CHEMISTRY OF EPA CONTAMINANT CANDIDATE LIST COMPOUNDS: DEGRADATION MECHANISMS AND PRODUCTS

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EFFECTIVENESS OF THE RETAIL BAN ON TBT BASED ANTIFOULING PAINTS IN THE WESTERN MEDITERRANEAN HARBORS

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Introduction

Environmental aspects of harbours are an important issue of their management since they are recipients of toxic chemical inputs from a wide variety of pollution sources and can affect marine coastal ecosystems by sediment dredging, seawater diffusion or advective sediment transport. Organotins (OTs) have been widely used during the last decades as biocides, polymer stabilisers, wood preservatives, and catalysts in a number of industrial processes[1-3]. Nevertheless, their main source in the marine ecosystem is related to their use as antifouling paint biocides. Therefore, OTs are transferred from wastewaters to sewage sludges produced in wastewater treatment plants (WTP) due to partial degradation of OTs[4]. Therefore, in urban coastal areas where raw sewage is disposed to only physical treatment, OT sources coming from sewage disposal could be not negligible. The high ecotoxicological risk of these contaminants on marine ecosystems is widely documented (i.e. imposex, oyster malformation, mussel larvae mortality) at very low concentration levels (few ng L^{-1})[5-7]. These negative effects on the aquatic environment were discovered in the Arcachon Bay (France) in the early 1980s[8]. As a consequence, the French authorities banned the use of antifouling paints containing tributyltin (TBT) on boats less than 25 m long in 1982. Similar regulations on the usage of TBT in paints came into effect few years later in other countries. As a consequence, TBT and triphenyltin (TPhT), which is also used as biocide in antifouling paints, have been included in the US EPA Environmental Endocrine Disrupters and in the European Union Priority Pollutant Lists (EU, Directive 76/464). Moreover, their global ban is under scrutiny in the forthcoming years (UNEP, POPS/INC/CEG, 1999).

The aim of this work is to provide recent data (e.g. 1995 to present) on the occurrence of TBT and TPhT, and their degradation products in the Western Mediterranean Sea. Surface sediments were analysed from harbours, marinas and sewage disposal sites (domestic and industrial) of the North-western Mediterranean Spanish coast to compare with previous data corresponding to late 1980s[9] in order to evaluate the effectiveness of the European Community regulations.

Area of Study

There are two study areas precisely distinguished; one corresponds to Northeast of the Spanish Mediterranean coast, the Catalan Sea, including four harbours: Masnou, Barcelona, Tarragona and Sant Carles. The other corresponds to the Southeast of Spain, namely the Alboran Sea, including eight harbours, located in Almería, Aguadulce, Almerimar, Marbella, Estepona, Banús, Duquesa and Sotogrande. Furthermore, three sewage disposal areas of different effluent characteristics (type of treatment and composition) were investigated corresponding to municipal (i.e. Barcelona and Almería) and industrial (Tarragona) WTP plants.

Sampling and Strategy

Surface sediment (0-5 cm) was collected from a vessel by using a small van Veen grab. Then, they were placed in aluminium foil plates, transferred to polyethylene bags and kept in a portable refrigerated freezer. To ensure that only the most recent sediment was sampled, only the top 2 cm of sediment was collected. After sampling, sediment samples were transported to the laboratory in refrigerated boxes and frozen at –20 ºC until analysis.

Sample preparation, extraction procedure and derivatization

Freeze-dried and sieved sediments (ca. 2 g; 120 mm mesh) were weighed and transferred to a glass centrifuge tube with a Teflon-lined cap previously wrapped with aluminium foil. Tripropyltin (TPrTCl) and tricyclohexyltin (TCyTCl) chlorides were added as recovery spike (surrogates) to the sample at a spiking level of 200 ng each. Details on the extraction process accomplished by sonication with toluene/HOAc (10:4) for 5 min and derivatization with Grignard reagent are described elsewhere [10]. Finally, evaporation down to 1 mL was carried out under a gentle stream of nitrogen. About 600 ng of TeBT was added to the sample as an internal standard prior to the GC-FPD determination.

