www.trjfas.org
ISSN 1303-2712
Turkish Journal of Fisheries and Aquatic Sciences 11: 649-660 (2011) DOI: 10.4194/1303-2712-v11_4_20

The Determination of Organotin Compounds Levels in Sediment Samples from Turkish Aegean Sea Coast

Aykut Yozukmaz[1], F.Sanem Sunlu[1,*], Ugur Sunlu[1], Meral Ozsuer[1]

[1] Ege University, Faculty of Fisheries, Department of Hydrobiology, 35100 Bornova, Izmir, Turkey.
.

* Corresponding Author: Tel.: +90.532 5956470; Fax: +90.232 3883685;
E-mail: f.sanem.sunlu@ege.edu.tr

Received 18 August 2010
Accepted 22 July 2011

Abstract

The purpose of this study was reveal of organic tin compounds (OTC) levels at different marinas choose from Turkish Aegean Sea coastline. The sediment samples were collected in a seasonal period and tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) concentrations were detected at the ng g^{-1} within sediment using by GC coupled MS. In this way, effects of the most important organic tin entry points of maritime activities were try to determine in the coastal line along the Aegean Sea. This study includes from the north to the southern part of all the Aegean Sea coast line from 8 stations and 16 samples with references points. Reference stations were picked in sea shores where far away from maritime traffic and using for human activities like beaches and ports. Station 1, 4, 6, 7 and 8 are the most popular marinas located in study area. Station 3 and 5 are small fishing port, station 2 is the only ship breaking site. Following winter sampling, mean concentration of ∑butyltin for all stations was 1,091.5 ng g^{-1} Sn. and average concentration of ∑butyltin for all reference points was 495.9 ng g^{-1} Sn. After summer sampling, mean concentration of ∑butyltin for all stations was 2,691.2 ng g^{-1} Sn. and mean concentration of ∑butyltin for all reference stations was determined as 1,343.9 ng g^{-1} Sn. Thus, both the highest and lowest OTC levels from the most intense areas in terms of maritime activities along the coast of the Aegean Sea were determined. At the end of the study, we determined that the total OTC concentrations in the sediment samples showed the significant spatio–temporal changes.

Keywords: Organic tin compounds (OTC), sediment, Turkish Aegean Sea, TBT, DBT, MBT.

Türkiye Ege Denizi Kıyılarından Alınmış Sediment Örneklerinde Organik Kalay Bileşiklerinin Seviyelerinin Belirlenmesi

Özet

Bu çalışmanın amacı Ege Denizi kıyı şeridinden seçilmiş farklı marinalardaki organik kalay bileşiklerinin (OTC) seviyelerini ortaya koymaktır. Sediment örnekleri mevsimsel periyotta toplanmış ve sediment içerisindeki tributilkalay (TBT), dibutilkalay (DBT) ve monobutilkalay (MBT) konsantrasyonları gaz kromotografi (GC/MS) cihazı kullanılarak belirlenmiştir. Bu yolla Ege Denizi'nde denizcilik faaliyetleri açısından en önemli organik kalay giriş noktalarının etkileri belirlenmeye çalışılmıştır. Çalışma tüm Ege Denizi sahil şeridinin en kuzeyinden en güneyine kadar olan kıyıdan seçilmiş 8 istasyon ve referans noktaları ile birlikte toplam 16 örnekleme istasyonunu kapsamaktadır. Referans istasyonları deniz trafiğinden uzak olan ve plajlar ile iskeleler gibi daha çok insan aktiviteleri için kullanılan sahile yakın bölgelerden seçilmiştir. İstasyon 1, 4, 6, 7 ve 8 Ege Denizi'nde bulunan en yoğun marinalardır. İstasyon 3 ve 5 küçük balıkçı barınakları iken, istasyon 2 ise Ege Denizi kıyı şeridi boyunca bulunan tek gemi söküm alanıdır. Kış örneklemesini takiben bütün istasyonlar için ortalama ∑butilkalay konsantrasyonları 1.091,5 ng g^{-1} Sn. iken referans noktaları için ise ortalama ∑butilkalay konsantrasyonları 495,9 ng g^{-1} Sn. idi. Yaz örneklemesinden sonra bütün istasyonlar için ortalama ∑butilkalay konsantrasyonları 2.691,2 ng g^{-1} Sn. ve bütün referans istasyonları için ise ortalama ∑butilkalay konsantrasyonları 1.343,9 ng g^{-1} Sn. olarak belirlenmiştir. Böylece Ege Denizi kıyılarında denizcilik faaliyetleri açısından en yoğun bölgelerde hem en yüksek hem de en düşük OTC düzeyleri ölçülmüştür. Çalışmanın sonunda sediment örnekleri içerisindeki toplam OTC konsantrasyonlarının zamansal ve mekansal olarak belirgin bir şekilde değişiklik gösterdiği saptanmıştır.

Anahtar Kelimeler: Organik kalay bileşikleri (OTC), sedimet, Ege Denizi, TBT, DBT, MBT.

Introduction

Although production of organic compounds was started at World War II, Sn metal and its alloys have been of importance to mankind since the beginning of the Bronze Age. While it has various physical, chemical and biological properties, Sn has a larger number of its organometallic derivatives in commercial use than that of any other elements. Over the last 50 years the use of organotin compounds has progressed in other important industrial commodities. Due to the widespread use of the OTC, considerable amounts of these compounds have inevitably been involved in various ecosystems (Ladislao, 2008; Hoch, 2001; Mora *et al.*, 2003; Jacobsen and Asmund, 2000).

Growth of aquatic organisms on vessel hulls create a layer of roughness which give rise to reduction of vessel speed per energy consumption. A 10 µm increase of the rough avarege vessel hull could cause fuel cconsumption to increase about 0.3-1.0% (Champ and Seligman, 1996). To reduce running shipyard costs, roughness of vessel hulls must be prevented. Primary marine antifouling paints used to be based on Cu_2O but such coatings became ineffective within a year and thus more effective biocides were needed. TBT was originally designed for use on the hulls of large ships to reduce the build–up of barnacles and improve speed and efficiency. However, an aggressive marketing program in the 1960's saw its worldwidely fashionable use on much smaller crafts both across the oceans and through inland waterways (Sayer *et al.*, 2006). A widespread use of TBT–based antifouling paints was started early 1970's for the demand. Various commercial applications gave rise to a drastic increase in the worldwide output of organotin chemicals from less than 5,000 tons in 1955 up to 50,000 tons in 1992 (Mercier *et al.*, 1996). In the United States the annual consumption of TBT in antifouling paints were reported to be about 450 tons in 1987 (Champ and Bleil, 1988). Thus approximately 7% of the tin metal was used to produce organo metallic derivatives (Donard *et al.*, 1988).

