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Leaching of organotin compounds from poly(vinyl chloride) (PVC) material

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The release of mono- and di-butyltin species (MBT and DBT) in water after leaching of five different poly(vinyl chloride) (PVC) materials was investigated under mild conditions over a period of one month in batch reactor systems. Results showed that inorganic tin, MBT and DBT compound were released from the material tested under experimental static leaching conditions. The total amount of inorganic tin and organotin compounds observed upon leaching varied considerably from one PVC material to another.

Keywords: Inorganic tin, monobutyltin, dibutyltin, PVC material, leaching

1 INTRODUCTION

Mono- and di-butyltin (MBT and DBT) are released into the environment through different sources. Most of the time, their occurrence is related to degradation pathways of the well-known tributyltin species (TBT), an efficient biocide used in antifouling paints. The stepwise degradation of TBT to DBT and MBT has been reported to be mediated by microbial activity[1] or to biological and photochemical reactions.[2,3] Another potential source may originate from the direct leaching of poly(vinyl chloride) (PVC) pipes.[4,5]

There is increasing evidence that mono- and dibutyltin compounds may be introduced directly into the environment via drainage water pipes or sewage water processing plants. Indeed, these compounds have been detected in areas where the use of TBT is unlikely. These areas included riverine sediments receiving mining effluents[6] and urban waste waters.[7,8]

Dialkyltin compounds are generally used as stabilizers of PVC material, e.g. for drainage and potable-water pipes. Some dialkyltin compounds used include dioctyltin(IV) dilaurate, dioctyltin(IV) dioctylthioglycollate, dibutyltin(IV) dilaurate,[9] indicated here in an increasing order of toxicity: LD_{50} to rats varies respectively from 6000 to 175 mg kg^{-1}. If diorganotin compounds are classically considered as being less toxic than their trialkylated counterparts, they may also alter fundamental metabolic activities. DBT (dibutyltin dichloride) has been shown to inhibit ADP-stimulated respiration of mitochondria significantly.[10]

The US production and consumption of organotin compounds foreseen in 1990 indicates that most of the organotin compounds produced (a little more than 60%) will be used as PVC stabilizers.[11] Almost no data are available on the amounts of organotin released into the environment during the manufacture or use of pipes, and even further, after their discharge as solid waste.[11] Moreover, little to no knowledge exists with regard to the importance of chemical leaching occurring from degradation of PVC material in dumping sites.

The degradation of PVC has been studied extensively in the past, but techniques used generally for the determination of tin species were neither sufficiently sensitive nor sufficiently selective. In this paper, we present the results of static leaching experiments over a period of one month for five types of PVC material from different manufacturers. These experiments were performed with a highly selective and sensitive apparatus coupling a simplified gas chromatograph with an atomic absorption spectrometry detector (GC AA).

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2 MATERIAL AND METHODS

2.1 Experimental design

Five different types of PVC were used in this study (referred in the text as PVC 1, 2, 3, 4 and 5). Unfortunately, no data were available with regard to the type of organotin stabilizer used. PVC chips (1 cm, total weight of 15 g) were introduced into 500 cm^3 acid-washed Pyrex glass bottles. The flasks were filled with tap-water and the concentrations of organotin species were monitored in the different batches of water over a period of one month. Aliquots of 50 cm^3 were collected for analysis after 1, 2, 5, 12 and 33 days. Intakes were replaced with equivalent volumes of tap-water and the dilution factor introduced was taken into account in each set of analyses. All the experiments were performed at room temperature and the flasks were kept exposed to daylight. Extreme care was taken to avoid cross-contamination of samples during the whole period of the experiment.