Results and Discussion

Organotin accumulation in sediments

The Catalan Sea

Organotin concentrations in sediments from this area varied widely depending on the location. Results for the 1995 sampling survey are shown in Fig. 1. Butyltins were predominant in the whole area of study and the higher levels were found in the Barcelona commercial harbour. Maximum levels for TBT (18700 ng g^{-1}), DBT (6860 ng g^{-1}) and MBT (1675 ng g^{-1}) were found Barcelona harbour. Concentrations of di- and triphenyltin were one or two orders of magnitude lower than butyltins but comparable

for MPhT. The highest phenyltin values were also detected in the Barcelona harbour.

As expected, in the Masnou marina, where pleasure boats are predominant, OT concentrations are lower than in the Barcelona commercial harbour. In MSN stations, butyltin concentrations average 204 ng MBT g^{-1}, 530 ng DBT g^{-1} and 920 ng TBT g^{-1}. In this area of study, the contamination for phenyltin is not relevant (average of 140 ng g^{-1} for all phenyltin species). Butyltin derivatives in Sant Carles harbour were higher than expected according to the harbour characteristics. Station SC1 is the most polluted, located in the marina with longer water residence time than sampling stations located closer to the harbour entrance. In any case, average values for butyltins are moderately high (200 ng MBT g^{-1}, 600 ng DBT g^{-1} and 1600 ng TBT g^{-1}). On the other hand, the station SC3 shows higher values for a fishing wharf (MBT: 202 ng g^{-1}, DBT: 955 ng g^{-1} and TBT: 1110 ng g^{-1}). Those results lead us to consider that fishing boats are using TBT-based antifouling paints.

The Alboran Sea

In the Alboran Sea, OT concentrations in sediments were determined for the first time. Nine harbours and twelve sites were selected in this study. Results are shown in Fig. 1. Almería harbour is the only commercial harbour where OTs were measured. It shows the highest values for butyltins among the harbours located into the southern basin, with maximum levels reaching 785 ng g^{-1} for MBT, 540 ng g^{-1} for DBT, and 2135 ng g^{-1} for TBT. Moreover, a remarkable difference in the concentration levels between this harbour and the Barcelona harbour is noticeable, attributable to the enormous contrast of traffic volume (4 10^6 t *versus* 28.5 10^6 t, respectively) and passenger traffic (i.e. Barcelona doubles Almería). All the rest of marinas from the southern Spanish coast analysed show values that average 975 ng g^{-1} of TBT, except Sotogrande that has a higher value over the average reaching around 3868 ng g^{-1} of TBT. Those values are reasonable because Sotogrande marina has a large number of moorings and also maximum length permitted for the boats.

Sewage disposal sites

Organotin values obtained from the different sewage disposal areas are also shown in Fig. 1. In Barcelona (BS), phenyltins are in the average of 25 ng g^{-1} with maximum levels for butyltins of 120 ng g^{-1}. In any case OT concentrations in Barcelona region are lower in comparison to the Almería sewage disposal site (ASO) analysed, reaching values of 600 ng g^{-1} for MBT, 80 ng g^{-1} for DBT and 270 ng g^{-1} for TBT. Those differences could be accounted for by wastewater treatment and the population served by each treatment plant. In our study, the WTP of Barcelona, which serves ca. 1.5 millions of inhabitants and its composition is 80% domestic, owns a physical-chemical treatment using basic conditions which could lead to an OT hydrolysis. On the other hand, the population of Almería is around 4.5 10^5 inhabitants but its municipal WTP has only primary treatment without alkaline flocculation conditions leading to a higher accumulation of OTs in sediments since their removal efficiency is presumably lower than in the Barcelona treatment plant.

In Barcelona and Almería sewage sludges, phenyltins are found at negligible levels due to the lack of domestic applications of these compounds. These results contrast with the OT composition in an industrial sewage disposal area located in the Tarragona commercial harbour. In this case, butyltin concentrations are similar to those of the Barcelona sewage disposal but phenyltins were identified at low concentrations, except for the station TRQ where values reached the 300 ng g^{-1} of MPhT, attributable to specific manufacturing activities undertaken at this chemical plant. Then, the discharge of OTs related to the disposal of urban and industrial sewage sludge into the coastal environment should not be neglected. In this concern, OTs could be bioavailable by desorption, resuspension or diffusion from sewage sludge into the water column triggering a variety of ecotoxicological effects.