General definition of organic groups with the tin atom is series of $RnSnX_4$–n regardless of their quantities which produces maximal anti biological activity against all species when n=3 (Blunden *et al.*, 1984; Dubey and Roy, 2003). In the aquatic environment, TBT is quickly removed from the water column down into bed sediments because it has a high specific gravity with about 1.2 kg L^{-1} at 20°C (Landmeyer *et al.*, 2004), low solubility (less than 10 mg L^{-1} at 20°C and pH 7.0) (Fent 1996), and log K_{ow} values near 4.4 at pH 8 (Meador, 2000). Additionally, TBT is ionisable and exhibits a pK_a acidity constant of 6.25 (Meador, 2002). TBT sorption/desorption in natural sediment can be strongly influenced by changing pH and salinity, which may be explained by the contrasting sorptive behaviour of the neutral and ionic species under given pH and salinity conditions (Arnold *et al.*, 1998; Meador, 2000; Hoch *et al.*, 2003; Burton *et al.*, 2004) similar to what has been reported for other ionisable hydrophobic organic contaminants in sandy sediments (Antizar–Ladislao and Galil, 2004). Because the adsorption of TBT on to sediments is reversible, contaminated sediments can act as a long–term source of dissolved–phase contamination to the overlying water column (Unger *et al.*, 1988). Furthermore, aging may be an important component of the fate of TBT in contaminated sediments, particularly in samples with high contents of organic carbon (3–5% w/w) (Burton *et al.*, 2006). The affinity of organotins for adsorption to sediments is positively correlated with the extent of organo–variability in the tin, such that increasing adsorption is seen for MBT<DBT<TBT (Landmeyer *et al.*, 2004).

In the aquatic environment, OTC's have low aquarious solubility and low mobility, and are easily adsorbed onto suspended particulate matter (SPM). Like in sediments, the TBT has a tendency to bond to particular matters in water. They are in the form of either particulate organic matter or attached to the mineral phase. Despite their high atomic weights and low aqueous solubilities, OTC's tend to adsorb onto particles and directly merge with sediment, where they accumulate and release back into water column by re–suspension of particles. TBT may have high toxic effect even in lower concentrations depending on variation and number of organisms in its environment and on impact range. Although sediments can be identified as ending points, desorption of TBT into solid particles is considered a feedback process. Therefore, sediments are actually not ending points for this toxic matter, but are renewable pollutant sources (Hoch and Schwesig, 2004). Due to the functional groups, organic matters can adsorb different pollutants thus the content of organic carbon in sediments should strongly influence their capability to retain the TBT. The mineral composition of the sediment, especially clay fraction components is important as they influence the adsorption of TBT. The maximum TBT adsorption in clay takes place at pH 6-7. A large proportion of the organotin contaminants are found to be associated with the clay fraction of particulate matter, indicating that concentration and adsorbtion onto this fraction is an important control mechanism for distribution and fate of the organotins in the environment. The particle concentration and salinity also have impact on the adsorption, from which it was found that the adsorption of TBT into the sediment was mostly affected by organic matters (both by the organic matter adsorbed to mineral particles and by the particulate organic matter). This is an important process in the fate of TBT in the aquatic system. The deposition of the SPM leads to organotin scavenging in sediments where considerable amounts of the tri–substituted organotins and their degredation products could be detected. Thus, sediments may serve as traps for these toxic contaminants. In the wastewaters having high amounts of suspended solids, the TBT is mainly associated with particulate matter. The adsorbed matters influence particularly the benthic organisms and the ones feeding by filtering the water. Organotin compounds taken from water and sediments may accumulate in the body of the organism. The accumulation as the result of both pathways is often proportional to concentration of the compound in the environment. The extent of bioaccumulation is further influenced by biodegradation based on excretion of the related organisms. Another factor of bioaccumulation is the pH. Since the pH of seawater is higher than 8, the dissolution of the TBT and the Triphenyltin (TPT) from body are low, and they have a tendency to accumulate in the tissues and organs of aquatic organisms (Rüdel, 2003).

As a result of the studies related to organic tin pollution in aquatic environments, legal restrictions have applied in the developed countries, especially those progressing in shipping, yacthing and ship–building. TBT, the reason for such prohibitions can directly spread from antifouling paints into the water and increase the level of contamination in water and sediment of the marinas, lakes and coastal areas.

Due to the impact on the exploitation of marine biological resources generated by chronic TBT contamination, there are to be some restrictions on using organotins. French government regulated the use of TBT–containing paints fort the first time in January 1982 for vessels up to 25 m length. In 1985, government of the United Kingdom prohibited the application of TBT–based antifouling paints to small vessels. Canada government regulated TBT's maximum daily release rate for antifouling paints of 4 μg TBT per cm^2 of hull surface in 1989. The restriction on TBT usage in antifouling coatings of boats and aquaculture nets was imposed in Japan in 1990. Furthermore, in November 1999, International Maritime Organization (IMO) accepted global prohibition aimed at harmful effects of antifoulings on ship coating and decided to constitute a system to replace them, which includes prohibition of the environmentally harmful TBT applications in anticoating systems in vessels by 1 January 2003 and their complete banning in 1 January 2008 (IMO, 2001).

The monitoring studies in the world show that the organotin pollution still goes on in the coastal areas, bays and open seas. The studies carried out in the coastal areas and the inland seas of Pacific, Atlantic and Indian Oceans emphasized the critical level of organotin pollution in the harbours and the marinas with an intensive maritime traffic. While most of the studies were based on the determination methods and on the amount of organotin compounds in sea water and in sediments, some others were carried out with sea organisms. Especially physical and functional damages were observed in the indicator sea organisms. The amount of organotin compounds accumulated in the organisms were determined, which showed that they were mostly accumulated in organs and tissues.

The importance of sediments in organotin pollution was noticed. The studies showed that the sediments were not the ending point but they were a renewable source (Kırlı, 2005; Ladislao, 2008; Quevauviller *et al.,* 1994; Lee *et al*., 2006; Buggy and Toblin, 2006). It was emphasized that this situation was the reason why sediments were significant factors in the continuation of organotin pollution in seas since at the same time removal of the dredging wastes caused additional pollutions.

In Turkey, public and private seaports and the increasing number of marinas constructed on the Bosphorus and Dardanelles Straits, Black Sea, Marmara Sea, Aegean Sea and Mediterranean Sea coasts are noteworthy regions to make research into organotin compounds and other biocides with antifouling effect. Although OTC's are extremely hazardous to aquatic ecosystem, there are very few data of them and their detrimental impacts on the marine environment of the Aegean Sea. The purpose of study is to determine tributyltin and it's derivatives' levels and assess the hot spots at the most important maritime points along the Turkish Aegean Sea coast where there are considerable maritime activities, e.g., fishing and yachting, involving the heavy commercial maritime processes. Especially, the ways in which the organisms living in the seas around Turkey are influenced by OTC's, the reflection of which on sea foods are subjects of further studies.

Materials and Methods

Sampling Area

Station 1, is located between 39°19′ N latitude and 26°41′ E longitude. Station 2 located in Aliaga coastal area which is around 1.5 km. long and has 26 ship wreckling facilities. In winter periods these facilities decompose ships less than in summer periods when a mean of 4-6 ships are decomposed per facility. Station 3 is located between 36°50'06" N–30°06'02" E latitude and longitude. Station 4, is located between 39°42′25″ N latitude and 27°04′04″ E longitude. Station 5, is located between 38°21′76″ N latitude and 26°20′42″ E longitude. Station 6 is a big hosting yacht and bonding area located between 38°19′30″ N latitude and 26°20′42” E longitude. Station 7 and Station 8 are located at 37°52′20″ N–27°15′46″ E and 37°02′00″ N–27°25′50″ E latitudes and longitudes respectively (Figure 1).

Sampling Method

Sediment samples were collected from 8 stations ranging from northern stretch of Aegean Sea from Station 1 in southern stretch to Station 8 along the coastal zone between March 2009 and August 2009. Reference stations were determined which are relatively far from the maritime activity where human and marine environment entwined as in beaches and piers.

