APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 239–245

Contamination of outdoor settled dust by butyltins in Malta

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Received 4 November 2006; Revised 6 November 2006; Accepted 16 September 2006

The presence of compounds of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) was determined in outdoor settled dust collected from several sites on the island of Malta, mainly from flat rooftops of school buildings. The dust was separated into three size fractions with diameters (μ*m*) >250, 125–250 and <125, and the two finer fractions were analysed for butyltins using extraction with glacial acetic acid followed by derivatization/solvent extraction with sodium tetraethylborate in the presence of iso-octane and quantitation by gas chromatography with flame photometric detection. The presence of TBT, DBT and MBT was established in most of the samples and TBT concentrations varied from non-detectable (<5 ng Sn g^{-1}) to highs of 15.5 and 18.7 μg Sn g^{-1} in Senglea and Marsaxlokk. TBT was generally found at concentrations significantly higher than reported hitherto in house dust collected from European homes. The geographical distribution of total organotins in both dust fractions suggests that TBT originates mainly from antifouling marine paint residues which contaminate the urban environment when ships' hulls are sand- or hydro-blasted during maintenance and repair at the drydocks facility in Grand Harbour. Other significant sources of TBT are located at Marsaxlokk fishing port and Wied iż-Żurrieq creek, both hosting sizeable communities of fishermen and leisure boating. The data also suggest that the municipal solid waste landfill at Maghtab is an inland source of butyltins. We suggest that dust containing harmful butyltins could possibly be ingested to expose humans to a risk which is probably of concern especially for young children living close to the hotspots of contamination. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: tributyltin; TBT; DBT; MBT; organotin; dust; urban environment

INTRODUCTION

The use of tributyltin (TBT)-based antifouling paints on marine vessels has led to widespread distribution in the marine coastal environment of TBT and its metabolites, mainly dibutyltin (DBT) and monobutyltin (MBT). Concerns about the toxicity of these compounds, in particular to marine species such as molluscs, have led to a ban by the International Maritime Organization, effective from 2003, forbidding the use of organotin-based antifouling paints. However, sediments are known to act as reservoirs of organotins and thus persistence of these compounds in the marine environment is expected even when the ban comes fully into force in 2008.

Past studies in our laboratory have mainly focused on the organotin contamination of the marine environment around Malta, an island in the Central Mediterranean.[1,2] In Malta, ship repair and maintenance activities take place at the drydocks which are located within the Grand Harbour area, in close proximity to densely populated urban zones. A preliminary unpublished study[3] carried out in our laboratory in 2000 had indicated the presence, in significant amounts, of MBT, DBT and TBT in settled urban dust collected from rooftops in two villages in the southeastern part of Malta, which is the site of the drydocks. In that study were found decreasing dust concentrations of organotins with increasing distance from the drydocks, thereby implicating this facility as a likely important contributor of organotins in urban dust in that area of Malta.

In this paper, we present the findings of a later, larger study which considered the extent of contamination by organotins

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of settled urban dust collected from various sites representing the entire geographical extent of the island of Malta and we use the distribution of contamination to infer likely sources and their relative strengths. The associated health risk to the Maltese population is also evaluated. Despite numerous studies performed on the environmental impact of TBT in seawater and on marine biota,[4] very few studies[5–9] have been directed at establishing the presence of this contaminant in the urban environment.

MATERIALS AND METHODS

Sampling of dust

The territory comprising the island of Malta was divided into grids of approximate size 7.8 km^2 and at least one sample was taken from each grid area (Fig. 1). A total of 32 dust samples were collected during the period October 2004 to April 2005. No samples were collected from Gozo and the other smaller islands of the Maltese archipelago. School buildings were chosen as sampling sites and dust was collected from their flat rooftops. When this was not possible, samples were collected from the school grounds. In two cases (samples B4 and C1.1), soil samples were taken from non-agricultural land in undeveloped areas. Samples were stored in sterile containers at −20 °C pending analysis.

