Pergamon

Marine Pollution Bulletin, Vol. 32, No. 2, pp. 238–240, 1996

0025-326X/96 $15.00+0.00

0025-326X(95)00183-2

The Distribution of Organotin Compounds in the North-Eastern Mediterranean

NILGUN KUBILAY, SEMAL YEMENICIOGLU, SULEYMAN TUGRUL and ILKAY SALIHOGLU
METU-Institute of Marine Sciences, P.O. Box 28, 33731 Erdemli-ICEL-TURKEY

In recent years the increasing use of organotin compounds in industry and agriculture, together with the development of sensitive and precise analytical techniques for the quantitative speciation of organotin compounds at environmental levels, have created great concern about the distribution, impact and fate of methylated tin and butyltins of anthropogenic origin. Organotin compounds are among those substances included in Annex I of the protocol of the Barcelona Convention for the Protection of the Mediterranean Sea Against Pollution from Land Based Sources (UNEP, 1982). A review of the properties and environmental behaviour of phenyltin, tributyltin and their derivatives, and of inorganic and methylated tins can be found in UNEP (1989) and Oceans'87 (1987).

Information concerning methylated tin species in the north-eastern Mediterranean is limited, and no data are available on butyltin species in this region. The present study provides information on the levels and speciation of both methyl- and butyltin compounds in the north-eastern Levantine Basin of the Mediterranean.

Water samples were collected by an inflatable craft from just below the surface as described in Gabrielides *et al.* (1990), from the stations shown in Fig. 1. Samples were stored in teflon lined screw-capped glass bottles (Pyrex) of 2 l capacity. In order to preserve the samples, 2 ml of glacial acetic acid was added and they were subsequently stored at 4°C. Sediment samples were collected with a Van-Veen grab. The samples were stored frozen in pre-cleaned polypropylene bags.

The samples were analysed by hydride derivatization, coupled to atomic absorption spectrophotometry. The details of the method used are published elsewhere (Yemenicioglu *et al.*, 1987; Gabrielides *et al.*, 1990). The METU-IMS laboratory has participated in an intercalibration exercise for the determination and quantification of individual butyltins, both in seawater and in spiked samples. The results were published by Gabrielides *et al.* (1990).

The data obtained for butyltins from the analysis of the subsurface seawater samples along the Turkish coast are shown in Table 1. No tributyltin was detected in the samples from Iskenderun and Mersin Harbours in July 1988 and February 1989, respectively, but in the other sampling periods tributyltin was detected at these sites in the range of 31–935 ng l^{-1}. These two harbours have heavy commercial shipping throughout the year and it is unlikely that a reduction in shipping activity is responsible for the decline in tributyltin concentrations in July 1988 and February 1989. Tributyltin undergoes degradation reactions which yield methyltins (Chau, 1980; Brinckman *et al.*, 1981) and other butyltins (mono- and dibutyltins). These reactions can be photolytic, or may be biologically or chemically induced (Blunden & Chapman, 1986; Lee *et al.*, 1987). The hydrophobic nature of butyltin causes its migration into the particulate fraction, and hence it precipitates rapidly into

