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Baseline

Occurrence and seasonal variation of butyltin species along the mediterranean coast of Turkey

Semal Yemenicioglu [a,*], Stephen de Mora [b]

[a] Middle East Technical University – Institute of Marine Sciences, P.O. Box 28, 33731 Erdemli-Mersin, Turkey
[b] Aromed Environmental Consulting Services Inc., 255 Melanie Avenue, Kingston, Ontario, Canada K7M 8C2

Organotin compounds are extensively used in industrial and agricultural applications, as disinfectants and antifouling additives. The use of TBT as an antifoulant additive in paints increases its level in seawater, especially near marinas and harbours. In general, progressive substitution of organic groups to the tin atom in any $R_nSnX_{(4-n)}$ series increases its toxicity and the maximum biological activity is produced when $n = 3$ (UNEP/FAO/WHO/IAEA, 1989). TBT has toxic effects on aquatic animals as well as aquatic plants (Nakatsu et al., 2006; Alzieu et al., 1986; King et al., 1989; Blanck et al., 1984; Fargasova and Kizlink, 1996; Huang et al., 1993; Miana et al., 1993). Once entered into seawater, TBT may be removed from solution either by adsorption on particulate matter (IPCS, 1990), by uptake, or by undergoing a series of chemical and biological degradation reactions (Blunden and Chapman, 1986; Seligman et al., 1988; Harino et al., 1998).

This study was carried out in the north-eastern Mediterranean at Iskenderun Bay, a semi-enclosed bay having limited exchange with the open sea (Collins and Banner 1979) and with heavy shipping traffic due to Iskenderun Harbour and the Iraq–Ceyhan and Azerbaijan–Ceyhan petroleum pipelines terminus (Fig. 1). Mersin Harbour is a busy port, and has a dry dock; Antalya Harbour is similar to Mersin Harbour from the oceanographic point of view, having good exchange with the open sea. In addition to the commercial harbour, there is a small marina (Marmaris Marina, an enclosed estuary).

Using a rubber boat, seawater samples were collected in 2002 just below the surface as described in Gabrielides et al. (1990) at the stations shown in Fig. 1. Samples were stored in Teflon lined screw-capped glass bottles (Pyrex) of 1 L capacity. To each bottle, 2 ml of concentrated hydrochloric acid (HCl 30% Merck Suprapure) was added to preserve the samples, which were stored at 4 °C until analysed. Samples were analysed as soon as possible by utilizing hydride derivatization, coupled with atomic absorption spectrophotometry. The details of the method used have been published elsewhere (Yemenicioglu et al., 1987; Gabrielides et al., 1990).

The results obtained in this study revealed that butyl tins concentrations and speciation in the studied area was variable in both space and time. Concentrations ranged from below the detection limit (2.92 ng TBT-Sn L^{-1}) to 33.18 ng TBT Sn L^{-1}. The highest values were measured in harbours and marinas. The reference station (Fig. 1) was sampled twice (in July and November, 2002). No butyl tin species were detected in the samples obtained from the reference station.

Two samples were obtained from each river estuary, namely the Goksu, Ceyhan and Berdan River estuaries. Dibutyltin (DBT) and TBT were not detected in these estuaries with the exception of the March sampling period from the Ceyhan river estuary (Fig. 2). The existence of monobutyltin (MBT) at the river estuaries in the absence of TBT and DBT indicated that additional sources other than TBT may exist. These rivers receive drainage from agricultural areas in the region. In addition, the Berdan River estuary also receives some industrial discharges. The Ceyhan River estuary is situated at Iskenderun Bay and it is very close to a small harbour where small fishing boats, yachts and trawlers take shelter. It is also on the sea route of ships visiting the Iraq–Ceyhan and Azerbaijan–Ceyhan crude oil pipe-line terminal. It is not unlikely that the waters of this small harbour and the shipping traffic of the crude oil filling terminal affects this estuary.

Antalya harbour and Marmaris marina were sampled only once, during October 2002. As expected, the TBT and its degradation products, DBT and MBT, were detected in these sampling regions (Fig. 2). These regions are occupied by pleasure boats and yachts throughout the year. The maintenance of these vessels is carried out within the marina.

The highest TBT concentration (33.18 ng TBT Sn L^{-1}) was measured at Iskenderun harbour (Fig. 3). The results from this location show that in June, July and February TBT is absent, that is below the detection limit of 2.92 ng TBT-Sn L^{-1} (Fig. 3). However, during the summer months (June and July), the degradation products of TBT, namely dibutyltin (DBT) and monobutyltin (MBT), were measured in relatively high concentrations, reaching to about 5-fold of their winter concentrations. It is a well-known fact that the main removal processes for TBT from the water column are via absorption on to particulate matter and degradation by photolytic or biologically induced reactions. Some authors have suggested that TBT is removed from the water column primarily by particle absorption (Blunden and Chapman, 1986; Seligman et al., 1988; WHO, 1990).