Analytical techniques

About 60 g of dust were collected from each site. A number of dust samples were inspected under the stereomicroscope (magnification ×30), paying particular attention to the presence or absence of coloured particles interpreted as representative of paint debris. A 0.2 g sub-sample was heated at 120 °C to constant mass for determination of humidity. The remainder of the sample was sieved (Endecots Octagon 200) such that the following fractions were separated: a 'fine dust' fraction (<125 μm), a 'coarse dust' fraction (125–250 μm) and 'granules' (>250 μm). The coarsest fraction (granules >250 μm) constituted 64.5% of the dust and consisted mainly of millimetric stony and glass granular matter and this fraction was not analysed; both the 'coarse dust fraction' (125–250 μm), which constituted 11.5% of settled dust, and the 'fine dust' (24%) were analysed separately for butyltins.

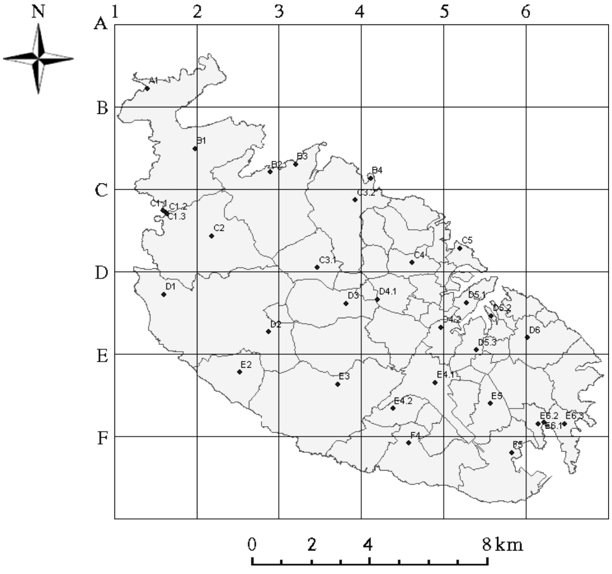

Figure 1. Map of Malta showing location of sampling sites.

The analytical method for organotin determination was based on that used by Carlier-Pinasseau *et al.*[10] for marine sediments, involving the simultaneous derivatisation and extraction using sodium tetraethylborate ($NaBEt_4$) followed by gas chromatography–flame photometric detection (GC-FPD). A 2 g sample of each fraction was treated with 20 ml glacial acetic acid for 4 h and the mixture was separated by centrifugation. To 5.0 ml of supernatant were added 30 ml of a 20% sodium acetate solution (to pH 4.6) and 50 ml deionized water, followed by spiking with tripropyltin chloride in hexane as recovery standard (100 μl; 1.86 ng Sn μl^{-1}). The mixture was then filtered through a 0.45 μm membrane filter and transferred to a specially designed reactor, consisting of a 250 ml conical flask to which a glass adaptor provided with a short vertical 4 mm diameter open glass column may be fitted where it was derivatized by addition of 200 μl of a $NaBEt_4$ solution (0.06 g ml^{-1}) in the presence of 1000 μl of iso-octane, and magnetically stirred for 20 min.[10] A sufficient amount of deionized water was then added to raise the iso-octane layer into the narrow part of the reaction vessel, from where it could be retrieved by Pasteur pipette and transferred to a small vial. To the extract was added 100 μl of a solution of tetrabutyltin in hexane as an internal quantification standard (0.883 ng Sn μl^{-1}) and the mixture was evaporated under nitrogen to around 100 μl. Gas chromatographic analysis was performed using a Perkin Elmer 8000 GC-FPD equipped with a 610 nm optical filter, an air–H_2 flame and He as carrier gas. The analytical column was a 25 m fused silica narrow bore capillary column having a non-polar bonded phase (BP1, SGE). Peak identities were established by comparison with retention times of known standards and peak heights were used for quantification. Blank runs were performed with each set of samples analysed. The limit of detection was established to be 5 ng Sn g^{-1} of dry dust based on a signal to noise ratio of 3.