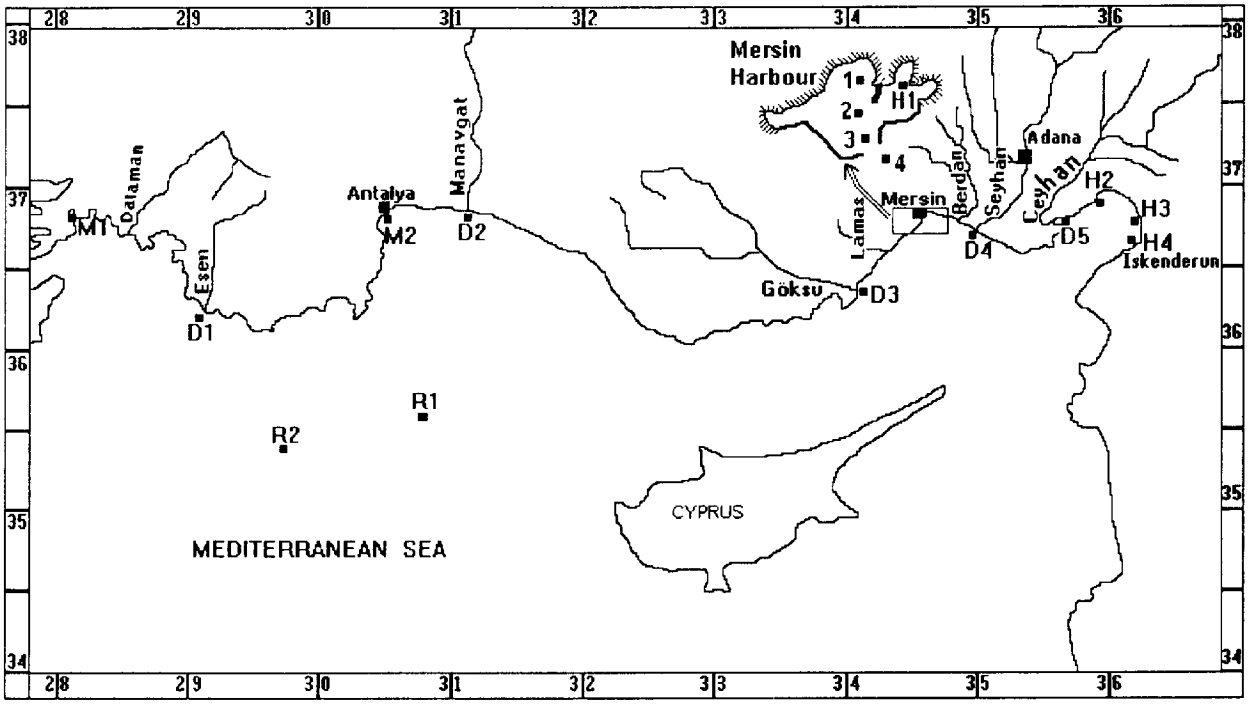

Fig. 1 Sampling locations for water and sediments.

TABLE 1

Butyltin concentrations (ng l^{-1} as chlorides) measured in the coastal waters of the north-eastern Mediterranean.

Sampling station	Sampling date	$BuSnCl_3$	Bu_2SnCl_2	Bu_3SnCl	T °C	S (‰)	Chl-a (mg l^{-1})
Iskenderun Harbour							
H4	May 1988	8*	56*	83*	19.46	37.13	2.78
	July 1988	2774*	484*	<8*	29.18	38.20	0.04
	Nov. 1988	8	23	31	19.26	39.13	0.39
	Feb. 1989	27	7	32	15.74	39.09	NA
Mersin Harbour							
H1	May 1988	30*	266*	935*	18.85	35.96	0.58
	Nov. 1988	12	44	31	20.83	39.15	NA
	Feb. 1989	13	<0.8	<8	15.95	39.10	NA
Dry dock							
1	Nov. 1988	84	133	59	NA	NA	NA
2		66	86	55	NA	NA	NA
3		60	55	42	NA	NA	NA
4		140	<0.8	9	NA	NA	NA
Botas							
H2	May 1988	140	<0.8	9	20.93	36.68	6.15
	Nov. 1988	311	<0.8	<8	19.12	39.12	1.43
Isdemir							
H3	May 1988	21	15	<8	19.82	37.64	5.33
	Nov. 1988	633	<0.8	<8	19.43	39.23	0.39
	Mar. 1988	77	<0.8	<8	16.63	38.99	NA
Marmaris Marina							
M1	May 1988	<0.4*	121*	11*	17.55	38.86	NA
	July 1988	<0.4*	742*	353*	24.35	38.96	0.08
	Dec. 1988	60	7	38	18.92	38.66	0.41
	Mar. 1989	5	4	23	15.88	39.04	0.57
Antalya Marina							
M2	May 1988	<0.4*	677*	154*	19.10	37.22	0.12
	July 1988	129*	121*	183*	24.93	38.91	0.04
	Feb. 1989	102	<0.8	<8	15.64	38.96	NA
Göksu River Delta							
D3	Oct. 1988	212	<0.8	<8	NA	NA	NA
	Feb. 1989	268	<0.8	<8	15.50	38.92	NA
Ceyhan River Delta							
D5	May 1988	<0.4	11	14	NA	NA	NA
Reference stations							
R2	July 1988	<0.4	<0.8	<8	25.89	39.17	0.08
R1	Oct. 1988	<0.4	<0.8	<8	NA	NA	NA

