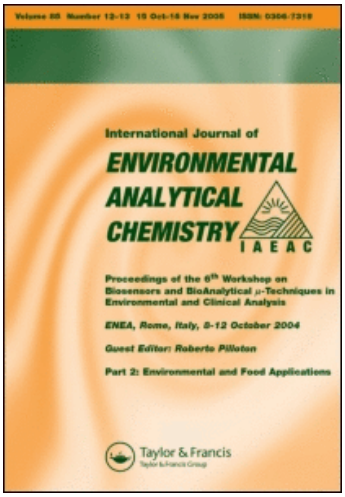

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DETERMINATION OF METHYLTIN AND BUTYLTIN COMPOUNDS IN ENVIRONMENTAL WATER AND SEDIMENT SAMPLES

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Although today most techniques for the determination of organotin compounds provide adequate precision, problems concerning the accuracy of data obtained from actual environmental samples still exist. Two important sources of error are the storage of samples and the extraction of organotin compounds from environmental matrices. The stability of methyl- and butyltin compounds in freshwater samples stored in polycarbonate containers was examined: storage at +10°C and freezing at −20°C both conserved original concentrations for some days, but resulted in losses after prolonged storage. For sediment samples, freeze-drying was found to be a reliable method of conservation. Extraction efficiency was evaluated for the extraction of sediment samples by refluxing in methanol/hydrochloric acid. Spiking and re-extracting a sediment may result in an overestimate of extraction efficiency. More accurate data can be obtained by using a method based on extracting sediment with varying volumes of solvent. Our data suggest that tin speciation, as well as the type of sediment, influence extraction efficiency significantly.

KEY WORDS: Organotin compounds, sediment extraction, stability of samples, tributyltin

INTRODUCTION

Due to the mounting interest in the role and fate of organotin compounds in the environment[1–4], numerous methods have been developed in recent years to determine trace levels of these compounds in water and sediments[5–13]. At the low concentrations at which these compounds are typically found in the environment (the ng/l and ng/g level in the case of natural waters and sediments, respectively), analytical precision and accuracy become especially difficult to achieve.

At present, the techniques used to determine organotin species in aqueous samples seem to be quite reliable. Quantitative recovery of organotin species from such samples is usually achieved, and standards can be easily prepared. However, other problems concerning the accuracy of these data exist and, moreover, often do not receive appropriate attention. The storage of water and sediment samples, usually necessary for logistical reasons, is such a critical factor. When certain container

materials are used, major loss of tributyltin (TBT) from water samples may occur within just a few hours[14,15]. Although storage times of more than a few hours are frequently required, data on the stability of tin compounds other than TBT in water samples have not been published. In the case of sediment samples, short-term storage may be less problematic as the concentration of tin compounds is usually higher, and the water can be eliminated by drying the samples. Here, the most important influence on data accuracy is the efficiency of the tin species extraction[13,16]. To date, a reliable and efficient method of extracting organotin species from sediments has not been developed and the absence of a representative reference material further complicates the process. Much of the published organotin data may not be accurate.

In the present publication, we investigate the effect of water and sediment sample storage on the precision and accuracy of organotin compound determination. We also investigate the effect of extraction efficiencies for organotin compounds from sediments on analytical accuracy. In the absence of a certified sediment reference sample, we establish the accuracy of our results in an intercomparison exercise.

METHODS

Apparatus

Analysis was performed by a modification of the method described by Randall *et al.*[8]: organotin compounds were derivatized to the corresponding hydrides by reaction with $NaBH_4$. These hydrides were purged by a stream of helium from the reaction flask to a cold trap (cooled with liquid nitrogen) which contained a chromatographic packing material. Species were separated by heating the trap up to +180°C and subsequently detected in the electrothermally heated quartz furnace of an atomic absorption spectrometer. Details of the apparatus, reagents and standards are given elsewhere[17].

Analytical procedure

A 100 ml water sample was placed in the reaction flask. 50 µl of 65% HNO_3 and 50 µl of an aqueous solution containing 1.6 ng (as tin) triethyltin bromide as an internal standard were added. The reactor was closed and secured with a stainless-steel clamp. The cold trap was cooled by liquid nitrogen to −196°C and the four-way valve adjusted to pass helium through the reactor. 2 ml of 8% (by weight) $NaBH_4$ solution were injected through the septum and the solution purged for about 5 min. Then the reactor was bypassed, the liquid nitrogen removed, the variable transformer for heating the cold trap was set at 32.4 V and the integrator was started. After about 3.5 min the temperature controller maintained a temperature of 180–190°C in the trap. Tin compounds elute within 4.5 min; during this time the next sample could be placed in the reactor.