Results obtained from Mersin Harbour (Fig. 4) show that although TBT concentrations were low (3–5 ng TBT-Sn L^{-1}, about 25% of winter concentrations of 20–30 ng TBT-Sn L^{-1}), during the summer months (June and July) TBT does not disappear completely. TBT can be removed from solution rapidly under intensive

* Corresponding author. Tel.: +90 324 5212406; fax: +90 324521 2327.
E-mail addresses: semal@ims.metu.edu.tr (S. Yemenicioglu), Stephen.deMora@gmail.com (S.de Mora).

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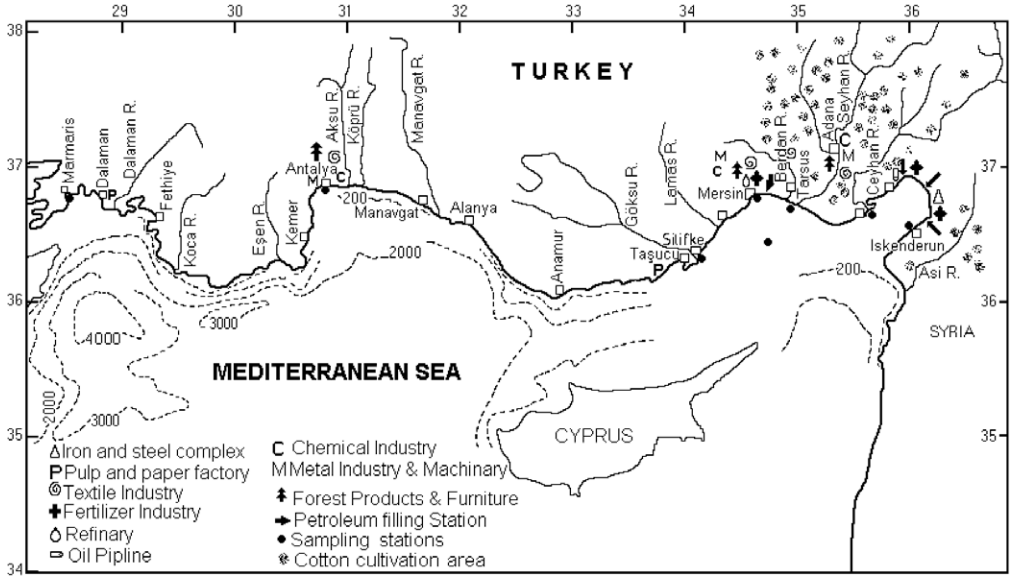

Fig. 1. Sampling locations.

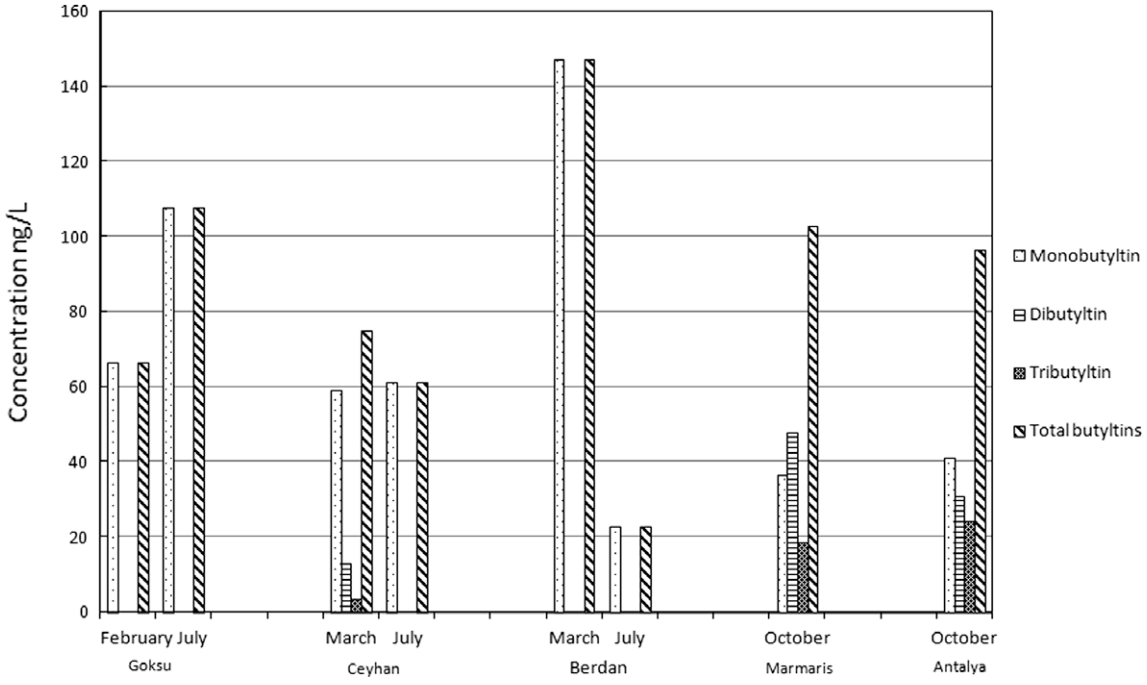

Fig. 2. Butyl tins concentrations measured at estuaries and marinas.

