

Organotins in Lake Sediment

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Organotin compounds are entering the aquatic environment due to their use in antifouling paints on boats and from municipal and industrial wastewaters [1]. Tributyltin (TBT) is highly toxic to aquatic life, particularly to marine molluscs (oysters) [2] and gastropods, leading to observed declines of dog-whelk populations on various coasts [3]. Chronic toxic effects on these organisms occur at aqueous concentrations of a few ng/l. TBT, dibutyltin (DBT), and monobutyltin (MBT) have been detected in the aquatic environment. Increased concentrations of TBT in water, sediment, and biota have been linked primarily to pleasure boating activities. In the water column, TBT concentrations were reported to lie in the high ng/l range for marinas, and in the low to medium ng/l range for open waters [4, 5]. TBT residues in sediments were found to be considerably higher, typically in the high $\mu\text{g}/\text{kg}$ range [4–6], and total butyltin concentration was shown to decrease with depth in sediment cores [7]. In the water column, TBT is biodegraded by successive dealkylation reactions leading to DBT as the principal degradation product with lesser amounts of MBT [6, 8]. In sediments, degradation was reported to be much slower with half-lives of 4 to 5.5 months [6–8].

To date, little is known about the occurrence and persistence of organotin compounds in sediments. Here, we report on the vertical distribution of a series of butyltins and phenyltins in the sediment of freshwater marinas of Lake Lucerne, Switzerland. The occurrence of phenyltin residues has not been previously reported. By using radiocesium isotopes in the sediment, we derive geochronological data. Con-

siderable concentrations of TBT in the upper part of the dated sediment core in conjunction with the low occurrence of DBT and MBT suggest that TBT is conserved in this sediment over a time period of years.

Several sediment cores up to 60 cm in length were taken on July 12, 1989, in the 2.5 to 3 m deep marina Lucerne. This marina was constructed in 1978, has berths for 456 pleasure boats, and is well flushed. The sediment was anoxic. The cores were taken with a gravity corer using Plexiglas tubes of 12 cm diameter for chemical and nuclide analyses, and PVC tubes of 6.3 cm diameter for sedimentological description and photography. Immediately after collection, a core of 12 cm diameter and 29 cm in length was extruded in 0.5 cm or 1 cm slices, split vertically into two subsamples, and stored in cleaned glass jars at -30°C . One portion of wet sediment was used for sediment organotin analysis. The other wet subsample was freeze-dried and used for porosity measurement, determination of organic and inorganic carbon (by Carlo Erba CNS-analyzer and Coulometer inorganic carbon analyzer), ^{134}Cs and ^{137}Cs by γ -counting using a Canberra well-type detector and multi-channel analyzer.

Details of the organotin trace analysis of water and sediment employing internal standards (IS) are given in [5, 9]. Briefly, the procedure consisted of the following steps: (a) acidification of the 500 ml water or sediment sample (5–15 g); (b) solid-phase extraction of the water sample, or diethyl-ether (containing 0.25% tropolone) extraction of sediment sample; (c) derivatization (ethylation by a Grignard reaction); (d) cleanup; (e) analysis by high-performance gas chromatography with flame photometric detection on a 30-m fused silica capillary column. For quantification, IS tripropyltin chloride, and mono-, di-, tri-, and tetrapentyltin

chloride in acetone were added to the samples prior to extraction. The detection limit for the butyl- and phenyltins was 2–20 ng/l of water and 0.05–2 $\mu\text{g}/\text{kg}$ (dry weight) of sediment. All the results are reported as mean values of duplicate or triplicate determinations and refer to the butyltin and phenyltin species as the ion. The concentrations were corrected for recovery by IS (60–95% for different species), and sediment data are given on a dry-weight basis.

First measurements in marina waters of Lake Lucerne during 1988 showed that TBT concentrations were remarkably high [10]. Considerable organotin concentrations were also measured on July 12, 1989. The concentration of TBT was 252 ng/l, DBT was 12 ng/l, and MBT was 13 ng/l in unfiltered water collected at a depth of 1 m. Additionally, triphenyltin (TPT), a biocide also employed in some (older) antifouling paints in addition to TBT, occurred in concentrations of 38 ng/l. TBT occurs in marina waters in the dissolved and particulate phase. In seawater, virtually all the TBT occurs in a dissolved form, however, there is also capacity for sorption to particulates as indicated by the reported distribution coefficients K_d between particulate and dissolved phases in the range of 3000 [8]. Our measurements indicate similar distribution ratios in the water of the marina investigated [11]. In addition, our study with municipal wastewater showed that the concentration of suspended particles was an important parameter controlling partitioning between dissolved and particulate phases [9]. In raw wastewater containing high concentrations of suspended solids, about 90% of the organotins were associated with the particulate phase, whereas in the secondary effluent containing a lower suspended solids concentration, it was only 53%. Thus, scavenging of TBT from the lake water column to sediment is assumed to occur on the basis of these observations.