Table 1 Reproducibility of the extraction of organotin species from freeze-dried and wet sediments (in % relative standard deviation; n = number of extractions).

Analyte	*Sediment 1 dry* ($n = 4$)	*Sediment 2 dry* ($n = 4$)	*Sediment 3 dry* ($n = 8$)	*Sediment 4 wet* ($n = 3$)
$MeSn^{3+}$	32	55	37	52
Me_2Sn^{2+}	50	—	19	—
$BuSn^{3+}$	21	11	25	16
Bu_2Sn^{2+}	24	5	8	16
Bu_3Sn^{+}	—	7	—	11

Sediment extraction

The extraction method was a modification of that described by Matthias *et al.*[7]. To 3 g of freeze-dried sediment in a round-bottom flask, 25, 50, 75 or 100 ml of methanol and 2% (by volume) of 30% HCl were added. A teflon-coated stirring bar was introduced and the mixture boiled under reflux for 30–40 min using a water bath. After cooling to room temperature, the mixture was transferred to two 30-ml polycarbonate centrifuge tubes and centrifuged for 20 min at 20,000 g. The supernatant was decanted. Solutions were kept in 30-ml polycarbonate bottles. Following the procedure of Cooney *et al.*[18], an aliquot of this extract was transferred to the hydride generator containing 100 ml of water (which had been tested to contain no tin compounds) and analyzed as described above. Each sediment sample was extracted and analyzed in duplicate. The reproducibility of the extraction step was evaluated by extracting multiple 3-g aliquots of three freeze-dried sediments and one wet sediment with 50 ml of methanol and 2 ml of HCl. Results are presented as relative standard deviations in Table 1. Variance for methyltin compounds is usually higher than for butyltin compounds, as peaks for those species often overlap with a large peak of inorganic tin.

Quantification

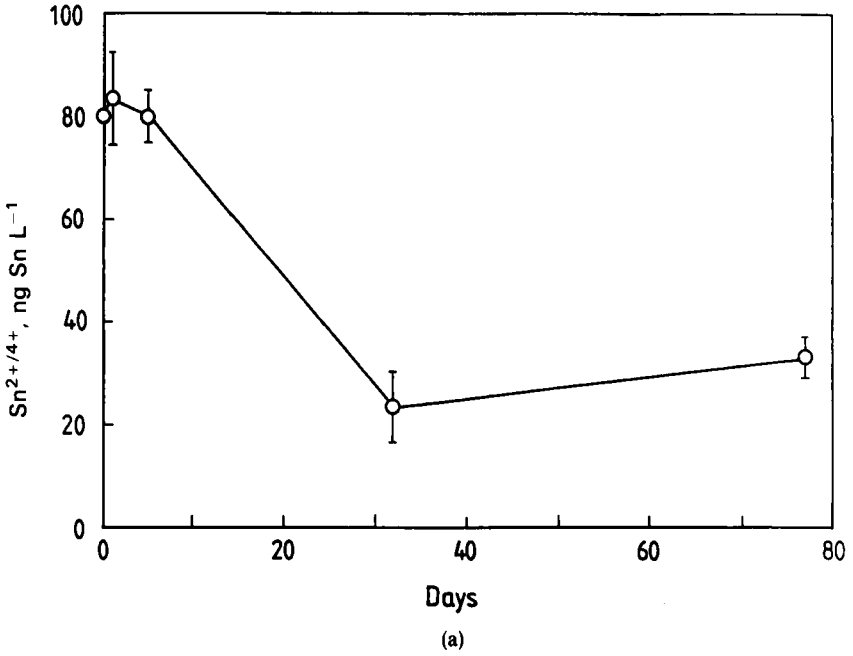
For water samples we used calibration curves based on peak areas which were determined daily. Calibration of Rhine water samples was made against standards added to Rhine water (whose content of tin compounds had been previously determined), thereby avoiding possible matrix effects. Quantification of sediment extracts was performed by standard addition, as the slopes of calibration curves for different extracts showed large variations. Quantification of inorganic tin proved to be difficult as most calibration curves for this species showed an extremely poor correlation. This would have resulted in a very high uncertainty of the analytical data; therefore no quantification of inorganic tin in sediment extracts was carried out.