Although we successfully validated the method of analysis for TBT and DBT using PACS-2, this certified reference material, a marine sediment, is not comparable to the dust samples and there exists no appropriate reference standard for such materials. In order to establish the efficacy of the analytical method for the samples, we submitted a fine dust and a coarse dust sample from a locality (Senglea) where TBT contamination was very high (>5 μg Sn g^{-1}) to three successive extractions and measured the concentration of TBT, DBT and MBT for each extract. For the fine dust fraction, the first extract contained 78% of the total extractable TBT (12.2 μg Sn g^{-1}) while the third fraction contained only 2%. Corresponding values for the coarse dust fraction (containing

DOI: 10.1002/aoc

a total TBT concentration of 7.96 μg Sn g^{-1}) were 73 and 3%, respectively. In light of these results, and considering the fact that the Senglea (and one other) sample contained about 10 to >200 times more TBT than found generally in the other samples, it was decided that one extraction would be sufficient to extract most of the organotins in the dust.

RESULTS AND DISCUSSION

Distribution of organotins in urban dust

Results for both size fractions of dust that were analysed are shown in Table 1. The code numbers in the table correspond to the grid sectors in Fig. 1.

It is fairly clear from the data that contamination by butyltins of settled dust in Malta is a ubiquitous occurrence and that the concentrations in certain areas, namely in the proximity of Grand Harbour and Marsaxlokk Bay, are high. In Table 2, we compare our data with that of Santillo *et al.*[7,8] and Fromme *et al.*,[9] who analysed house dust in European homes for organotins. Table 2 also shows ranges and median values for all samples collected in this work and, separately, that for the sub-set taken from within 3 km of Grand Harbour. Whereas the organotins found in European house dusts (which also contained octyl and phenyltins) were dominated by MBT and DBT, presumably deriving from an indoor source, namely poly(vinylchloride) (PVC) floorings

Table 1. Abundance, in ng Sn g^{-1}, of organotins in the fine and coarse fractions of settled dust from Malta

		Organotins in fine dust fraction (<125 μm)			Organotins in coarse dust fraction (125–250 μm)		
Code	Locality	MBT	DBT	TBT	MBT	DBT	TBT
A1	Ċirkewwa[a]	18	28	54	11	10	24
B1	Mellieħa	8	8	41	23	n.d.[3]	77
B2	St Paul's Bay	19	25	97	15	19	76
B3	Buġibba	137	79	151	174	137	391
B4	Baħar iċ-Ċagħaq[b]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C1.1	Għajn Tuffieħa[b]	n.d.	n.d.	n.d.	n.d.	n.d.	24
C1.2	Għajn Tuffieħa[a]	n.d.	24	144	n.d.	n.d.	n.d.
C1.3	Għajn Tuffieħa	n.d.	n.d.	n.d.	18	17	97
C2	Mġarr	21	47	102	21	41	52
C3.1	Mosta	26	34	213	n.d.	n.d.	160
C3.2	Baħar iċ-Ċagħaq	57	49	81	69	62	100
C4	San Ġwann	31	49	70	27	28	31
C5	Sliema	12	22	31	12	35	77
D1	Baħrija	91	51	13	154	n.d.	n.d.
D2	Rabat[a]	21	25	78	18	9	59
D3	Attard	39	34	48	44	31	30
D4.1	Mrieħel	33	61	143	51	56	79
D4.2	Marsa	81	274	980	143	370	241
D5.1	Floriana	n.d.	118	1861	35	49	52
D5.2	Senglea	1892	6982	9630	895	2226	5798
D5.3	Paola	36	321	2107	112	173	734
D6	Żabbar	250	368	1917	24	87	1976
E2	Dingli	28	17	27	34	22	31
E3	Siġġiewi	16	14	92	n.d.	n.d.	n.d.
E4.1	Luqa	20	49	62	19	24	45
E4.2	Mqabba	26	6	29	n.d.	n.d.	17
E5	Għaxaq	20	63	259	29	86	467
E6.1	Marsaxlokk[a]	1903	2441	6880	4232	6439	11 828
E6.2	Marsaxlokk	172	170	174	180	158	165
E6.3	Delimara[a]	n.d.	n.d.	35	n.d.	n.d.	56
F4	Żurrieq[a]	12	52	289	42	116	217
F5	Birżebbugia	37	42	84	14	34	30

[a] Dust collected from the ground not from a roof top.
[b] Soil sample (there were no built structures in the area).
[3] n.d. = level below detection limit.