sunlight (Blunden and Chapman, 1986; Harino et al., 1998; Olson and Brinckman, 1986). The observed reduction in TBT concentrations can be attributed to an increased rate of removal (due to increased degradation rates and absorption on particulate matter) during the hot summer months. TBT was detected constantly in the samples from Mersin harbour, indicating a continuous input. The only exception was the February sampling period. This is an unexpected result, since this location is a very busy harbour containing an active dry dock. Commercial ships, fishing boats, yachts and trawlers also take shelter in this harbour. The absence of TBT in February could be the result of high amounts of total suspended sediment (TSS) load (TSS = 251.5 mg/L) compared with measurements made in November (TSS = 60 mg/L). In addition, storm water drains and sewage from Mersin city drain into this harbour. The half-life of TBT in the water column is supposed to be in the order of 20 days, but the actual rate of break down of TBT depends on many factors, such as the intensity of sunlight, concentration of suspended matter, the phytoplankton population and intensity of bacterial activity (Olson and Brinckman, 1986; Lee et al., 1987). Seligman et al. (1988) proposed a half life for TBT in the range 6–7 days.

In general, TBT concentrations were highly variable and tended to be greatest in marinas and harbours, confirming previous work. For example, TBT concentrations reported by King et al. (1989) were in the range of below detection limit (0.005 μg TBT-Sn L^{-1}) to 0.32 μg TBT-Sn L^{-1} in coastal Northland and Auckland, New Zea-

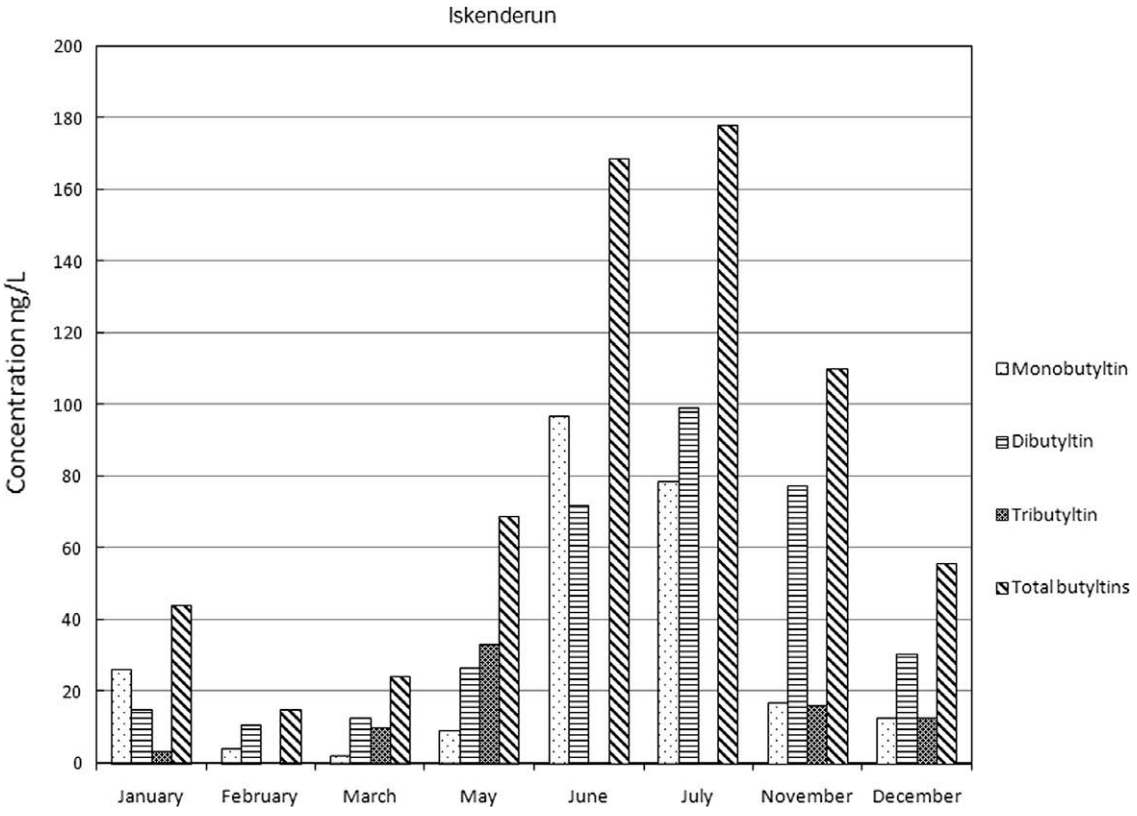

Fig. 3. Butyl tins concentrations measured at Iskenderun harbour.