*Gabrielides *et al.* (1990).
NA, Not analysed.

sediments. The absence of tributyltin but the co-presence of comparatively large amounts of monobutyltin in July 1988 in Iskenderun Harbour and in February 1989 in Mersin Harbour (Table 1) suggests that tributyltin was removed from the water column by these processes. According to Seligman *et al.* (1988), the degradation of tributyltin is induced largely by biological processes and the half-life was estimated at 6–7 days. Olson & Brinckman (1986) found an increase in the degradation rate of tributyltin under intense light and warm temperatures, as are found locally. The existence of monobutyltin in the water samples from the Göksu River delta might imply butyltin input from local sources into the river. The Göksu River also receives triphenyltin compounds, which are extensively used in the local agriculture as fungicides.

In sediments, triphenyltin may undergo transformation reactions, to yield trimethyltin (Chau, 1980). To evaluate the influence of butyltins on the distributions and fates of methyltin species in water, simultaneous methyltin and butyltin measurements were performed (Table 2). No monomethyltin was detected in the seawater samples, while dimethyltin was found to be present only in October and November 1988. However, trimethyltin was detected in most of the samples. Yemenicioglu *et al.* (1987) reported all forms of methyltins in the coastal waters of the north-eastern Mediterranean during the summer season, dimethyltin being the dominant species.

In the sediment samples taken, only methyltins and monobutyltin were determined quantitatively (Table 3). Although these data suggest that the concentrations of methyltins and monobutyltin at the sites studied have increased by two orders of magnitude within 4 years, it is interesting to note that the ratios of monomethyltin to trimethyltin, and dimethyltin to trimethyltin, were consistent with those reported by Tugrul *et al.* (1983). In the present study methyltin species were found to increase in concentration in the order monomethyltin <

TABLE 2

Methyltin concentrations in seawater samples (ng l^{-1} as chlorides).

Sampling station	Sampling date	Methyltin concentrations		
		$MeSnCl_3$	Me_2SnCl_2	Me_3SnCl
H4	May 1988	<0.30	<0.15	7.4
	Oct. 1988	<0.30	<0.15	13.7
	Feb. 1989	<0.30	<0.15	<0.25
H2	May 1988	<0.30	<0.15	5.3
	Oct. 1988	<0.30	<0.15	17.1
H3	Nov. 1988	<0.30	1.0	2.8
	Mar. 1989	<0.30	<0.15	<0.25
H1	Oct. 1988	<0.30	<0.15	39.7
M2	Oct. 1988	<0.30	4.4	44.2
	Mar. 1989	<0.30	<0.15	<0.25
D3	Oct. 1988	<0.30	<0.15	27.5
	Feb. 1989	<0.30	<0.15	<0.25

TABLE 3

Methyltins and monobutyltin concentrations (as chlorides) in sediment samples (ng g^{-1} dry wt).

Sampling station	$MeSnCl_3$	Me_2SnCl_2	Me_3SnCl	$BuSnCl_3$
Manavgat D2	15	36	143	100
Esen D1	38	58	107	260
Seyhan D4	65	81	159	100
Göksu D3	375	477	1696	980
Marmaris M1	22	36	87	142
Iskenderun H4	26	56	81	359

dimethyltin < trimethyltin. The results obtained by Tugrul *et al.* (1983) in polluted sediments suggest methyltin transport to sediments from the overlying waters by adsorption on to sinking particulate organic matter (Donard & Weber, 1985).

The results of this study differ from those described by Dahab (1988) in the Alexandria coastal belt, where monomethyltin was the predominant species. Dahab (1988) used an acidic solution to extract organotin species from the sediment samples. In the present study double-distilled water was used for the extraction of organotins, as the use of acidic solutions would generate CO_2 from these sediments, which exhibit a high carbonate content, causing the loss of volatile organotin species.

Most of the studies on the distribution of butyltin species in the polluted coastal waters of marinas, harbours and estuaries have demonstrated that butyltins are almost omnipresent, tributyltin usually being the predominant species (FAO, 1988; Krone *et al.*, 1989; Bacci & Gaggi, 1989). Although the present study demonstrated the existence of all forms of butyltins with tributyltin as the dominant species in some sampling periods, the findings suggest not only the substantial and rapid transformation of tributyltin to dibutyltin and monobutyltin in polluted waters, but also the possibility of land-based inputs of the latter two species of tin.