2.2 Analysis

Inorganic tin and organotin compounds were determined by hydride generation/cryogenic trapping/gas chromatographic separation and detection in a quartz cell of an atomic absorption spectrometer (Perkin–Elmer 5000).[12,13] Careful attention was paid to obtain a good long-term reproducibility of measurements. The calibration was done by the method of standard additions in tap-water, using the same stock solution (stored at −20°C) of which the stability was verified with a fresh solution at the end of the experiments. Other details of the analytical procedure are described elsewhere.[14] The repeatibility of the method as assessed with five replicate analyses of tap water (50 cm^3) containing 10 ng (as Sn) respectively of inorganic tin, mono- and di-butyltin compounds. Relative standard deviations were found to range between 6 and 10%. The long-term reproducibility (RSD) over the total period of the experiment is higher in the case of TBT only. The blank in tap-water was monitored over the whole study and traces of neither MBT nor DBT could be detected; the blank therefore contained amounts of inorganic tin less than 2 ng dm^3. All the analyses were performed in duplicate (2×25 cm^3) and the results are reported as the mean and standard deviation of these duplicate measurements. Detection limits measured in tap-water were respectively 0.5 ng dm^{-3} (as Sn) for inorganic tin, 0.6 ng dm^{-3} (as Sn) for MBT and 0.5 ng dm^{-3} (as Sn) for DBT.

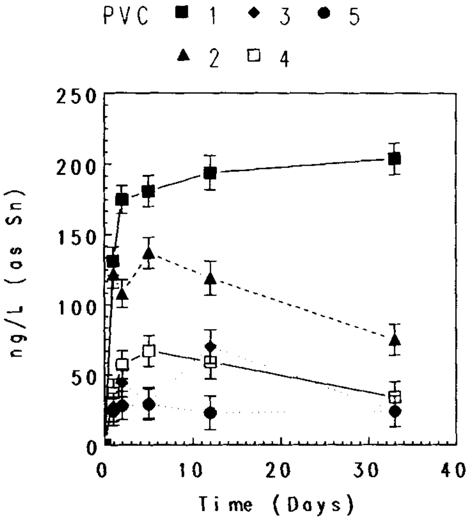

Figure 1 Leaching patterns of total tin (sum of inorganic tin, MBT and DBT) in each different PVC material tested (materials 1, 2, 3, 4 and 5). The concentrations are given in ng dm^{-3} (as Sn). ■, PVC1; ▲, PVC 2; ◆, PVC 3; □, PVC 4; ●, PVC 5.

3 RESULTS AND DISCUSSION

3.1 Kinetics of release

The time pattern for release of total tin (sum of inorganic and organo- tin amounts) is presented in Fig. 1. Results indicate that all PVC materials tested under these leaching experimental conditions released significant amounts of tin. The release observed was rapid in all the cases, since up to 80% of the total tin leached was released within two days. After five days of leaching, the concentrations of total tin stabilized or slightly decreased. This first set of results allows us to distinguish two types of material: two PVC materials presented a high leaching capacity (PVC 1 and 2) whereas another group (PVC 3, 4 and 5) released significantly less tin. In the first group of materials, total tin concentrations obtained upon leaching reached an average of 150 ng dm^{-3}, whereas the average concentrations found in the second group were less than 50 ng dm^3. This probably reflects a difference in the chemical formulation of the organotin stabilizers used in the PVC tested.

A closer examination of the distribution of the different tin species observed upon leaching is presented in Fig. 2(a)–(e) which highlights the different leaching capacities of the PVC tested: inorganic tin is the dominant species in all the leachates and contributes from 30 to 60% of the total tin content. Other species are MBT and DBT. Methylated tin species were not detected.

On the basis of the distribution of the different tin species, one may also distinguish between the quality of the PVC tested (i.e. the different natures of the stabilizers used): PVC materials 1 and 2, presenting the higher leaching rate of total tin, displayed also a high release of DBT. The other materials tested (3, 4 and 5) presented much lower leaching rates and the predominant organotin species released was MBT.

Adsorption processes have to be considered in this study of leaching dynamics as the results may be partially biased by such pnenomena. With the exception of PVC 1, of which the tin distribution suggests a continuous leaching over the whole period of the study, all PVC materials displayed a plateau or a slight decrease in the tin concentrations measured over time. This indicates that a possible equilibrium between the leaching rate and the adsorptive capacities of the glass walls of the flasks may have occurred. It is impossible to state whether a continuous leaching of tin species occurred in these PVC materials since the tin compounds may have been adsorbed either on the glass walls or on the surface of the PVC chips.