In the sediment of this marina, considerable concentrations of a series of butyltins and phenyltins occurred. The organotins were only present at the top of the core, which points to a recent source. As in the water column, the major compound detected was TBT. Figure 1 shows the butyltin profiles down to a depth of 12 cm. Concentra-

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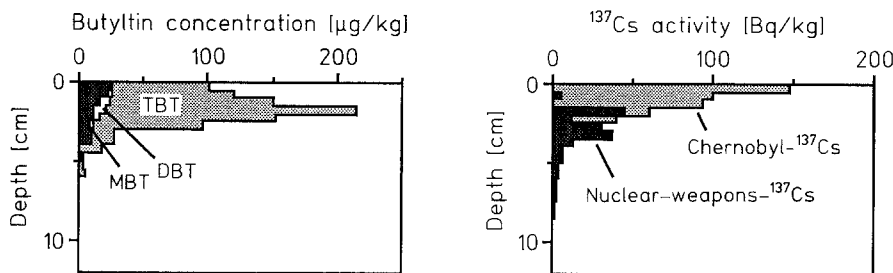


Fig. 1. Butyltin and ^{137}Cs profiles in sediment core of marina Lucerne. *TBT* tributyltin, *DBT* dibutyltin, *MBT* monobutyltin. Zero values occurred below 12 cm

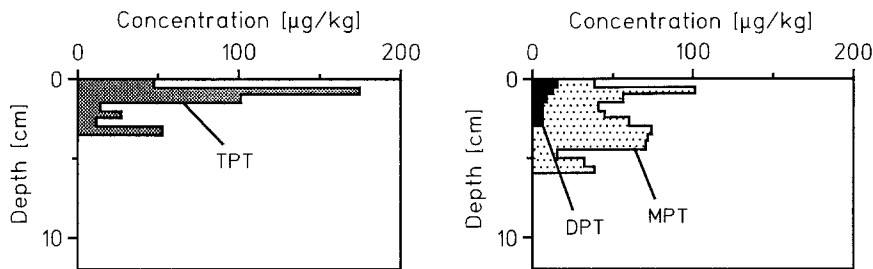


Fig. 2. Phenyltin profiles in sediment core of marina Lucerne. *TPT* triphenyltin, *DPT* diphenyltin, *MPT* monophenyltin. No phenyltins occurred below 6 cm

tions of TBT increased from 101 $\mu\text{g}/\text{kg}$ at the top to 215 $\mu\text{g}/\text{kg}$ at a depth of 1.5 to 2.0 cm. Between 2.5 and 5.5 cm, concentrations decreased significantly from 96 to 5 $\mu\text{g}/\text{kg}$, and at 6 cm and down to 29 cm, no butyltins were detected. The decrease in TBT concentrations was paralleled with decreases in DBT and MBT ranging between 1 and 26 $\mu\text{g}/\text{kg}$ and 0.5 and 25 $\mu\text{g}/\text{kg}$, respectively. Both the low proportion of degradation products, DBT and MBT, and the concentration decrease with depth, indicate a low degradation of TBT in this sediment.

Phenyltins have not previously been reported to occur in lake sediments. Our data in Fig. 2 show that considerable concentrations of TPT and its likely degradation products, diphenyltin (DPT) and monophenyltin (MPT), occurred. TPT was only present in the uppermost 3.5 cm in concentrations ranging between 12 and 174 $\mu\text{g}/\text{kg}$. DPT was only present in the top 3 cm, and MPT was detected to a depth of 6 cm. The proportions of degradation products relative to the parent compound were different between phenyltins and butyltins. MPT as a TPT degradation product occurred in higher proportions than MBT or DBT relative to TBT,

which suggests a higher degradation rate of TPT than TBT.

Much higher butyltin residues have been detected in the top 3 cm of a 20-cm-long sediment core, taken with other cores in the 2.5-m-deep marina Stansstad, another marina in Lake Lucerne. The sediment was anoxic. From the surface down to 3 cm, concentrations of TBT were in the range of 1158 to 1589 $\mu\text{g}/\text{kg}$. Similar to marina Lucerne, proportions of MBT and DBT relative to TBT were only low, with concentrations in the range of 50 to 220 $\mu\text{g}/\text{kg}$. In addition, considerable concentrations of TPT in the range of 71 to 188 $\mu\text{g}/\text{kg}$ occurred. The concentrations of MPT and DPT were in the range between 9 and 33 $\mu\text{g}/\text{kg}$.

In previous studies, no vertical organotin profiles in conjunction with ^{137}Cs profiles were reported. Here, we use the ^{134}Cs and ^{137}Cs isotopes to develop geochronological data. ^{134}Cs originates solely from the Chernobyl accident (April 1986), but ^{137}Cs derives from both Chernobyl and prior nuclear weapons testing in the atmosphere peaking in 1963–1964. ^{137}Cs profiles in the sediment core of marina Lucerne are illustrated in Fig. 1. Chernobyl- ^{137}Cs was calculated by using the well-