RESULTS

Storage experiments

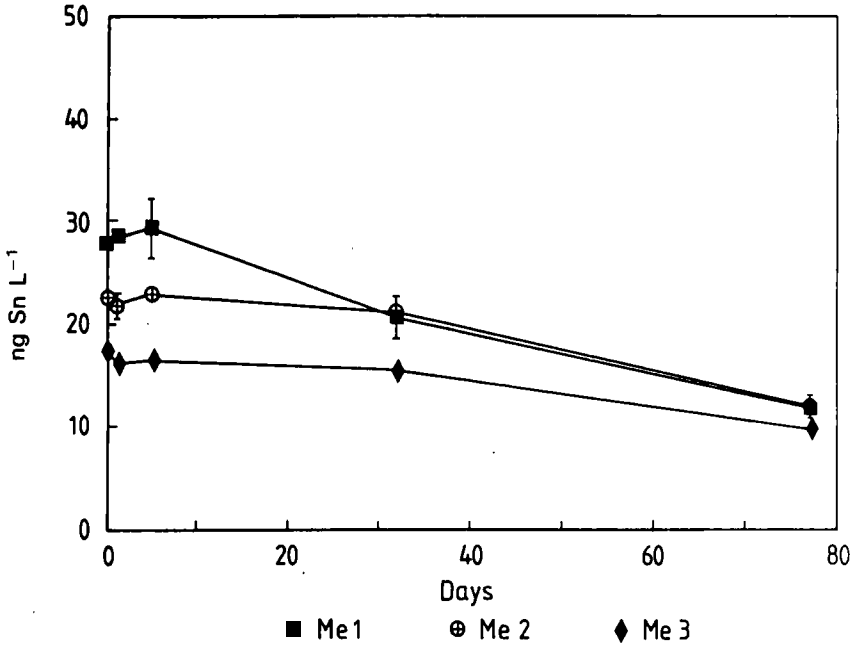
For storage, all samples, as well as standards, were kept in the dark to avoid breakdown of organotin compounds by UV irradiation.

Stability of water samples during storage. Adsorption of tributyltin on different materials has been reported. The material to which the least losses were observed is polycarbonate[14,15]. To test the stability of fresh water samples, Rhine water in polycarbonate bottles was spiked with a known amount of organotin compounds and inorganic tin. Samples were analyzed shortly after spiking and again after several days of storage. Samples were kept either in a refrigerator at a temperature of +10°C or in a freezer at −20°C. Changes in concentration were monitored over a period of 77 and 57 days, respectively. Results from the spiked samples stored at +10°C are presented in Figures 1a–c. Concentrations of inorganic tin and the methyltins are relatively stable within the first five days of storage. While the content of inorganic tin and monomethyltin in the sample decrease rapidly thereafter, concentrations of di- and tributyltin remain approximately constant for some 30 days. After this period, concentrations of di- and tributyltin also decline. Mono- and dibutyltin show a loss of about 30% after five days of storage and a further decline after prolonged storage.



(a)

Figure 1 Changes in the concentration of inorganic tin and organotin compounds in a river water sample stored at +10°C: (a) inorganic tin, (b) methyltin compounds, (c) butyltin compounds.



