is necessary, because each group has its own peculiarities in the calculation of hull areas. In Table 1, the mean number of ships calling daily into the Port of Piraeus are listed. For all these ships, docking daily in the port, the mean underwater area was calculated according to Normand's formula (eq.1), which takes into consideration the ship's dimensions and the vessel's draught under loaded or ballast conditions (19,20)

$$S = L \times [1.5 \times d + (0.09 + c_b) \times B] \quad (1)$$

where S = underwater area; L = length of the ship at its water line; B = breadth; d = draught; c_b = coefficient of fineness (ratio of the volume of ship's displacement to the volume of the circumscribing block of constant rectangular section, having the same length, breadth and draught as the ship)

The total ship's underwater area per category was obtained from these calculated mean values of the underwater ship's area and the corresponding number of ships. Furthermore when the percentage of time spent daily by moored ships in the port was introduced, the effective mean underwater area per day for each ship category could be calculated. Finally, the whole effective mean underwater area of all ships staying the daily mean in the port of Piraeus came to 214.6 x $10^3 m^2$/day.

For three probable leaching rates, 0.3, 0.2 and 0.1 $\mu g/cm^2$/day the calculated total daily inputs of TBT (expressed as TBTO) from the whole effective mean underwater area of all moored ships could be calculated, taking into account the port's water volume (Table 2).

This calculation, however, is simplified, and it doesn't take into consideration the simultaneous degradation of TBT. Various degradation investigations have been carried out (21-23), which led to degradation half lives ($t_{1/2deg.}$) for TBT in aquatic systems from 4 to 60 days, depending on the temperature of the seawater, the light (UV) conditions, and the biological activity. Assuming first order degradation kinetics for TBT (21), the rate of TBT release is given by the following differential equation:

$$\frac{dm}{dt} = i - km \quad (2)$$

where i = the daily constant TBT release rate from the SPC paints [g/d], k = the degradation rate constant [d^{-1}], m = mass of TBT [g]. For $t=t_{1/2deg}$ the degradation half life reduces to

Table II. Calculated daily TBTO leaching by ships moored in Piraeus port without taking into consideration any degradation (total actuall underwater ship's area = $214.6 \times 10^6 m^3$, water volume of the port = $13.095 \times 10^6 m^3$)

Probable TBTO daily leaching rates	Quantity of TBTO leached daily	Calculated TBTO leached daily from all moored ships in the water volume of the port
r_i [$\mu g/cm^2$/day]	i [g/day]	[ng/L]
0.3	643.8	49.2
0.2	429.2	32.8
0.16	341.8	26.1
0.1	214.6	16.4

$$t_{1/2deg} = (\ln 2)/k \quad (3)$$

Equation (2) can be integrated to give for the total mass of TBT after time t, m_t:

$$m_t = m_o e^{-kt} + i(1 - e^{-kt})/k \quad (4)$$

where m_o = the initial mass of TBT leached from ships' hulls into the port [g]. In eq. 4, the first term expresses the first order degradation of TBT and the second the daily TBT input from the ships' hulls into the port.

The experimental measured TBT concentration corresponds therefore to the equilibrium value, m_{equ}, between the new TBT input and the TBT remaining from the degradation, and it can be calculated from eq. 4 for $t \to \infty$

$$m_{equ} = i/k \quad (5)$$

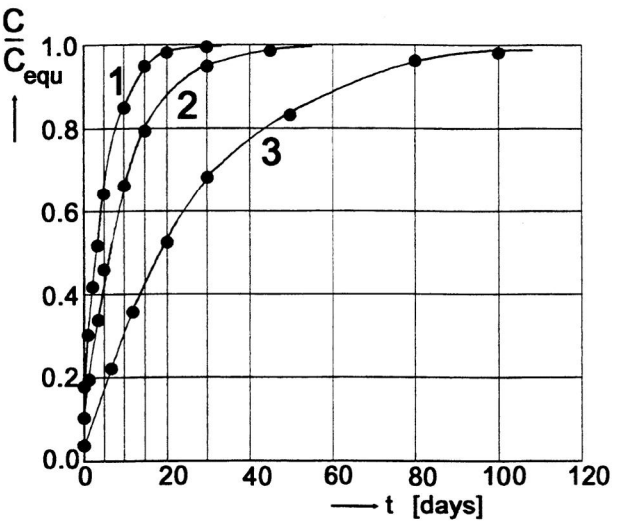

Figure 2. Leaching rate curves for three different $t_{1/2deg}$, normalized by their corresponding equilibrium values (1: $t_{1/2}$=4 days, 2: $t_{1/2}$=7 days 3: $t_{1/2}$=20 days). c_{equ}=equilibrium concentration of TBTO.