The concentrations of monobutyltin determined in oxic delta sediments were found to be similar to those in polluted sediments from Iskenderun and Mersin Harbours, indicating butyltin sources in the river catchments.

This work was initiated in the framework of the long-term programme for pollution monitoring and research in the Mediterranean (MED POLL-Phase II), and was continued after the completion of this programme.

Bacci, E. & Gaggi, C. (1989). Organotin compounds in harbour and marina waters from the Northern Tyrrhenian Sea. *Mar. Pollut. Bull.* **20**, 290–292.

Blunden, S. J. & Chapman, A. (1986). Organotin compounds in the environment. In *Organometallic Compounds in the Environment* (P. J. Craig, ed.), pp. 111–149. Longman Group Ltd, Essex, UK.

Brinckman, F. E., Jackson, J. A., Balin, W. R., Olsen, G. J. & Iverson, W. P. (1981). Ultra trace speciation and biogenesis of methyltin transport in estuarine waters. Paper presented at the *NATO Symposium, Trace Metals in Sea Water*. Erice, Sicily, 30 March–3 April 1981.

Chau, Y. K. (1980). Biological methylation of the tin compounds in the aquatic environment. Paper presented at the *Third International Conference on Organometallic and Coordination Chemistry of Germanium, Tin and Lead*. University of Dortmund, Germany, July 1980.

Dahab, O. A. (1988). Speciation of tin compounds in sediments of the Alexandria, Egypt coastal belt. *Water Air & Soil Pollut.* **40**, 433–442.

Donard, O. F. X. & Weber, J. H. (1985). Behaviour of methyltin compounds under simulated estuarine conditions. *Environ. Sci. Technol.* **19**, 1104–1110.

FAO (1988). Report of the FAO/UNEP/IAEA/WHO review meeting on the Organotin Pilot Survey, Erdemli, Turkey, 7–9 November 1988. Food & Agricultural Organisation, Rome.

Gabrielides, G. P., Alzieu, C., Readman, J. W., Bacci, E., Dahab, O. A. & Salihoglu, I. (1990). MED POL survey of organotins in the Mediterranean. *Mar. Pollut. Bull.* **21**, 233–237.

Krone, C. A., Brown, D. W., Burrows, D. G., Chan, S. & Varanassi, U. (1989). Butyltins in sediment from marinas and waterways in Puget Sound, Washington State, USA. *Mar. Pollut. Bull.* **20**, 528–531.

Lee, R. F., Valkirs, A. O. & Seligman, P. F. (1987). Fate of tributyltin in estuarine waters. In *Oceans'87 Proceedings, International Organotin Symposium*, Vol. 4, pp. 1411–1415. The Institute of Electrical & Electronics Engineers, NY.

Olson, G. J. & Brinckman, F. E. (1986). Biodegradation of tributyltin by Chesapeake Bay microorganisms. In *Oceans'86 Conference Record, Organotin Symposium*, Vol. 4, pp. 1196–1291. The Institute of Electrical & Electronics Engineers, NY.

Oceans'87 (1987). *Proceedings of International Organotin Symposium*, Vol. 4. The Institute of Electrical & Electronics Engineers, NY.

Seligman, P. F., Valkirs, A. O., Stang, P. M. & Lee, R. F. (1988). Evidence of rapid degradation of tributyltin in a marina. *Mar. Pollut. Bull.* **19**, 531–534.

Tugrul, S., Balkas, T. I. & Goldberg, E. D. (1983). Methyltins in the marine environment. *Mar. Pollut. Bull.* **14**, 297–303.

UNEP (1982). Convention for the Protection of the Mediterranean Sea Against Pollution and its Related Protocols. United Nations Environment Programme, Geneva.

UNEP (1989). Assessment of Organotin Compounds as Marine Pollutants in the Mediterranean. MAP Technical Report Series 33, United Nations Environment Programme, Geneva.

Yemenicioglu, S., Saydam, C. & Salihoglu, I. (1987). Distribution of tin in the Northeastern Mediterranean. *Chemosphere* **16**, 429–443.