Table 2. Concentrations (μg Sn g^{-1}) of organotin compounds in settled dust from Malta and in European household dust (ranges; values in brackets are medians)

	N	MBT	DBT	TBT	Total organotins[a]
UK Housedust[7]	15	0.18–2.39 (1.05)	0.17–0.89 (0.46)	0.004–0.19 (0.022)	0.49–3.48 (1.78)
Five European countries housedust[8]	10	0.08–1.20 (0.65)	0.03–0.33 (0.22)	0.004–0.16 (0.03)	0.14–5.81 (1.36)
German housedust[8]	28	0.005–1.50 (0.05)	<0.005–5.60 (0.03)	<0.005–0.08 (0.008)	0.01–7.18 (0.10)
Malta dust, all island	32	<0.005–6.14 (0.052)	<0.005–9.21 (0.076)	0.005–18.7 (0.14)	0.024–33.7 (0.25)
Malta dust, within 3 km of Grand Harbour	8	0.024–2.79 (0.09)	0.057–9.21 (0.31)	0.11–15.4 (1.57)	0.19–27.4 (2.10)

[a] For household dust, values include octyl and phenyltins; only values above the detection limit are given.

and carpets (treated against bacteria, moulds, fungi and dust mites), the most abundant organotin in Malta dust was TBT. It is very unlikely that TBT in outdoor settled dust would derive, to any significant extent, from TBT-treated timber constructions since wood is not a significant construction material in Malta and even window frames are largely made from aluminium or steel. The concentrations of TBT found in dust from the Grand Harbour area were significantly greater than any reported from other European house dusts and the source of such contamination appears highly likely to be TBT-containing antifouling marine paint that is removed routinely by sand- or hydro-blasting at the drydocks, which are located on the coastline of Grand Harbour next to the town of Senglea. This conclusion is strongly supported by Fig. 2, which depicts contour maps showing, respectively, total butyltin concentrations in the fine and coarse dust fractions: the isopleths clearly indicate a source of TBT centred at the site of the drydocks facility. The most prevalent wind direction locally is the northwesterly,[11] and this accords with the distribution observed for both the coarse, but especially the fine fraction of dust which travels more effectively by wind action, where high concentrations of butyltins persist for over 3 km in the downwind direction.

Microscopic examination (Fig. 3) of dust samples from Dingli (E2) and Senglea (D5.2) revealed that there is a marked difference in aspect between dust from the highly polluted and the less-polluted sites: both dust fractions from Dingli, containing low levels of butyltins, consisted of yellow to yellow-brown granules with occasional black amorphous bodies (interpreted as combustion-derived products) while the highly contaminated Senglea sample consisted of a similar matrix but also containing frequent highly coloured (red, blue, orange, green) particles that were interpreted as paint slivers released during paint-stripping operations from ships' hulls in preparation to repainting.

Statistical analysis (linear regression, ANOVA) of the analytical data (taking $p = 0.05$ as the level of significance) showed that distance from the drydocks is a significant predictor ($p < 0.01$) for determining the concentration of butyltins in dust at any particular location in Malta, although diagnostic tools confirmed what is also fairly apparent from Fig. 2, namely that values at E6.1 (Marsaxlokk) were outliers and influential points, and indicated Marsaxlokk, an important fishing village in Marsaxlokk Bay in the southeast of Malta, as a significant additional source of butyltins. The concentrations of MBT, DBT and TBT in the fine and coarse fractions of dust were found not to vary significantly ($p = 0.995$, 0.342 and 0.357, Mann–Whitney test). On the other hand, the ratio log ([MBT]/[TBT]) was found to increase significantly with distance from the drydocks (linear regression, $p = 0.032$): since MBT, like DBT, is a degradation product of TBT, this information suggests that debutylation is ongoing in street dust as observed in aquatic sediments. There was no statistically significant relation between the ratio log([DBT]/[TBT]) and distance from the presumed source.