Sediment samples were collected by standard

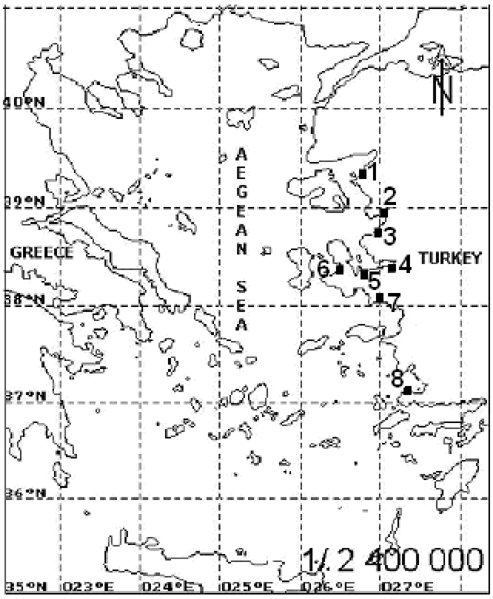

Figure 1. Map of the sampling area.

(6x6x6) stainless steel Ekman Grab® from 0–10 cm surface of the sediment layer and 1–10 m. depth of the sea surface according to difference in geological composition between the station areas. Sample analyses were carried out using GC/MS, HP Agilent 6890–coupled 5973N Mass Selective Detector (non–detected–nd. limits for MBT, DBT, TBT were 0.003, 0.001, 0.001 ng g^{-1} Sn respectively).

To avoid contamination, grab and spatula were washed with methanole and pure water between different sampling stations and collected samples put into pre–cleaned (methanole and pure water) glass container with stainless steel spatula. Glass containers were covered with alimunium stretch to prevent solar rays and with cotton plaster to avoid contamination from plastic material. Collected samples were stored at –4°C along the way then at –18°C in the deep freeze until the day of analysis.

Analytical Methods

Following open air drying for 4 days, sediment samples were shived through a 1 mm mesh and 5–10 g was oven dried at 110°C. 0.1 M NaOH solution was poured into a 50 ml baloon joje as a solvent for determining OTC's. 17,5 molarity, 0,2 M acetic acid (1142 µl) was poured into a 100 ml baloon joje to prepare a buffer solution. 17 g sodium acetate was measured and added to 100 ml baloon joje, the pH of which this mix should be 5.4. If pH level is not acceptable it should be rearranged in a way to use a suitable acid or alcali (NaOH).

95% purity butiltin trichloride, 96% purity tributiltin chloride and 96% purity dibutiltin dichloride are sequentially used for preparing standards, after bought from Aldrich. These standards were prepared in acetic acid/methanol solution of 3:1 ratio in such a way that it could be 1000 ppm. Amber glass tubes were selected to eliminate light factor.

Sediment sample of 0.5 g was weighed and placed into a glass tube. Acetic acid/methanol solution of 4 ml at a rate of 3:1 was added into it and treated with ultrasonic shredder for 10 min. Meanwhile, standards were prepared for analyses. 100 µl was taken from each standard and mixed standard was prepared in the same way.1000 µl was completed by adding acetic acid/methanol solution of 700 µl at a rate of 3:1 into the mixed standard. Sample of 200 µl taken from the ultrasonic shredder was put into two separate tubes. 100 µl of 10 ppm standard was added to a sample of one tube and buffer solution of 4 ml added into each tubes. Later, derivation was started. 0.5 ml sodium tetraetilborate solution was added into both tubes and they were treated with ultrasonic shredder for 10 min., after which by the addition of 1 ml Hexane they were vortexed for a while to be mixed and then entire portion of the supernatant of the samples, held in shaker at 250 rpm. for 1 hour, was taken and 5 µl of it injected into the device for GC analysis.

GC/MS which consists of a 5973N Mass Selective Detector connected to Agilent 6890 GC, was used for analysis. Column type was HP5MS (30 m x 250 mm x 0.2 µm). Oven initial temperature was 40°C (the first 1 minute) and samples were burned with a gradual increase at 20°C of per minute up to 300°C as a final temperature. Flow rate was 1.2 ml a minute and injection amount was 5 µl. but the mixed standard of 1µg ml^{-1} was injected. The lowest level to be detected was 0.001 for MBT, 0.003 for DBT and 0.0009 ng g^{-1} for TBT and retention times were 4.76 for MBT, 5.52 for DBT and 6.17 min. for TBT.

In order to quality control of the analytical results, CRM–462 (Coastal Sediment for Butyltins) provided from IRMM (Institute for Materials and Measurements) and analyses of CRM–462 proved that the method was able to accurately determine levels of OTC's (Table 1).

Sediment sample of 0.2–0.5 g was put into glass tube for the determination of the amount of carbon (%) in it. 10 ml ultra pure water, 20 ml (H_2SO_4 + 6.6 g Ag_2SO_4), 0.5 g $HgSO_4$ and 1N $K_2Cr_2O_7$ was added into it and treated with shredder for 10 min before heat up to 160°C for 2 hours. After that, all samples were taken into 400 ml conical flask then, 150 ml of distilled water and 10 ml H_3PO_4 (75% purity) were added and were left to cool down. This solution was titrated with mohr salt ($Fe(NH_4)_2(SO_4)_2 6H_2O$) by the help of 3 drops of ferroin indicator until its' color return from green to red and consumptions were determined. Carbon (%) values were calculated using the following formula (Egemen, 1999);

$$\text{Carbon (\%)} = \{[(N-N')\text{x } 0.12] / \text{Sediment val.}\} \text{ x } 25/\text{Tit. cons. val.}$$

N = Blank consumption.
N' = Sample consumption.

Results

As a result of the winter sampling, the highest ∑butyltin level was detected from Station 4 (1927.6 ng g^{-1} Sn). The lowest ∑butyltin level was measured from Station 5 (nd.) with a mean concentration of ∑butyltin for all stations being 1091.5 ng g^{-1} Sn. The highest concentration of ∑butyltin was detected in Station 1 (1464 ng g^{-1} Sn) and the lowest concentration was measured in the Stations 7, 3, 4 and 5 from the reference points (nd.). A mean concentration of ∑butyltin for overall reference points was 495.9 ng g^{-1} Sn.

While all values from the reference Station 4 were below the detection limits (nd.), the most concentrated organic tin derivates were found to be 928.4 ng g^{-1} Sn DBT – 999.2 ng g^{-1} Sn TBT in Station 4. In Station 2, levels of OTC's were found to be 704.4 ng g^{-1} Sn DBT – 1050.0 ng g^{-1} Sn TBT and were measured as 505.2 ng g^{-1} Sn DBT – 442.0 ng g^{-1} Sn TBT in reference station 2. 518.4 ng g^{-1} Sn DBT – 828.4 ng g^{-1} Sn TBT were measured and 900.8 ng g^{-1} Sn DBT– 563.2 ng g^{-1} Sn TBT were detected in Station 1 and reference station 1 respectively. Detected concentrations were 892.4 ng g^{-1} Sn DBT – 778.4 ng g^{-1} Sn TBT from the Station 6 and 455.2 ng g^{-1} Sn DBT –444.0 ng g^{-1} Sn TBT from the reference station 6.

In Station 8 160.0 ng g^{-1} Sn MBT, 410.0 ng g^{-1} Sn DBT and 530.0 ng g^{-1} Sn TBT were measured and the reference station's values were 400.0 ng g^{-1} Sn DBT – 280 ng g^{-1} Sn TBT. After the winter sampling, only DBT values were detected in Station 3 as 808 ng g^{-1} Sn. OTC levels in reference station 3 were nd. While the levels were 788.0 ng g^{-1} Sn DBT and 431.2 ng g^{-1} Sn TBT in Station 7, all the values were below the detection limits in reference station 7. Levels of OTC's were nd both for reference and sampling Station 5 (Figure 2).