established $^{134}\text{Cs}/^{137}\text{Cs}$ ratio of 1.9 ± 0.2 [12]. All values have been corrected for nuclear decay (May 1, 1986), and the detection limit of ^{137}Cs (half-life 30.17 a) was 0.122 Bq/kg. The occurrence of ^{134}Cs with a half-life of 2.06 a proves its origin from the Chernobyl accident. The profile of Chernobyl- ^{137}Cs shows maximum activities in the top of the core, gradually decreasing to zero values at 2.5 cm. The shape of the profile suggests mixing of at least the uppermost 2 to 2.5 cm of the sediment column. Homogenization and/or an erosion process can also be deduced from the irregular shape of the profile of nuclear-weapons- ^{137}Cs . A first peak of nuclear-weapons- ^{137}Cs occurs at 2 cm, where Chernobyl- ^{137}Cs is still present and a second peak occurs from 2.5 to 3.5 cm, followed by a gradual decrease to zero. Disturbances are most likely caused by anthropogenic processes such as motor propellers of boats within the shallow marinas, but also by bioturbation processes by benthic biota. However, as can be deduced from the vertical distribution of Chernobyl- and nuclear-weapons- ^{137}Cs , the depositional structures are not completely disturbed in the core. The top layer of 2 to 2.5 cm may represent approximately 3 to 4 years prior to the date of sampling, and it is assumed that the sediment is built up of homogenized sections of approximately 2 to 2.5 cm. This leads to the conclusion that the occurrence of considerable concentrations of TBT in the sediment presumably correlates with the construction of the marina in 1978. At this time TBT-containing antifouling paints were already in use, but the annual amount used is not known. The increase in the organic carbon content at this sediment depth (Table 1) may also indicate the construction of the marina in 1978 and a subsequent change of this littoral environment by cutoff from the rest of the lake. These observations and the geochronology of the core provide evidence that TBT (and TPT) are stored in this sediment over remarkably long periods of time. The persistence of TBT is also indicated by the low occurrence of its degradation products. In previous studies, low degradation rates of TBT, especially in anoxic sediment, were found in freshwater [6] and marine sediments [7]. Sediments may therefore represent a sink, and under

certain circumstances, a source of TBT and TPT through desorption for several years after inputs cease.

The ecotoxicity of marina waters and sediments is mainly based on their TBT and TPT concentrations. On comparison with organisms living in the water column, little is known about the toxicity of organotins to benthic organisms. TBT concentrations in the sediment of marina Stansstad may be harmful to benthic organisms. The LD₅₀ (48 h) of the oligochaete *Tubifex tubifex*, a representative organism, was reported to lie in the range of 5 and 50 ppb [13]. However, data in this study are unclear as to whether this value holds for sediment or water concentrations. This oligochaete was not observed in the sediment cores taken from marina Stansstad. However, absence of this worm may also be caused by long-term anoxic conditions at this site. In addition, it was shown that uptake of TBT from contaminated sediments by oligochaetes takes place [6], thus making sediment-associated TBT available to the benthic food chain. Further studies, however, are required to determine the degradation processes of TBT and TPT in sediments, and to determine the ecotoxicological implications of TBT- and TPT-contaminated sediments to benthic organisms.

We would like to thank J. Perlinger, EAWAG, for reading the manuscript, and to the anonymous reviewers for helpful comments. The study was sup-

Table 1. Water content, porosity, and organic carbon content in sediment core of marina Lucerne

Depth [cm]	Water content [%]	Porosity [vol. %]	Organ. C [wt %]
0– 0.5	79	0.90	4.75
0.5– 1.0	76	0.89	4.54
1.0– 1.5	75	0.89	3.66
1.5– 2.0	75	0.88	3.72
2.0– 2.5	72	0.87	3.06
2.5– 3.0	70	0.86	2.49
3.0– 3.5	69	0.85	2.41
3.5– 4.0	63	0.81	1.53
4.0– 4.5	61	0.80	1.41
4.5– 5.0	60	0.80	1.21
5.0– 5.5	60	0.79	1.37
5.5– 6.0	60	0.79	1.36
6.0– 10.0	59– 56	0.79– 0.76	1.30– 1.08
10.0– 29.0	55– 46	0.75– 0.66	1.22– 1.12

ported in part by the Kanton Luzern, Amt für Umweltschutz (P. Stadelmann).

Received October 12, 1990 and February 6, 1991

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Sensitivity to Odors in Wistar Rats Is Reduced After Low-Level Formaldehyde-Gas Exposure

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Formaldehyde is an irritant, often causing eye irritation, and runny noses, as well as chronic respiratory problems [18]. There is also evidence for the involvement of formaldehyde in cancer [7, 8], at least in high concentrations.

Experimentally induced long-term exposure to formaldehyde at a dose of approximately 15 ppm has been associated with the development of nasal cancers in Sprague-Dawley and Fischer rats [13, 16]. Even a lower concentra-

tion of about 6 ppm formaldehyde has been found to induce lesions in the nasal area, the trachea, and the bronchial bifurcation of the rhesus monkey [10]. There is no experimental evidence, however, for noxious effects of low-level formaldehyde-gas exposure. Therefore, a promising approach to the investigation of possible harmful effects of low-level formaldehyde concentrations may be the analysis of olfactory sensitivity.

In a psychophysical study, five male Wistar rats (Group I) were exposed to 0.25 ppm formaldehyde gas from post-natal day 30 until 160; exact birth dates were available for all animals. Experi-