The fact that the DBT amounts presented a general decrease, without a corresponding increase in MBT moieties, suggests that little to no degradation of this compound occurred during the experiment. This result is consistent with the higher adsorptive capacities observed for DBT in comparison with MBT and TBT during storage experiments on natural waters.[14]

3.2 Degradation pattern

Organotin compounds are usually considered to be rather stable with regards to chemical strain. However, in dialkyltin substitutes, R_2SnX_2, the anionic radical X may be easily cleaved by simple hydrolysis.[15] In comparison, the tin–carbon bond is considered to be much more stable. The analytical method only allowed us to identify the cationic forms of inorganic tin or MBT and DBT in the samples. Therefore it was not possible to assess the importance of changes in the anionic composition of the compounds. The generally accepted degradation pathway for DBT is a stepwise debutylation to MBT and finally to inorganic tin. The results of Fig. 2 suggest that two alternative pathways could have occurred, considering the respective distribution of tin species:

(a) the organotin stabilizers obtained upon leaching were rapidly degraded to harmless inorganic tin under the experimental conditions used; or
(b) inorganic tin was also leached directly from the PVC materials along with the butyltin species.

The second hypothesis is most likely since the Sn–C bond is not thought to be easily broken under these conditions. In both cases, the detection of these compounds in the leachates suggest that a possible long-term weakening of the PVC material to chemical attack may occur.

CONCLUSIONS

The present study clearly demonstrates that the release of inorganic and organic tin compounds from leaching of PVC materials is a pathway which may occur in the environment. This release significantly differs from one PVC type to another, which is probably to be related to the different nature of the stabilizers used. The effects of this leaching may affect the long-term stability of the PVC material, due to a possible enhancement of its porosity and vulnerability to chemical attack.

Although DBT is considered to be less toxic than the trialkyltin species, the rapid increase in the production and use of PVC and its consequent disposal will lead to an accumulation of these compounds in the environment and to possible long-term effects on man and biota. These results should therefore offer encouragement towards the monitoring of these species in aquatic ecosystems, including ground and sewage waters.