At the end of the summer sampling, the highest total ∑butyltin level was seen in Station 2 (4278.4 ng g^{-1} Sn). The lowest ∑butyltin level was measured at Station 5 (983. 6 ng g^{-1} Sn) with a mean concentration of ∑butyltin for all stations being 2691.2 ng g^{-1} Sn. For the reference stations, the highest and lowest

Table 1. The mean results of analyses of CRM–462 which used for test of the reliability of the device and method of analyses

	BCR 462 Coastal Sediment		
	Certificated Value (µg kg^{-1})	Confidance Interval (µg kg^{-1})	Measured Value (µg kg^{-1})
Tributiltin	54	±15	58.73 (7 repetition)
Dibutiltin	68	±12	56.33 (7 repetition)

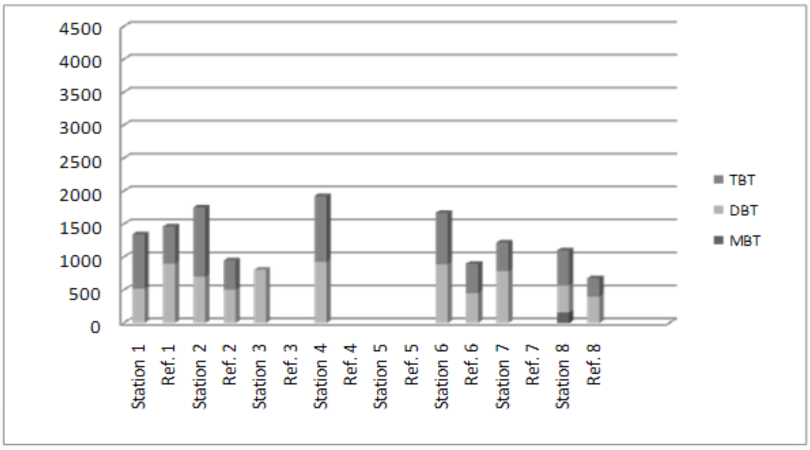

Figure 2. Levels of organic tin derivates in winter sampling period at sampling and reference stations.

levels of ∑butyltin were measured 2207.6 ng g^{-1} Sn for Station 4 and nd. for Station 7 respectively. A mean concentration of ∑butyltin for all reference stations was determined as 1343.9 ng g^{-1} Sn.

Following the summer sampling, the highest OTC's were found to be 453.6 ng g^{-1} Sn MBT, 816.2 ng g^{-1} Sn DBT and 3008.6 ng g^{-1} Sn TBT in Station 2. The levels of MBT, DBT and TBT were 409.8, 835.4 and 227.8 ng g^{-1} Sn in reference station 2 seriatim. Those in Station 1 were measured as 620.2 ng g^{-1} Sn MBT, 1043.0 ng g^{-1} Sn DBT and 2200.2 ng g^{-1} Sn TBT. While the concentrations were 425.4 ng g^{-1} Sn MBT and 914.6 ng g^{-1} Sn DBT, TBT level was nd. In Station 8 301.8 ng g^{-1} Sn MBT, 918.9 ng g^{-1} Sn DBT and 1609.4 ng g^{-1} Sn TBT and in reference station 8 416.2 ng g^{-1} Sn MBT, 821.8 ng g^{-1} Sn DBT and 250.2 ng g^{-1} Sn TBT were detected. 316.2 ng g^{-1} Sn MBT, 598.2 ng g^{-1} Sn DBT and 1275.4 ng g^{-1} Sn TBT were measured in Station 3 while 428 ng g^{-1} Sn MBT, 473 ng g^{-1} Sn DBT and 202.2 ng g^{-1} Sn TBT detected in reference station 3.

In Station 4, 506.8 ng g^{-1} Sn MBT, 1003.8 ng g^{-1} Sn DBT and 1225.4 ng g^{-1} Sn TBT were determined; MBT was nd., DBT was 945,4 ng g^{-1} Sn and TBT was 1262.2 ng g^{-1} Sn in reference station 4. Station 6's levels were 892.4 ng g^{-1} Sn DBT and 778.4 ng g^{-1} Sn TBT while 455.2 ng g^{-1} Sn DBT and 444.0 ng g^{-1} Sn TBT were detected in reference station 6.

In Station 7, MBT, DBT and TBT levels were 565.4, 1371.3 and 996.6 ng g^{-1} Sn repectively while all values nd. in reference station 7. MBT was not detected in Station 5 and DBT level was 471.8 ng g^{-1} Sn and TBT level was 511.8 ng g^{-1}. In reference station 5 MBT, DBT and TBT levels were 304.0, 730.6 and 615.8 ng g^{-1} respectively. 2598.9 ng g^{-1} Sn MBT, 976.6 ng g^{-1} Sn DBT and 320.6 ng g^{-1} Sn TBT were measured in Station 6 and 455.0 ng g^{-1} Sn MBT, 847.4 ng g^{-1} Sn DBT and 186.6 ng g^{-1} Sn TBT were measured in reference station 6 (Figure 3).

The majority of metal contaminants partition onto particulate matter such as clay minerals, Fe and Mn oxides/hydroxides, carbonates, organic substances (e.g., humic acids) and biological materials (e.g., algae and bacteria) (Calmano *et al.*, 1993). Research has shown that Fe and Mn oxides/hydroxides along with organic matter are important binding sites for metals in oxic sediment and It is well known that many pollutants generally increase with decreasing particle size and metals bound to organic matter in sediment (Saulnier and Mucci, 2000; Li *et al.*, 2000; Zoumis *et al.*, 2001; Fan *et al.*, 2002).

Organic and organometallic contaminants preferentially partition to organic matter in sediment. Therefore, the carbon (%) amounts which found in sediment samples from all stations were determined for compare to the total OTC levels (Table 2).

The total OTC levels and the amount of carbon (%) contents in the samples which taken from stations have been identified in similar changes between the summer and winter seasons (Figure 4).

As a result, a strong lineer correlation was found

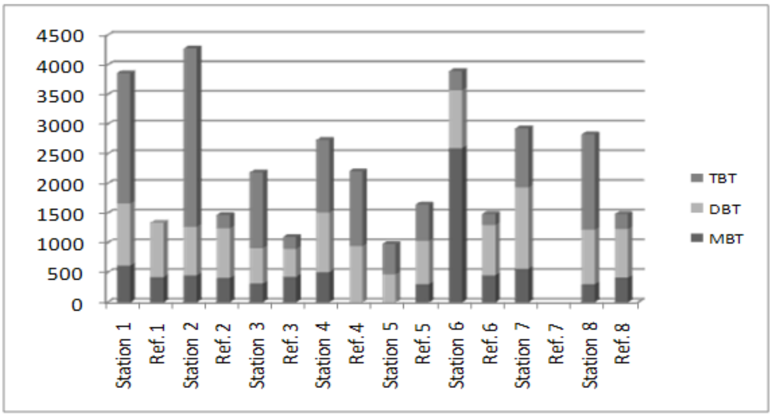

Figure 3. Determined OTC levels in sampling and reference stations after summer sampling period.