In Fig. 2 , the leaching rate curves, calculated for three different $t_{1/2deg}$ from eq. 4 and normalized by their corresponding equilibrium values, are illustrated.

Experimental

Sampling

During the time period from August to November 1993, samples of seawater were collected from different sites of the port of Piraeus (Fig. 1). For each sampling point, bulk water samples of about 45 L were taken at 0.5 m sub-surface with close-open-close samplers of 25 L capacity each, consisting of high density polyethylene. The temperature of the seawater was in the range of 21–24°C.

Analytical Procedure

The determination of TBT in the seawater samples was performed according to a voltammetric method with a preconcentration step (9). The procedure was further optimised for improvement of the detection limit. For the preconcentration of TBT, the unfiltered samples were passed, with a flow rate of 25 mL/min, through an ion exchange column filled with 50 mL of the cation exchanger DOWEX 50 W-X8 (Serva, Germany), in the Na-form, 100-200 mesh. After washing of the resin with distilled water, until chloride was no longer detectable in the effluent, TBT was eluted with 50 mL 3 N HCl in methanol. For the determination of TBT, the eluate was then extracted with 8 mL dichloromethane, adding also 20 mL dist. water for phase separation. In the organic phase of dichloromethane, TBT was now directly determined by alternating current polarography (ACP), as is described in detail elsewhere (12). The whole analytical procedure for the TBT determination in seawater samples is shown schematically in Figure 3.

Results and Discussion

In Table 3, the concentrations of TBT (expressed as TBTO), found at the selected sampling sites in the harbour area of Piraeus, are listed. These represent the mean value of three replicate measurements of each sampling point. The recovery of TBT for the developed procedure had been found for artificial sea water to be about 85% (9). The TBT concentrations found in the port are relatively low in comparison to published concentration values from other harbours of the Mediterranean coast line (1,24,25), where in some cases the TBT concentration reaches the 1000 ng/L level.

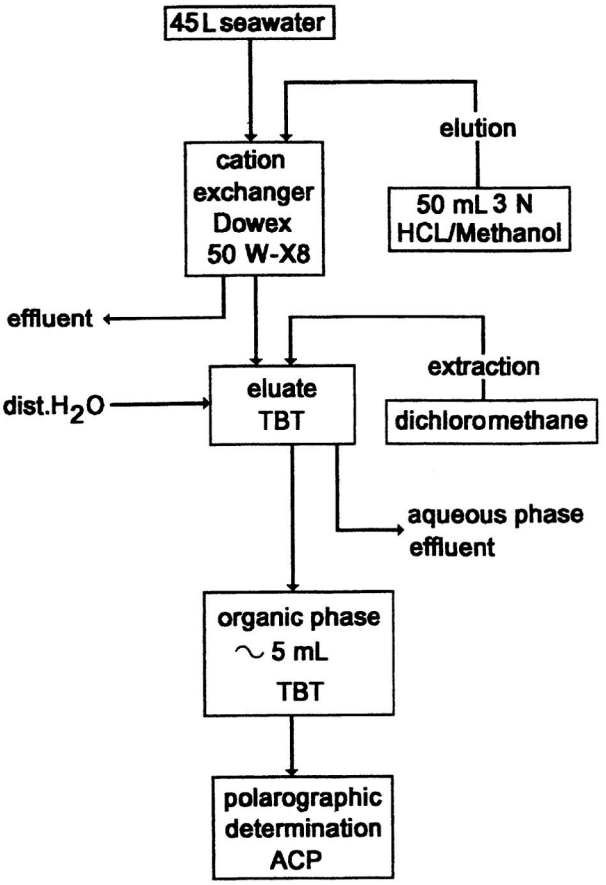

Figure 3. Flow sheet for the TBT determination in seawater.