As indicated previously, Marsaxlokk dust was also high in butyltin pollution, especially affecting the coarser sized particles. Microscopic examination of the dust again revealed abundant highly coloured particles. Marsaxlokk sea port hosts a significant fleet of fishermen's boats and maintenance of sea craft and fishing tackle takes place on the shore front and is a constant source of activity in the area. Marsaxlokk Bay is also the site of one of Malta's power stations, although as far as we could determine, no TBT-containing products are used at the power station. The contour diagram (Fig. 2) also suggests that there is another minor source of TBT-pollution originating in the vicinity of Żurrieq (F4). This village lies approximately 2 km north of Wied iż-Żurrieq, another site of important boating activity connected with fishing and the tourist/leisure industry. This minor high might again relate to release of antifouling paint residues during maintenance activities by the boating community.

An intriguing aspect of these results is the apparent presence of an inland source of butyltins contamination centred somewhere within grid areas B3 and/or C3 and defined by the contour lines at 400 and 600 ng Sn g^{-1} in Fig. 2(a) and (b), respectively. This area coincides with the site of the Maghtab municipal landfill, which spans roughly the upper half of grid area C3 in Fig. 1. For several decades, the landfill has received both municipal and industrial solid wastes, dominated by construction and demolition limestone material and has now actually become a positive topographic