Table 2. The amount of determined carbon (%) in the sediment samples and, biotope–structure content of the sediment from the stations′

Station	Coordinates	Biotop+Structure	% Carbon
1	39°19′ N–26°41′ E	Muddy gravel	4.01
2	38°52′45″ N–26°54′48″ E	Mud	11.58
3	36°50′06″ N–30°06′02″ E	Muddy gravel	2.85
4	39°42′25″N–27°04′04″ E	Mud	4.53
5	38°21′76″ N–26°20′42″ E	*Posidonia* sp.+ Mud	1.67
6	38°19′30″ N–26°20′42″ E	Muddy gravel + *Coulerpa* sp.	8.21
7	37°52′20″ N–27°15′46″ E	Mud	4.94
8	37°02′00″ N–27°25′50″ E	Muddy gravel	4,61

when compared total OTC levels against to the values of carbon (%) from summer and winter periods from all the stations (F= 6,115 $P<0.05$ for winter; F= 6,832 $P<0.05$ for Summer. F_t= 5.59 for degrees of freedom:1–7).

Discussion

In this study, possible OTC–contaminated areas were predetermined along the Aegean Sea coast and TBT, DBT and MBT concentrations measured. Revealed hot points emphasized the areas to be further studied.

Large number of research has showed that sediment is not a storage place but serves as a renewable source for OTC's (specially TBT) (Hoch, 2001; Diez *et al.*, 2005; Kırlı, 2005; Buggy and Tobin, 2006; Berto *et al.*, 2007; Ladislao, 2008).

Sampling station 2 is a place where retired ships wait for paint removal process on the ground. Because antifouling paint remove operation is conducted without any precaution, 20 25 firms cause an uncontrollable TBT contamination. The highest value of TBT (1,050.0 ng g^{-1} Sn in winter and 3008.6 ng g^{-1} Sn in summer) confirmed the related risky situation in the aforementioned site. Continuous ship entrance, thrice demolition rate in summer and removal process in the sea water during grounding of ships could be responsible for such a considerable contamination. In reference station of previously mentioned site, 505.2 ng g^{-1} Sn DBT and 442.0 ng g^{-1} Sn TBT were measured in winter period and 409.8 ng g^{-1} Sn MBT, 835.4 ng g^{-1} Sn DBT and 227.8 ng g^{-1} Sn TBT were measured in summer period. Furthermore, reference station values were higher in summer than in winter because of the area being an open bay and anchored ships in the bay being much more in summer than in winter (in winter period no ships have been observed but in summer period 25 ships have been detected to be anchored). DBT and MBT are not used as biotoxin on ships but are found in high quantity depending on the fact that this region is the industrial zone and TBT to DBT and MBT decomposed by bioactives. Every ship grounding process could lead to the transportation of remobilized TBT into water by mixing sediment (Hoch, 2001).

Although 928.4 ng g^{-1} Sn DBT and 999.2 ng g^{-1} Sn TBT were measured in Station 4 (75 ship capacity) in winter sampling, 506.8 ng g^{-1} Sn MBT,1003.8 ng g^{-1} Sn DBT and 1225.4 ng g^{-1} Sn TBT were detected in summer sampling. The high TBT values in summer period may be consequent of launching ships into the sea especially in summer time and discharging scraped paints into sea without any treatment in spring. After winter sampling, all OTC values were below the concentration limits. The difference between station and reference station may caused by position of Station 4 in the middle of the inner bay and by the adjacent İzmir Harbour and ferry port. The low levels of reference station in winter sampling may be caused by situation of reference station 4 near the mouth of the bay and thus by being away from the ferry traffic and water movements. In the summer sampling OTC levels were determined as 945.4 ng g^{-1} Sn DBT and 1262.2 ng g^{-1} Sn TBT in reference station 4. Differences in summer and winter period levels between reference station and station could be result of OTC compounds in the adjacent river Bostanlı which flushes off industrial waste into bay during heavy rains in spring.

After winter sampling, OTC levels were 518.4 ng g^{-1} Sn DBT and 828.4 ng g^{-1} Sn TBT in Station 1 (240 boat capacity). Despite the high boat capacity, OTC levels in Station 1 were lower than Station 4 due to the intensive marine traffic both in summer and winter periods in Izmir Bay. Levels of organic tin compounds were determined to be higher than in other marinas because the marina is mostly set as yacht marina, it is less effected from waves based on its location in inland sea, especially after connecting Dolap Island with mainland circulation has ended in stopping the branch stream from flowing through the bay and after all arriving and departing waters in straits remained too weak to undercurrent in the bottom of marina. The levels were 620.2 ng g^{-1} Sn MBT, 1043.0 ng g^{-1} Sn DBT and 2200.2 ng g^{-1} Sn TBT after summer sampling, which may be induced by maximum usage of capacity in summer season.

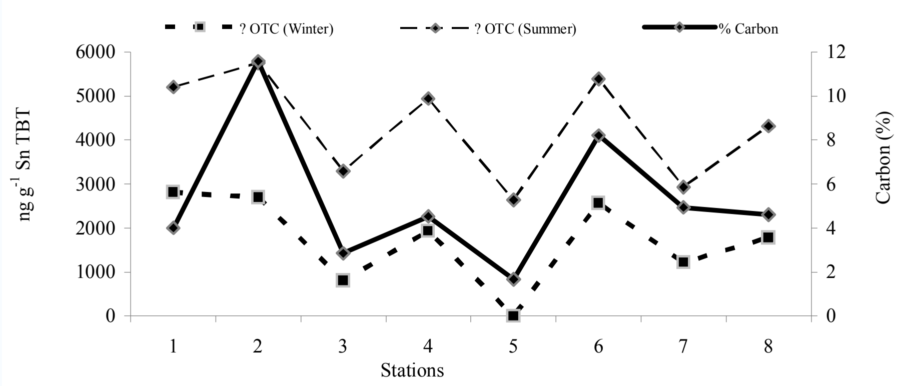

Figure 4. The amount of total OTC with carbon content changes in summer and winter seasons from the stations.

Painting activities in dock yard (100 boat capacity) in spring could also be a major source of contamination. Maximum release rate of biocid occur from the newly painted hulls (Hoch, 2001), which could explain the high accumulation levels in this site. 900.8 ng/g DBT and 563.2 ng g^{-1} Sn TBT were determined in reference station 1 after winter season. In summer period, while 425.4 ng g^{-1} Sn MBT and 914.6 ng g^{-1} Sn DBT were measured TBT was not detected. The close structures of the bay and many harbours, boat yard and overwintering places located in the area may cause considerable levels of the compounds. TBT's undetectable levels in reference station in summer and occurance of MBT both in reference station and marina could suggest that TBT is degredated by bioactivity in the area.

892.4 ng g^{-1} Sn DBT and 778.4 ng g^{-1} Sn TBT were measured in Station 6 in winter period while 2598.9 ng g^{-1} Sn MBT, 976.6 ng g^{-1} Sn DBT and 320.6 ng g^{-1} Sn TBT were detected in summer season. The marina (180 boat capacity) was constructed as Turkey's first private marina in 1974. The marina has been maintained for a couple of times since its establishment and serves for the pleasure craft for the longest period of time in Turkey, which was quite likely to lead to accumulation of OTC's. The values were 455.2 ng g^{-1} Sn for DBT and 444.0 ng g^{-1} Sn forTBT in reference station 6. In summer time 455.0 ng g^{-1} Sn MBT, 847.4 ng g^{-1} Sn DBT and 320.6 ng g^{-1} Sn TBT were determined. DBT concentrations was almost same as TBT concentrations may suggest that TBT has been broken by bioactivity (especially phytoplankton) in the area. The high MBT concentration (2598.9 ng g^{-1} Sn MBT) suggest that there could be acceleration of bioactivity because of the sea warming in summer.