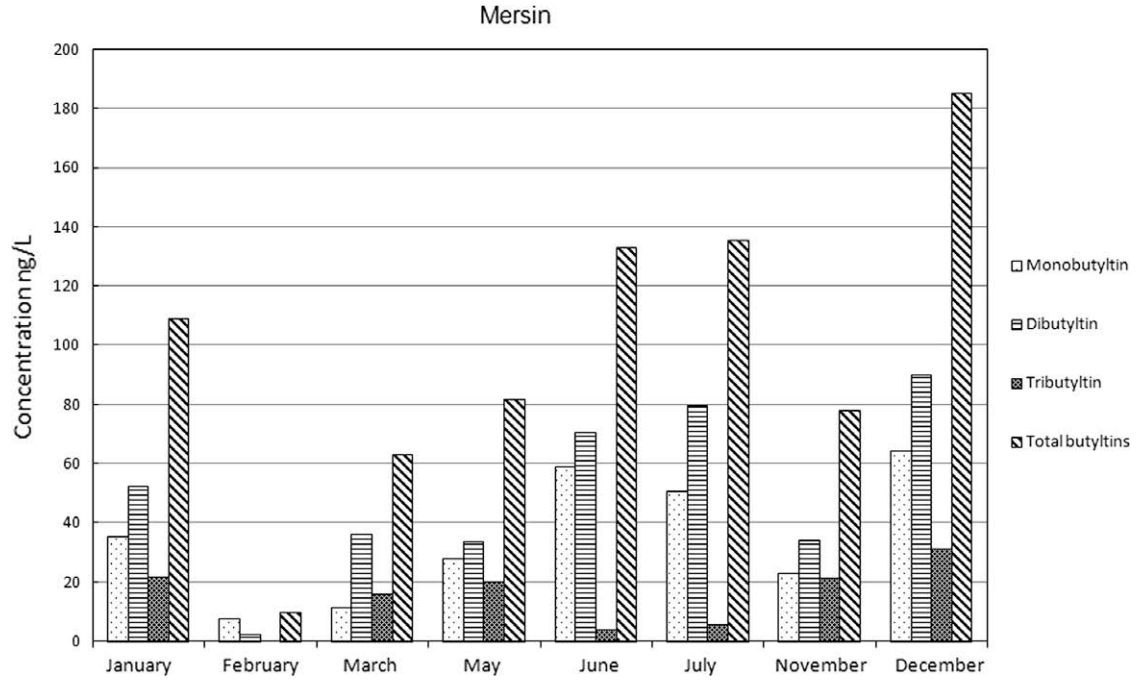

Fig. 4. Butyl tins concentrations measured at Mersin harbour.

land. In south-west England, Cleary and Stebbing (1987) reported that the maximum level of TBT was 0.18 μg TBT-Sn L^{-1}. Waldock and Miller (1983) measured 0.62 μg TBT-Sn L^{-1} in the Essex marina in south-east England.

The ratios of MBT to total butyltins were calculated in the present study. For Iskenderun harbour during March, May and November, the ratio was small (0.08–0.15) indicating recent discharge of TBT. However, for Mersin harbour the ratio was small only in the

March sampling period (0.18). As mentioned previously, this harbour receives sewage and storm runoff also. For the river estuaries the ratio was unity, indicating the absence of TBT discharge.

The results obtained from this work suggest that TBT concentrations in seawater samples collected along the Turkish coast of the Mediterranean Sea were highly variable over time and space. The absence of TBT, and an increase in the concentrations of DBT and MBT during the summer months (June and July) in Iskenderun harbour supported the suggestion that increased temperature and intensive sunlight increase the rate of TBT degradation. However, in Mersin harbour the TBT concentration during these months did not fall below the detection limit, concentrations being reduced almost 25% compared to winter concentrations. DBT and MBT increased 5-fold over their winter concentrations indicating not only rapid transformation of TBT to MBT and DBT but also the possibility of anthropogenic inputs of the latter two species.

The absence of TBT and DBT, but the existence of MBT in the samples from Goksu, Berdan and Ceyhan River estuaries indicated that there may be other sources for MBT in the region. Lastly, the absence of butyl tins at the reference stations indicated that these species are removed from solution very rapidly before their transportation to the open sea.

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