DOI: 10.1002/aoc

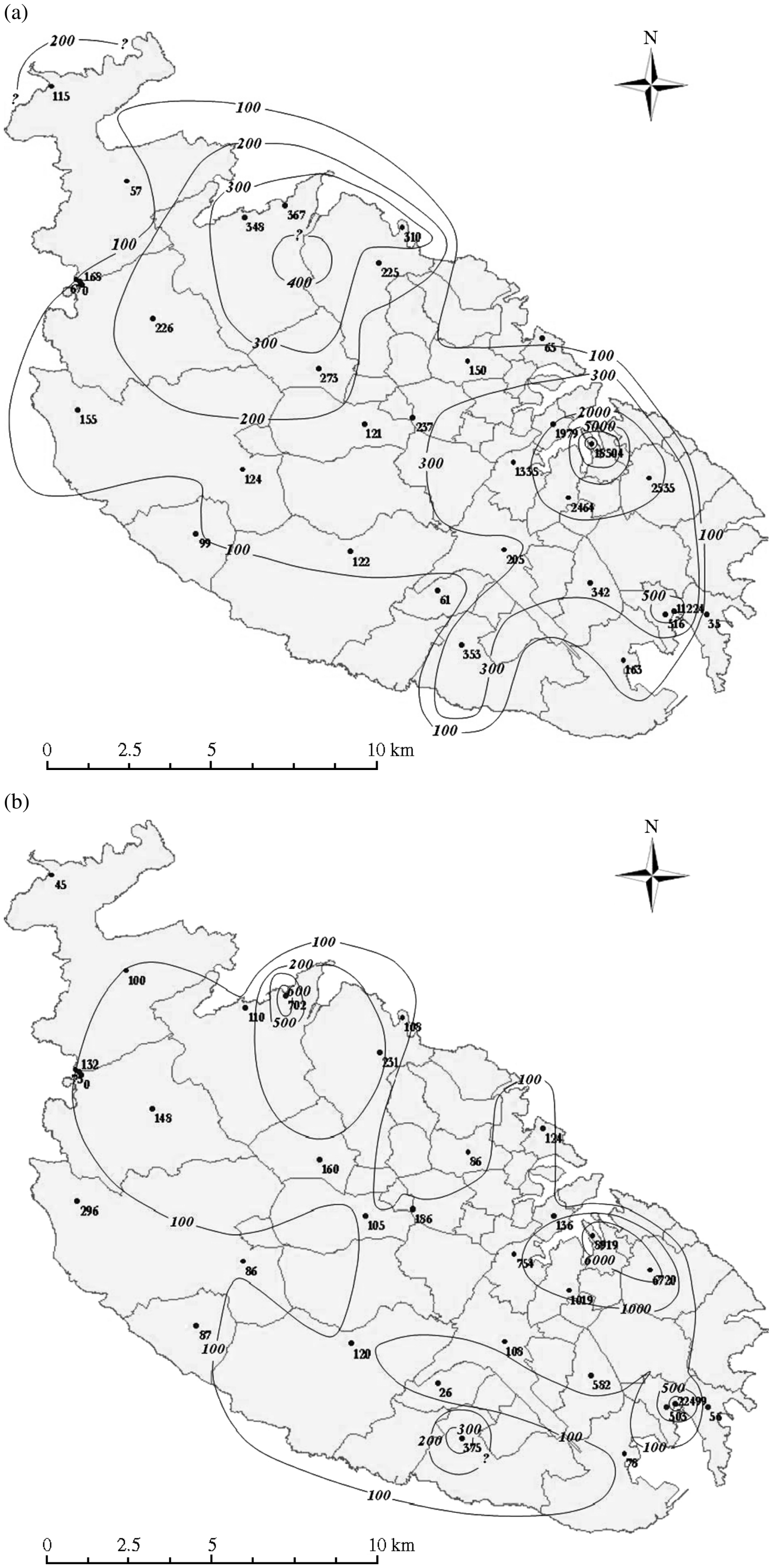

Figure 2. Contour maps showing total concentration of organotins (TBT + DBT + MBT) in ng Sn g^{-1} in (a) the fine fraction and (b) the coarse fraction of settled dust in Malta.

DOI: 10.1002/aoc

feature. The landfill has also received spent grit contaminated with paint shavings from the drydocks and also empty containers of antifouling paint which, inevitably, contain some residual material. We suggest that these sources could have contaminated the waste mass with paint-derived TBT. The landfill is also a repository of other butyltin-containing wastes, such as products made from polyvinyl chloride (PVC) and polyurethane polymers, which are important sources of MBT and DBT (and other organotins). Such materials could have contaminated the limestone rubble in the landfill which, through wind whipping of the uncovered deposit, could have provided a dust laden with butyltins originating in the northern part of the island away from the port areas.

Toxicological risk from butyltin-contaminated dust

Although there is no evidence that organotins are carcinogenic, they are known to produce immunotoxic and teratogenic effects in mammalian systems, even at low doses,[12] with DBT often appearing more toxic than TBT. DBT is also neurotoxic to mammalian brain cells.[13] Environmentally relevant doses of TBT have recently been shown to exacerbate airway inflammation in mice and TBT appears to present a significant risk for the induction of allergic diseases.[14] For humans, the tolerable daily intake (TDI) for TBT has been estimated to be[15] 0.25 μg tributyltin oxide kg^{-1} bw day^{-1}, which is equivalent to 0.1 $\mu g\,Sn\,kg^{-1}\,day^{-1}$. In order to estimate roughly the toxicological significance of human exposure to the contaminated dust, we considered the worst case situation defined by the following conditions: (a) assume house dust to be similar in composition to settled outside dust; (b) assume only street dust with diameter <250 µm is fine enough to be ingestible; (c) assume that there is 100% absorption of organotins in the gastro-intestinal tract; and (d) assume the TDI for DBT is equal to that of TBT. Then, since it is known that adults ingest about 20 mg of house dust per day,[16] an average adult weighing 60 kg and residing in Senglea (Grand Harbour area) where ingestible dust has a concentration of (TBT + DBT) of 17 $\mu g\,Sn\,g^{-1}$ would be exposed to 0.3 $\mu g\,Sn\,day^{-1}$; this is equivalent to 5% of TDI. For small children, exposure to dust is of greater concern: the ingestion rate is 100 mg per day,[17] they have a lower TDI due to smaller body mass and they are more sensitive subjects due to their developing immune system and also their playing habits. For a child with a body mass of 20 kg living in Senglea, dust ingestion could contribute about 85% of TDI, which is a very considerable amount with a very narrow margin of safety. These estimated doses do not include any organotin contributions from food and other sources, especially indoor sources[9] related to PVC tiling, plastic ware, biocide-treated carpets and so on, which would further narrow the margin of safety.