In winter 160 ng g^{-1} Sn MBT, 410.0 ng g^{-1} Sn DBT and 530.0 ng g^{-1} Sn TBT were determined while 301.8 ng g^{-1} Sn MBT, 918.9 ng g^{-1} Sn DBT and 1609.4 ng g^{-1} Sn TBT after the summer period analysis in Station 8 with 450–500 boat capacity. 400.0 ng g^{-1} Sn DBT and 280 ng g^{-1} Sn TBT were detected in the reference station in winter period and in summer period, with 416.2 ng g^{-1} Sn MBT, 812.8 ng g^{-1} Sn DBT and 250.2 ng g^{-1} Sn TBT being measured. Although the marina (450–500 boat capacity) is running at full capacity both in winter and summer seasons, the relative low levels of TBT in winter could be a reason for intense degredation in winters. In this case, detecting both MBT values in marina and DBT level 1.5 times more than TBT level in reference station 8 are shown as evidence. The high TBT level measured in summer may be the result of heavy marine traffic, boat yard inputs and cruise ships of large tonnage. The reason for low levels of TBT in marinas may be due to the small boat yard as compared with the other marinas. The determined high levels of DBT and MBT in summer season could be consequence of bioacitvity.

The levels of DBT and TBT were 788.0 and 431.2 ng g^{-1} Sn in winter season respectively while 565.4 ng g^{-1} Sn MBT, 1371.3 ng g^{-1} Sn DBT and 996.6 ng g^{-1} Sn TBT were measured in summer. In reference station, levels of all OTC's were founded below the detection limit both in winter and summer. The low levels of TBT and DBT both in summer and winter seasons may be caused by bioactivity. In winter period, level of DBT was almost 2 times more than that of TBT in marina and in summer period measured DBT (1371.3 ng g^{-1} Sn) and MBT (565.4 ng g^{-1} Sn) values were higher could indicate that bioactivation starting at the end of the winter period continuously increases in summer period in the region. Reference station 7 is opened to usage as beach by people and located far from maritime activities, which may explain for values less than previously measured values.

Station 3 is located in an open bay and consists of pier along the cost line, which is distinguishable from other marinas and ports. Following the winter sampling period, only DBT was measured as 808.0 ng g^{-1} Sn in and around harbour, the reason for which until 2005 there were no customs gates in the region and foreign boats to the region especially preferred Cesme Marina (Station 6) and similar ports, there existed military zone prohibited for ships to enter and thus no suitable boat yard in the region. Although the region has the biggest trawl fleet of Aegean zone, maintenance facilities for fishing vessel and gear nearest to Foca is in Cakalburnu. All ships in the region head for different places for maintenance and repairment. Most effective concentration of TBT mixed into water is within the first 1–2 weeks. Because ships are maintained in different regions, go out for fishing and then prefer the port, Cakalburnu to protect vessels from weather conditions, values of tin compounds may be found to be low in Station 3. Winter analyses determined only DBT concentration because of either transformation of low level TBT to DBT due to biodegradation or continental convection. At Foca Harbour (Station 3) 316.2 ng g^{-1} Sn MBT, 598.2 ng g^{-1} Sn DBT and 1275.4 ng g^{-1} Sn TBT values were determined but in reference station 428.0 ng g^{-1} Sn MBT, 473.0 ng g^{-1} Sn DBT and 202.2 ng g^{-1} Sn TBT values were determined. During summer period, 4 large passenger ferry boat continuously cruise between Greek Islands and Foca Harbour in Aegean Sea and wait for their turns anchored in Foca Harbour, which may explain for higher values of OTC's in analyses of summer period.

In winter period, OTC's limits measured in Station 5 were determined below those from other stations. However, in summer period 471.8 ng g^{-1} Sn DBT and 511.8 ng g^{-1} Sn TBT values were determined by analysis of samples gathered from pier. While determined values for each derivative of organic tin compounds levels were under measurement levels in winter period in reference station 5, MBT 304.0 ng g^{-1} Sn, DBT 730.6 ng g^{-1} Sn and TBT 615.8 ng g^{-1} Sn were determined in summer period. The fact that the differences ocur between summer and winter periods could be accounted for by additional number of boats anchored to the pier and near reference station 5 and thus acceleration of vessel traffic in the region in summer. Inputs of OTC's into reference station 5 may be result of convection caused by wave motions or anthropogenic effects.

Such high levels of OTS's determined at all stations in summer–winter periods along Aegean Sea seashore were because of too much affiliated boats in the region (in summer–winter almost 100% capacity utilization or higher at all marinas) and due to TBT easily likely to be connected to sediment, levels of OTC's were higher. Also, since the worldwidely introduction of prohibitions concerning usage of TBT in vessel paints, the regular observation has shown that TBT–based paints are stil used on boats less than 25m illegally and may therefore lead to high levels of TBT concentrations especially in marinas (Ceulemans *et al.*, 1998). Contamination in Aegean Sea with OTC's could be concequence of the fact that either TBT–based paints are illegaly used on boats less than 25 m or vessels were already treated by TBT–based paints because effective periods of paints are relatively long (5–7 years) prior to the related sanctions.

In all stations levels of other organic tin compounds (MBT and DBT) may be determined high because of decomposition of TBT by biological separators. Especially in summer increased levels of MBT and DBT may indicate that biological separators are more than in summer period than the winter period. Also reference stations may have been contaminated with TBT carried down by currents from the marinas. In addition, these areas may contaminated with organic tin compounds because of existing transport activities at the ports in the region and such seashores being used for stopover by tourist cruise ships especially in summer.

Conclusion

In the late 1970's, creation of problems for the marine ecosystem by OTC's was first found only after oyster population collapsed in Arcachon Bay, France. Urgent measures taken in February 1982 were applied succesfully (Alzieu, 2000). In the following years, world nations, mainly European countries have been trying to take precautions for existing levels of pollution by determining the organic tin in seas. In 1989, the European Union declared a prohibition of TBT for boats less than 25 m (89/677/CEE). Following the prohibition of TBT–based antifouling paints, monitoring programs were developed in most developed countries to determine the effectiveness of current arrangements, which indicated that tin compounds were found anywhere in aquatic organisms and marine systems.

Until 2008, it is not surprising that high levels of organic tin compounds were found in harbours, marinas and dry pools, because of the main active substance, Tributiltin in antifouling paints used for removal surface of ships from the negative effects of organisms which cling to marine vehicles and therefore increase in fuel consumption, transporting of species between environment, etc. However, although there were laws in many countries regulating the use of organic tin, the related contaminants continue to create a risk to many terrestrial and aquatic ecosystems. Furthermore, neither prohibitions have not put into effect yet nor controls are properly done in developing countries.

It follows from values obtained in this study that located on the shores of the Aegean Sea, most important marinas, harbours, fishing shelters and slipways involving maritime and fisheries activities across shores of the Aegean Sea have already been contaminated with OTC's. On the other hand, even less active and smaller shelters farther away from the maritime activities at the Aeagen Sea coastline have been found to be affected by pollution. Especially, coastal marine environment utilized by people as beaches and piers suitable for swimming have been too much contaminated with OTC's caused by flows of convection, biological fragmentation, maritime activities or terrestrial inputs.

High levels of tin compounds measured in summer–winter period along the Cost of Aegean Sea may be result of the numerous marinas (operating 100% or more capacity almost all year long) and strong adsorption tendency of TBT. Additionally, high concentrations of TBT suggesting the illegal usage of TBT–based antifouling paints on ships smaller than 25 m (Ceulemans *et al.*, 1998). Furthermore, ongoing contamination of Aegean Sea could be consequence of leaching from the boat painted before the ban, or the compounds' long–lasting effectiveness time (5–7 years).