Historical Trends

Organotin concentration for the 1988 and 1995 surveys are shown in Fig. 2. In the Barcelona harbour, the comparison with the data obtained in 1988 shows that OT levels in all stations in 1995 are even higher than those reported previously [9]. Since the first sampling, Barcelona has become a relevant commercial port in the Mediterranean Sea and nowadays, most of the docks are used for cargo boats or for international passenger ferries. Therefore, the growth in boat traffic observed during the last ten years is the reason for the increase of TBT concentration inside the Barcelona harbour. As a brief example, in 1988, 60 ng g^{-1} of TBT were found in BCN3 increasing to 5410 ng g^{-1}; and 975 ng g^{-1} in BCN1 are now close to 19000 ng g^{-1}. As we know all those freighters and ferries are longer than 25 m, so restrictions on TBT-based anti-fouling paints do not affect them. Moreover, the great maritime traffic of ships coming from convenience flag countries where no legislation might be another reason.
In the Masnou marina, a decrease of the levels reported in 1988 [9] was found. In all the stations, OT concentrations declined, in more of the cases, even more than half of the value obtained in the previous sampling. Consequently, the Masnou marina seems to show an effective fulfilment of the TBT regulation. However, in order to estimate the theoretical concentrations assuming reported degradation rate kinetics, actual sediments are exceeding the expected levels.

In Sant Carles marina (SC1), sediment concentrations of OTs were higher than previous data. Consequently, in contrast to Masnou, butyltin values increased enormously from 1988 to 1995 (MBT from 7 to 448 ng g^{-1}, DBT from 24 to 1327 ng g^{-1} and TBT from 12 to 5226 ng g^{-1}). In Sant Carles fishing wharf (SC3) we do not have previous data to compare, but high levels found on it in 1995 also indicate the requirement to implement a monitoring program to control an ecological area of its importance. Finally, in the Barcelona sewage outfall, the sediment analysis accomplished in the late 1980s compared with actual values show no large differences, in both cases values are close to 30 ng g^{-1} in the OT analysed.