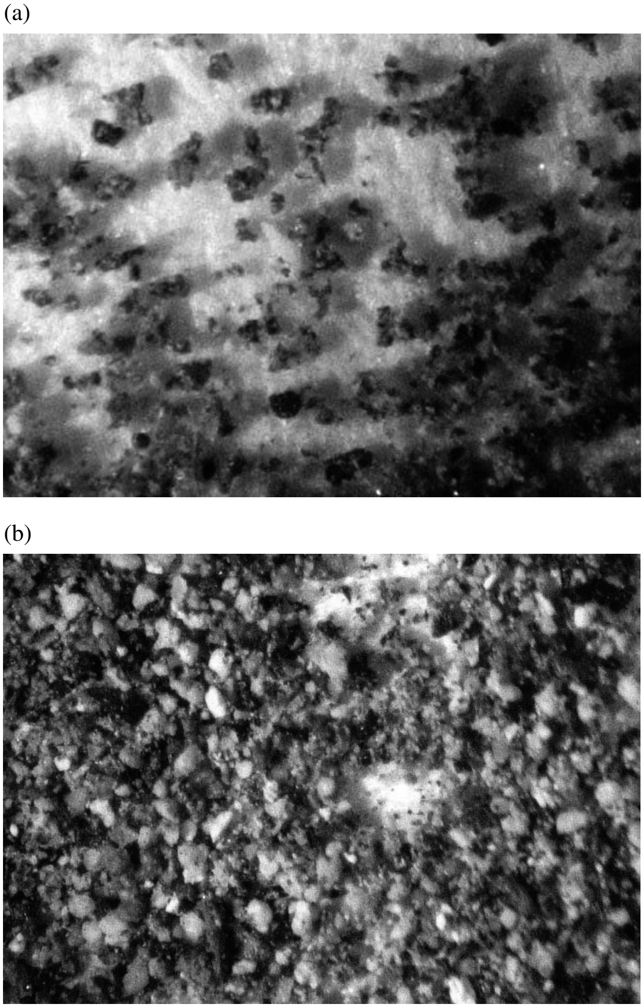

Figure 3. Fine dust from (a) Dingli and (b) Senglea. Magnification ×30 (photographs by Jonathan Henwood, Department of Biology, University of Malta).

The area around Grand Harbour is densely populated[18] (for Senglea, Birgu and Bormla, the density is about 22 000, 5800 and 6600 persons km^{-2}) and the total coastal population is about 73 000. Considering further that the effects of exposure to very low levels of organotins over a long period are unknown,[4] and that synergistic effects with other pollutants cannot be excluded, the state of contamination of the urban environment by butyltins in Malta may be of concern. The ban on the use of TBT should allow relaxation and possible eventual resolution of the problem, although it is difficult to say how long this will take. In aquatic sediments, the half-life of TBT is of the order of a few years:[4] that in settled dust under the relatively dry and sunny conditions of Malta is unknown. For this reason, it may be that the problem of contamination by organotin of the urban environment in Malta will not resolve for several years yet.

CONCLUSIONS

The present study has demonstrated the occurrence of butyltins in settled dust in Malta in levels ranging from low ng Sn g^{-1} to several tens of µg Sn g^{-1} and including considerable quantities of TBT. These toxic contaminants are ubiquitous and are found in settled dust from practically everywhere on the island, deriving mainly from biocidal marine paint residues scraped off ships' hulls during maintenance. A major source of such contamination appears to be the drydocks facility in Grand Harbour and dust containing total butyltin at levels of low µg Sn g^{-1} is found at distances of 3 km downwind from this source. The greater the distance from the drydocks, the more MBT is found in the dust, presumably resulting from ongoing degradation by debutylation of TBT and DBT. Boating activities in coastal fishing villages, mainly at Marsaxlokk and Wied iż-Żurrieq appear to generate similarly contaminated dusts, but high concentrations of butyltins are more localized, implying a weaker source strength. The data also suggest that the municipal landfill at Maghtab constitutes an inland source of butyltins. A preliminary evaluation of the extent of exposure of the population to butyltins from ingestion of contaminated dust suggests that, especially for children living in the densely populated area of the Grand Harbour region, the problem may be significant and is likely to persist for years even after a complete ban on TBT-containing marine paint had taken effect.

Acknowledgements

The authors wish to thank Dr L. Camilleri (Department of Statistics, Faculty of Science, University of Malta) for his assistance with the statistical analysis of the results.

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DOI: 10.1002/aoc