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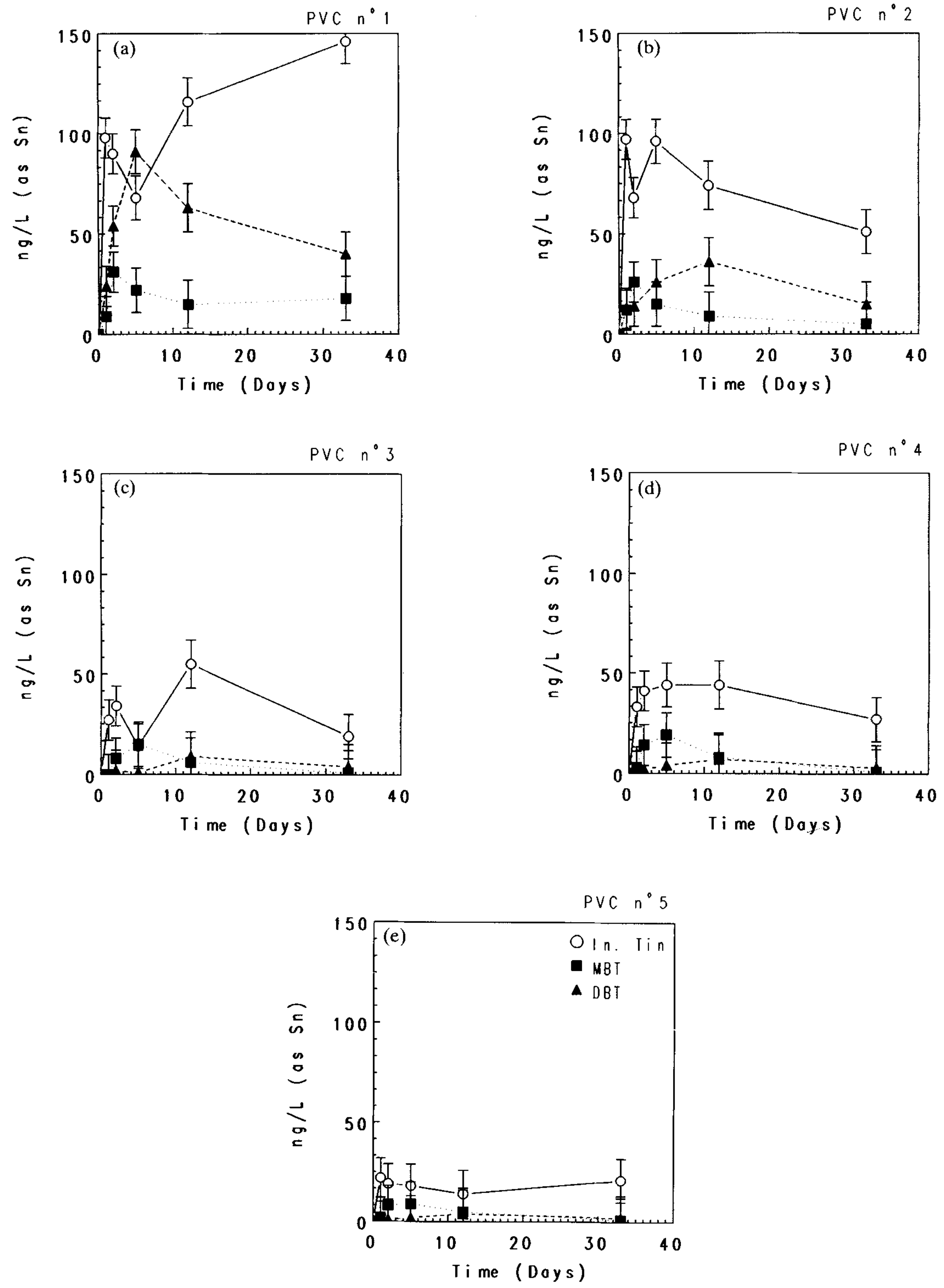

Figure 2 Distribution of inorganic and butyl tin species leached from each PVC material over a period of one month: (a) to (e) correspond to the materials 1 to 5 respectively. ○, Inorganic tin; ■, MBT; ▲, DBT.

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REFERENCES

1. Olson, G J and Brinckman, F E *Proc. Oceans 86 Organotin Symp.*, 1986, Washington, DC, 23–25 Sept. 1986, p 1196
2. Maguire, R J and Tkacz, R J *Agric. Food Chem.*, 1985, 33: 947
3. Takahashi, K, Yoshino, T and Ohyagi, Y *J. Chem. Soc. Japan*, 1987, 2: 181
4. OMS Publication No. 15, Geneva 1980
5. Boettner, E A, Ball, G L, Hollingworth, Z and Aquino, R EPA-600-SI-81-062 EPA Health and Effects Res. Lab., Cincinnati, 1982
6. Quevauviller, Ph, Lavigne, R, Pinel, R and Astruc, M *Environ. Pollut.*, 1989, 57: 149
7. Schebek, L PhD Dissertation, Johannes-Gutenberg-Universität, Mainz, 1990
8. Donard, O F X, Quevauviller, Ph and Bruchet, A *Water Res.* (submitted)
9. Lawson, G In: *Organometallic Compounds in the Environment*, Craig, P J (ed), Longman, Harlow, 1986, p 308
10. Cain, K, Hyams, R L and Griffiths, D E *FEBS Lett.*, 1977, 82: 23
11. Wilkinson, R R *Neutoxicology*, 1984, 5: 141
12. Donard, O F X, Randall, L, Rapsomanikis, S and Weber, J H *Inter. Anal. Chem.*, 1986, 27: 55
13. Donard, O F X In: *5. Colloquim Atomspektrometrische Spurenanalytik*, Weltz, B (ed), Bodenseerwerk Perkin–Elmer, 1989, p 395
14. Quevauviller, Ph and Donard, O F X *Fres. Z. Anal. Chem.*, in press
15. Plum, H *Information Chimique*, 1981, 220: 135