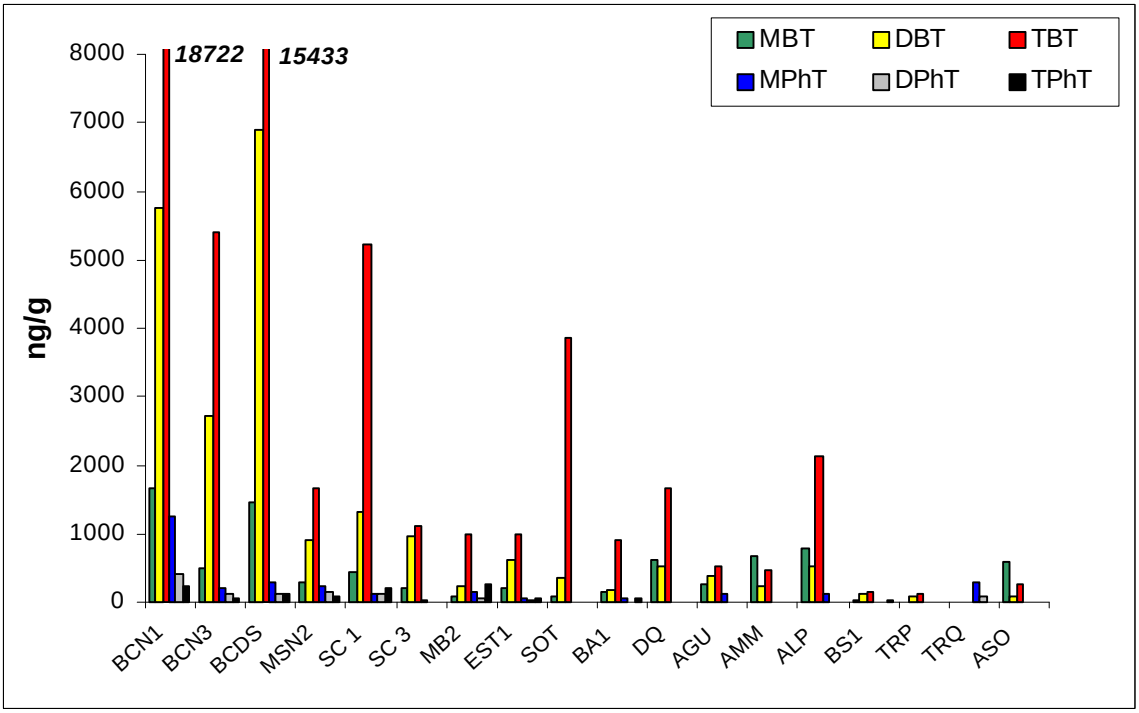
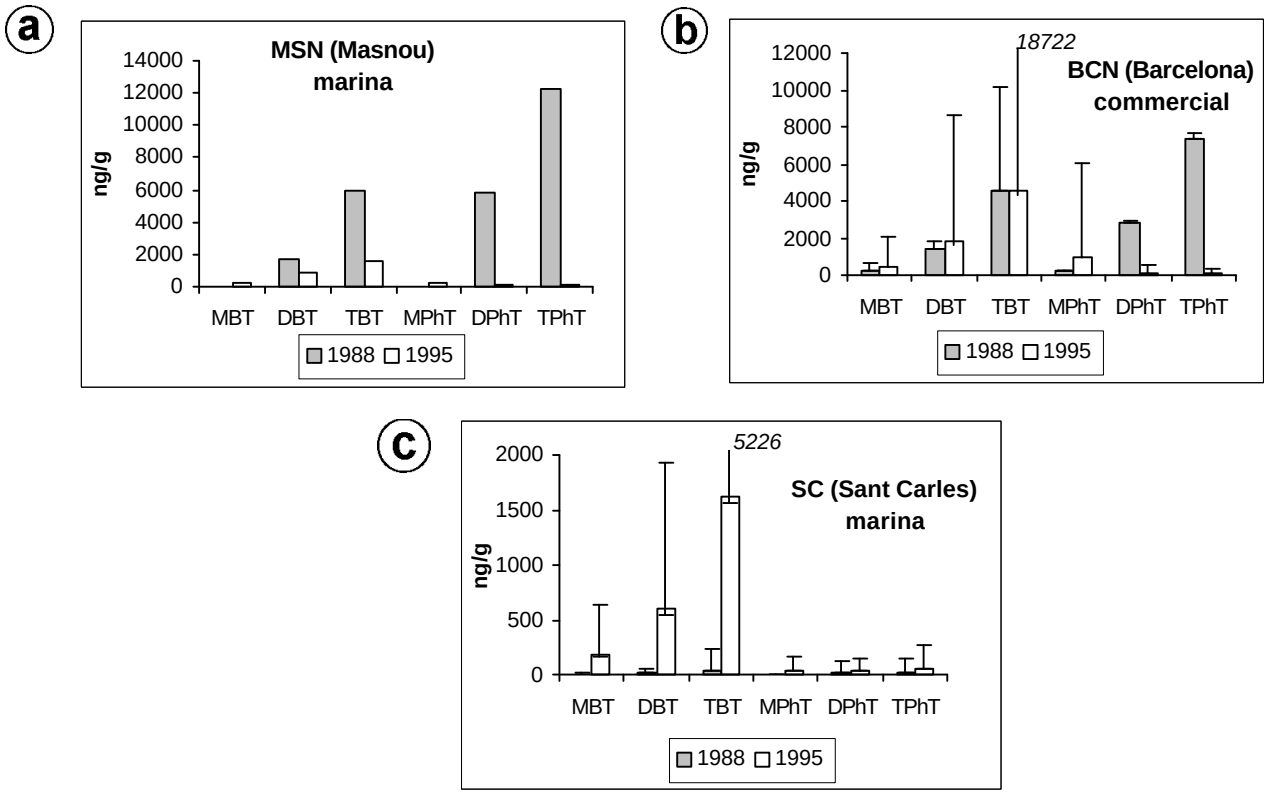


Figure 1. Organotin concentrations (ng g^{-1} dry wt) in all the marinas sediments of the northern (BCN: Barcelona, MSN: Masnou, SC: Sant Carles) and southern Mediterranean Spanish coast (MB:Marbella, EST: Estepona, SOT: Sotogrande, BA: Banús, DQ: Duquesa, AGU: Aguadulce, AMM: Almerimar, ALP: Almería commercial port) and in the sewage outfall in Barcelona (BS), Tarragona (TRP, TRQ) and Almeria (ASO) collected in the 1995-2000 sampling campaigns.



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