It is apparent that residues of butyltin species remain at depth in the sediments over 30 years after deposition, which reflects the long half lives of these compounds in anaerobic conditions. Their presence in sediments may in itself not be an immediate problem, however, if material is disturbed it may result in subsequent desorption of bound contaminants to the water column where they will be more readily bioavailable (Batley, 1996). The binding of organotin species to sediments has been demonstrated to be a reversible process involving particulate organic matter in the sediments and desorption occurs readily. For this reasons, knowledge about the deposition rate of the sediment reveals its' accumulation history, and this is important to show what the fate of OTC in the environment is (Table 3).

TBT and DBT levels specially in marinas and concentrations of all stations were also found as high as in harbour with heavy traffic across the world. Survey research from all over the world reported that organic tin pollution is still a matter of concern. The two–way research revealed that there are still significant TBT pollution along coastal zones of Pacific, Atlantic, India Oceans and of marinas and harbours.

In conclusion; comparison of levels between measured OTC's levels along Turkey Coast of Aegean Sea with those levels previously found in marinas along the Mediterranean shows that they are rather high (Table 4). In addition, a strong positive correlation was found between change of the carbon (%) and total OTC levels in sediment ($r = 0.711$ for winter and $r = 0.735$ for summer, $P<0.05$). At the end of the study, we determined that the total OTC concentrations in the sediment samples showed the significant spatio–temporal changes.

Recommendations

This study emphasized importance of sediment in marine pollution with organic tin compounds. This study also showed that the sediment is not the ending place for the organic tin compounds in the marine environment rather a renewable resource, indicating the sediment to be an important factor for continuation of OTC's concentration in marine environment and emphasizing that disposal of emerged wastes after scanning the bottom of harbours could cause additional contaminations (Hoch, 2001).

It is important to conduct comprehensive studies to determine level of OTC's pollution along entire coast of Turkey. Across Black Sea, Straits of Bosphorus and Dardanelles, Marmara, Aegean and Mediterranean coasts, public and private sector ports are established and increasing number of marinas are worth investigating in terms of OTC's and other effective antifouling biocides.

Unfortunately, current and future regulations will not of course eliminate TBT suddenly. In some countries despite prohibition or regulation in use of TBT, marine environmental pollution has continued and environmental concentrations have reached such high levels that the present situation could unfortunatelly continue this way. While member nations of IMO banned usage of TBT–based antifouling paints, developing countries which have not developed legal restrictions against using TBT–content antifouling paints or pesticides based on TPT continue to employ effective biocide and produce OTC's. The presence of OTC's should be determined and ongoing research need to be done on pollutants by following methods in natural systems, their kinetics and durability. Pollution in terrestrial ecosystems is the major cause of growing concern about industrial applications of organic tin compounds and their release into the environment.

Problems that may arise after the legal regulations to prohibit use of OTC's in antifouling effective ship paints should be discussed. The most important issues to emerge on employment of new chemicals possible to create harmful effects should also be debated concerning damages in the aquatic environment and misuse of antifouling chemicals

Table 3. Sediment deposition rates of different areas of Aegean Sea

Region	Sediment Deposition Rate (cm yr^{-1})	Reference
Northern Aegean Sea	0.200	Kanellopoulos *et al.*(2009)
Middle Aegean Sea (Izmir Bay)	0.104	Ichedef *et al.* (2007)
Southern Aegean Sea	0.321	Ugur *et al.* (2007)

Table 4. Reported butyltin compounds' levels from the world (ng g^{-1} Sn d.w.) (Ladislao, 2008)

Sampling Areas	Levels of OTC (ng g^{-1} Sn)		
Regions	MBT	DBT	TBT
Marinas of the U.S.A.			
East–West Canada Coast	nd.–330	nd.–100	nd.–5100
Crystal Lake, USA	21.3–320	59–350	1.5–14,000
Asian Marinas			
Osaka Harbor	nd.	nd.	10–2100
Malaysian Coast	5.0–360	3.8–310	2.8–1100
West cost of India	n.a.	nd.–469	5–2384
Vietnam Coast	3.9–30	8.1–42.7	8.3–51
European Marinas			
North–west Sicily coastline	nd.	nd.	3–27
Portuguese coast	5.2–78	5.3–65	3.8–12.4
North coastline of Spain	860–2870	150–710	50–5480
South–west of France	1.0–125	nd.–87	nd.–89
Marinas of Turkey			
Aegean Sea (In this study)	nd.–2598	nd.–1371	nd.–3008

which will become costly in fuel consumption leading to increase in the marine transport.

Acknowledgements

This research was financially supported by the Foundation of Scientific Research of the Ege University (BAP Project Number: 2009/SUF/018) and special thanks are extended to The Scientific and Technical Research Council of Turkey (TUBITAK–ATAL) for their technical contributions.

References

Alzieu, C. 2000. Environmental impact of TBT: the French experience. The Science of the Total Environment, 258: 99–102.doi:10.1016/S0048-9697(00)00510-6.

Antizar–Ladislao, B. and Galil, N.I. 2004. Biosorption of phenol and chlorophenols by acclimated residential biomass under bioremediation conditions in a sandy aquifer. Water Res., 38: 267–276. doi:10.1016/j.watres.2003.09.032.

Arnold, C.G., Ciani, A., Muller, S.R., Amirbahman A. and Schwarzenbach, R.P. 1998. Association of triorganotin compounds with dissolved humic acids. Environ. Sci. Technol., 32: 2976–2983. doi:10.1021/es980114z.

Batley, G. 1996. Distribution and fate of tributyltin in the marine environment. Tributyltin: Case Study of an Environmental Contaminant. S.J. de Mora. Cambridge University Press: Cambridge: 139–166. doi:10.1017/CBO9780511759772.006.

Berto, D., Giani, M., Boscolo, R., Covelli, S., Giovanardi, O., Massironi, M. and Grassia, L. 2007. Organotins (TBT and DBT) in water, sediments, and gastropods of the southern Venice lagoon (Italy). Marine Pollution Bulletin, 55: 425–435. doi:10.1016/j.marpolbul.2007.09.005.

Blunden, S.J., Hobbs, L.A. and Smith, P.J. 1984. The environmental chemistry of organotin compounds. In: H.J.M. Bowe (Ed.), Environmental Chemistry, The Royal Society of Chemistry, London: 49–77.

Buggy, C.J. and Tobin, J.M. 2006. Seasonal and spatial distributions of tributyltin in surface sediment of the Tolka Estuary. Dublin, Ireland. Environ. Pol., 143: 294–303. doi:10.1016/j.envpol.2005.11.025.

Burton, E.D., Phillips, I.R. and Hawker, D.W.S. 2004. Absorption and desorption behavior of tributyltin with natural sediments. Environ. Sci. Technol., 38: 694–700. doi:10.1021/es049291s.

Burton, E.D., Phillips, I.R. and Hawker, D.W. 2006. Tributyltin partitioning in sediments: effect of aging. Chemosphere, 63: 73–81. doi:10.1016/j.chemosphere.2005.07.048.

Calmano, W., Hong, J. and Forstner, U. 1993. Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. Water. Sci. Technol., 28(8-9): 223–235.

Ceulemans, M., Slaets, S. and Adams, F. 1998. Speciation of organotin in environmental sediment samples. Talanta, 46: 395–405. doi:10.1016/S0039-9140(97)00403-7.