Table III. Experimental concentrations of TBTO, found at the selected sampling sites of the Pireaeus Port

Station Nr.	Concentration of TBTO [ng/L]
1	34.6
2	35.4
3	34.2
4	30.0
5	8.6
6	n.d.
7	37.0
8	18.2
9	25.1
10	11.5
Mean	26.1±10.8

The mean concentration in the port for the investigated time period was about 26 ng/L TBTO or 25 ng/L TBT (Bu_3Sn^+). In places with high density of moored ships, the TBTO concentration reached about 35 ng/L,

which represents the lower values within the concentration range published by other authors for sea water (1). In some sampling points (Nr.5 & 10), where a low density of moored ships existed, the concentrations were only about 10 ng/L. In the sampling point Nr.6, no TBT could be detected, mainly due to the existence of a municipial waste water discharge at this site. For this sample, it was necessary to filter the collected seawater prior to the analysis in order to avoid blocking the ion exchange column by the particulated matter. As reported (26), 90% of the butyltins are associated with suspended solids in the effluent, and also the degree of degradation of TBT to less toxic butyltin compounds (DBT, MBT) and to inorganic Sn depends strongly on the microbiological activity and microalgae present in high numbers (1). In general, the photolytic and biological effects under light conditions are the main routes for the environmental degradation of TBT.

From Table 2, a TBTO daily mean leaching rate of 0.16 $\mu g/cm^2/day$ from all moored ships could be extrapolated for the measured mean TBTO concentration in the port of Piraeus. This value is within the range of the probable TBTO daily leaching rates and corresponds to an input of about 342 g/day TBTO in the port. However, for the actual leaching rate, the degradation of TBT has to be taken into consideration too.

Assuming a half life time for TBT of about 4 days (23), which can be tentatively applied to Piraeus port, and using the found mean TBTO concentration as the equilibrium value, the actual leaching rate of TBTO results from eq. 5. Under the mentioned conditions, an initial daily leaching rate for TBTO of 0.028 $\mu g/cm^2/day$ could be calculated, which is about 5.5 times lower than the corresponding value without taking into consideration any TBT degradation. This corresponds to an input of about 59 g TBTO/day within the port. In Fig. 4, the dependence of the actual leaching rates on the degradation half life for the found mean TBTO concentration is demonstrated. As the degradation half life increases, the daily leaching rate of TBTO, r_j, should decrease for the observed TBTO concentration in the port. For degradation half lives of more than two days, the leaching rates are less than 0.1 $\mu g/cm^2/day$, corresponding to the leaching rate values stated by the United States Navy and the UK Royal Navy.

Due to the achieved enrichment factor of about 9000 by the preconcentration procedure, the detection limit obtained by the described analytical procedure, was improved to 5 ng/L, showing that this technique can be applied to the determination of very low concentrations of TBT at the level of environmental quality targets. The accuracy, the reproducibility and the selectivity of the voltammetric analytical technique had been proved earlier against synthetic TBT reference materials obtained by BCR (Bureau of Reference Community) (12).

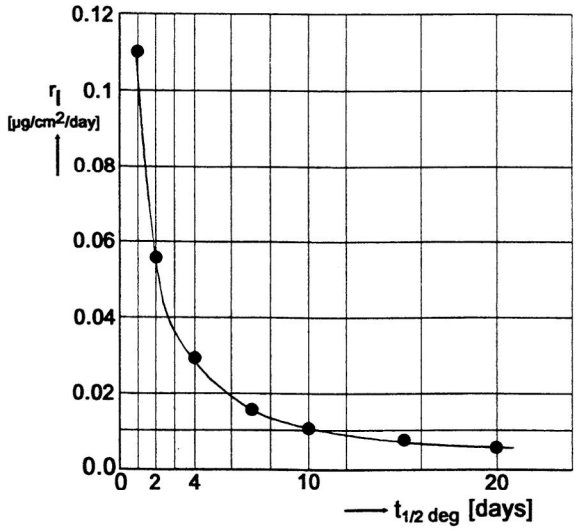

Figure 4. Dependence of the actual leaching rates from the degradation half lives for the found TBTO concentration in Piraeus port of 26.1 ng/L.

Conclusions

The obtained experimental results for tributyltin from moored ships in the Piraeus Port show a relatively low concentration of this toxic butyltin compound in the investigated area. This can be mainly explained by the fast degradation of tributyltin in this area, due to the elevated temperature of the seawater, the strong light (UV)- conditions, and the biological activity in the port. Also, it is observed that the antifouling paints used for the ships' hulls in Piraeus port, contain, in addition to TBT, cuprous oxide as an effective biocide.

For the experimentally observed TBT concentration in the port of Piraeus, a low leaching rate of this compound for the moored ships could be estimated, taking into consideration the degradation of TBT. The theoretical calculations performed in this study allow one to relate estimated TBT inputs to the concentrations, which have been observed in a nearly closed marine environment.

The developed voltammetric analytical technique proved to be a useful tool for the determination of TBT in natural sea water samples.

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