Champ, M.A. and Bleil, D.F. 1988. Research needs concerning organotin compounds used in antifouling paints in coastal environments. Science Appl. Int. Corp. US Department of Commerce, NOAA, Rockville.

Champ, M.A. and Seligman, P.F. 1996. An introduction to organotin compounds and their use in antifouling coatings. Organotin Environmental Fate and Effects, 1: 1–25. doi:10.1007/978-94-009-1507-7.

De Mora, S.J., Fowler, S.W., Cassi, R. and Tolosa, I. 2003. Assessment of organotin contamination in marine sediments and biota from the Gulf and adjacent region. Marine Pollution Bulletin, 46: 401–409. doi:10.1016/S0025-326X(02)00481-2.

Diez, S., Lacorte, S., Viana, P., Barcelo, D. and Bayona, J.M. 2005. Survey of organotin compounds in rivers and coastal environments in Portugal 1999–2000. Environ. Pol., 136: 525–536. doi:10.1016/j.envpol.2004.12.011.

Donard, O.F.X., Quevauviller, P., Ritsema, R. and Ewald, M. 1988. Sampling organotin variability in estuarine and coastal environments: a review. Proceedings of the International conference of Heavy Metals in the Hydrological cycle, Lisbon: 401–412.

Dubey, S.K. and Roy, U. 2003. Biodegradation of tributyltins (organotins) by marine bacteria. Appl. Organometal Chem., 17: 3–8. doi:10.1002/aoc.394.

Egemen, Ö. 1999. Çevre ve Su Kirliliği Ders Kitabı, Ege Üniversitesi Su Ürünleri Fakültesi, Bornova–İzmir, 42: 75-77.

Fan, W., Wang, W–X., Chen, J., Li, X. and Yen, Y–F. 2002. Cu, Ni and Pb speciation in surface sediments from a contaminated bay of northern China. Mar. Pollut. Bull., 44: 16– 32. doi:10.1016/S0025-326X(02)00069-3.

Fent, K. 1996. Ecotoxicology of organotin compounds. Crit. Rev. Toxicol., 26: 3–117. ISSN 1040-8444.

Hoch, M. 2001. Organotin compounds in the environment an overview. Applied Geochemistry, 16: 719–743. doi:10.1016/S0883-2927(00)00067-6.

Hoch, M., Alonso–Azcarate, J. and Lischick, M. 2003. Assessment of adsorption behavior of dibutyltin (DBT) to clay–rich sediments in comparison to the highly toxic tributyltin (TBT). Environ. Pollut., 123: 217–227. doi:10.1016/S0269-7491(02)00402-5.

Hoch, M. and Schwesig, D. 2004. Parameters controlling the partitioning of tributyltin (TBT) in aquatic systems. Applied Geochemistry, 19: 323–334. doi:10.1016/S0883-2927(03)00131-8.

Ichedef, M., Yener, G., Uğur, A., Büyükışık, B., Özden, B. and Köksal, E. 2007. Sedimentation Rates in Inner Part of İzmir Bay. CIESM–38th Congress, Book of Abstracts, İstanbul, 17 pp.

IMO, 2001. İnformation about International convention on the control of harmful antifouling systems on ships. http://www.imo.org/Conventions/mainframe.asp?topic_id=529 (accessed 13 February 2009).

Jacobsen, J.A. and Asmund, G. 2000. TBT in marine sediments and blue mussels (*Mytilus edulis*) from central-west Greenland. The Science of the Total Environment, 245: 131-136. doi:10.1016/S0048-9697(99)00438-6.

Kanellopoulos, T.D., Kapsimalis, V., Karageorgis, A., Anagnostou, C., Poulos, S. and Angelidis, M.O. 2003. Impact of recent human activities in the evolution of the Evros River delta and its adjacent marine area, NE Aegean Sea, Greece. ComDelta, Open Conference on Comparing Mediterranean and Black Sea Prodeltas, Aix–en–Provence, France: 52–53.

Kırlı, L. 2005. Organotin pollution in the marine environment. G.U. Journal of Science, 18(3): 517–528.

Ladislao, B.A. 2008. Environmental levels, toxicity and human exposure to tributyltin (TBT)–contaminated marine environment. A review. Environment International, 34: 292–308. doi:10.1016/j.envint.2007.09.005.

Landmeyer, J.E., Tanner, T.L. and Watt, B.E. 2004. Biotransformation of tributyltin to tin in freshwater river–bed sediments contaminated by an organotin release. Environ. Sci. Technol., 38: 4106–4112. doi:10.1021/es030697z.

Lee, C.-C., Hsieh, C.-Y. and Tien, C.-J. 2006. Factors influencing organotin distribution in different marine environmental compartments, and their potential health risk. Chemosphere, 65: 547–559. doi:10.1016/j.chemosphere.2006.02.037.

Li, X., Shen, Z., Wai, O.W.H. and Li, Y–S. 2000. Chemical partitioning of heavy metal contaminants in sediments of the Pearl River Estuary. Chem. Speciat. Bioavailab., 12(1): 17–25. doi:10.3184/095422900782775607.

Meador, J.P. 2000. Predicting the fate and effects of tributyltin in marine systems. Rev. Environ. Contam. Toxicol., 166: 1–48.

Meador, J.P. 2002. Determination of a tissue and sediment threshold for tributyltin to protect prey species of juvenile salmonoids listed under the US Endangered Species Act. Aquat. Conservation. Marw. Fresh. Ecosys., 12: 539–51. doi:10.1002/aqc.520.

Mercier, A., Pelletier, E.E. and Hamel, J. 1996. Toxicological response of the symbiotic sea anenome *Aiptasia pallida* to butyltin contamination. Mar. Ecol. Prog. Ser., 144: 133–146. doi0:10.3354/meps144133.

Quevauviller, P., Donard, O.F.X. and Etcheber, H. 1994. Butyltin distribution in a sediment core from Arcachon Harbor (France). Environmental Pollution, 84: 89–92. doi:10.1016/0269-7491(94)90074-4.

Rüdel, H. 2003. Case Study: bioavailability of tin and tin compounds. Ecotoxicology and Environmental Safety, 56: 180–189. doi:10.1016/S0147-6513(03)00061-7.

Saulnier, I. and Mucci, A. 2000. Trace metal remobilization following the resuspension of estuarine sediments: Saguenay Fjord, Canada. Appl. Geochem., 15: 191–210. doi:10.1016/S0883-2927(99)00034-7.

Sayer, C.D., Hoare, D.J., Simpson, G.L., Henderson, A.C.G., Liptrot, E.R. and Jackson, M.J. 2006. TBT causes regime shift in shallow lakes. Environ. Sci. Technol., 40: 5269–75. doi:10.1021/es060161o.

Uğur, A., Yener, G., Aközcan, S., Çatal, E., Gönülalan, F., Özden, B., İçhedef, M. 2007. 210Po and 210Pb in the Turkish Coast of the Aegean Sea Ecosystem. CIESM–38th Congress, Book of Abstracts, İstanbul, 61 pp.

Unger, M.A., MacIntyre, W.G. and Huggett, R.J. 1988. Sorption behaviour of tributyltin on estuarine and freshwater sediments. Environ. Toxicol. Chem., 7: 907–15. doi:10.1897/1552-8618(1988)7[907:SBOTOE] 2.0.CO;2.

Zoumis, T., Schmidt, A., Grigorova, L. and Calmano, W. 2001. Contaminants in sediments: remobilisation and demobilisation. Sci. Total. Environ., 266: 195–202. doi:10.1016/S0048-9697(00)00740-3.