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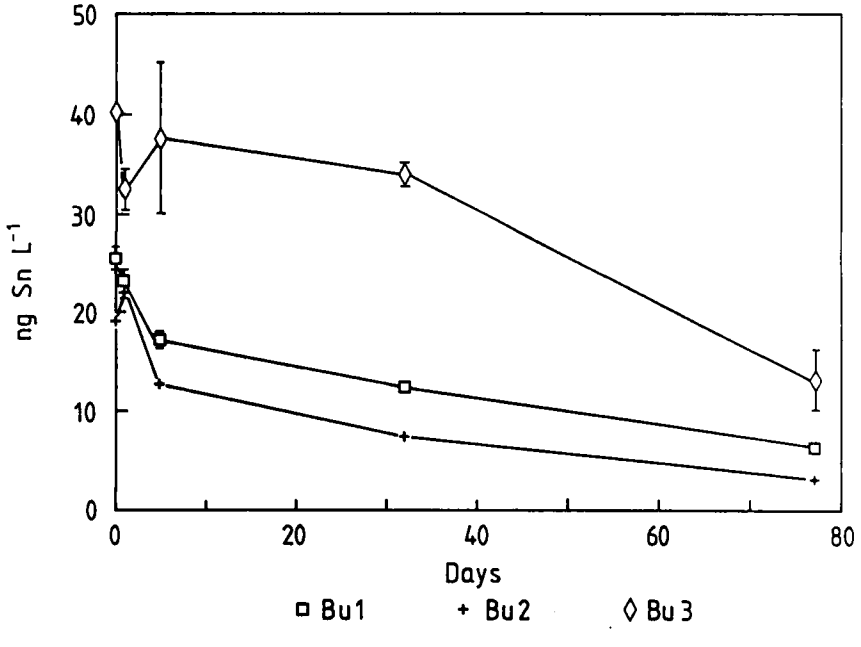


(c)

The behaviour of tributyltin in the first days of storage is uncertain due to large variability. A mean value for the first five days of storage would indicate a loss of about one third, on the same order of magnitude as in the work of Blair *et al.*[14], who found a loss of 25% from 30 μg/l tributyltin solution within 48 h of storage in a polycarbonate container. A larger decrease in concentration of tributyltin, however, is seen after more than a month of storage.

Freezing the spiked samples (Figures 2a–c) resulted in a better preservation of mono- and dibutyltin. Concentrations of methyltin compounds, in contrast, already decline after three days of storage. Tributyltin shows a 37% loss in its original concentration after eight days of storage, the same as observed with the sample stored at +10°C. After longer storage, however, losses of tributyltin are smaller in the frozen sample. The most dramatic change in the sample after freezing is seen with inorganic tin which drops about 60% after three days of storage.

The amounts of spike added, some tens of ng/l for the different species, are about one order of magnitude above those found in waters from the Rhine river, but are similar to those in more polluted samples, e.g. waste waters and harbour waters[17]. The relatively high spike concentrations were imperative because of the high analytical precision required for this type of investigation. Depending on the mechanism for the loss of the organotin species during storage (e.g. biological uptake, adsorption to a small number of specific sites, or to a large number of non-specific sites), the amount of tin species lost may increase with decreasing concentration. We have no concrete evidence for such behaviour. Neverthless, we caution that our conclusions

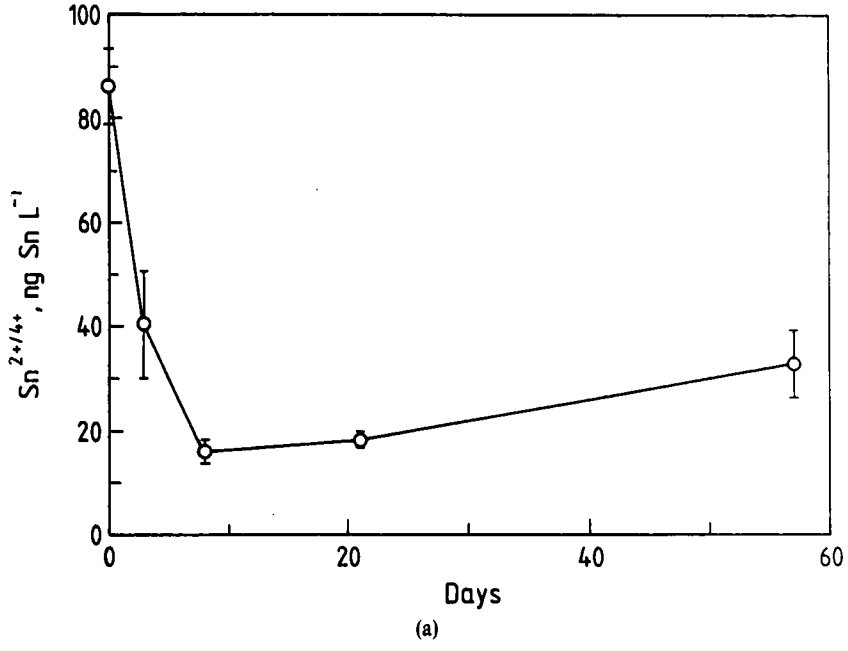
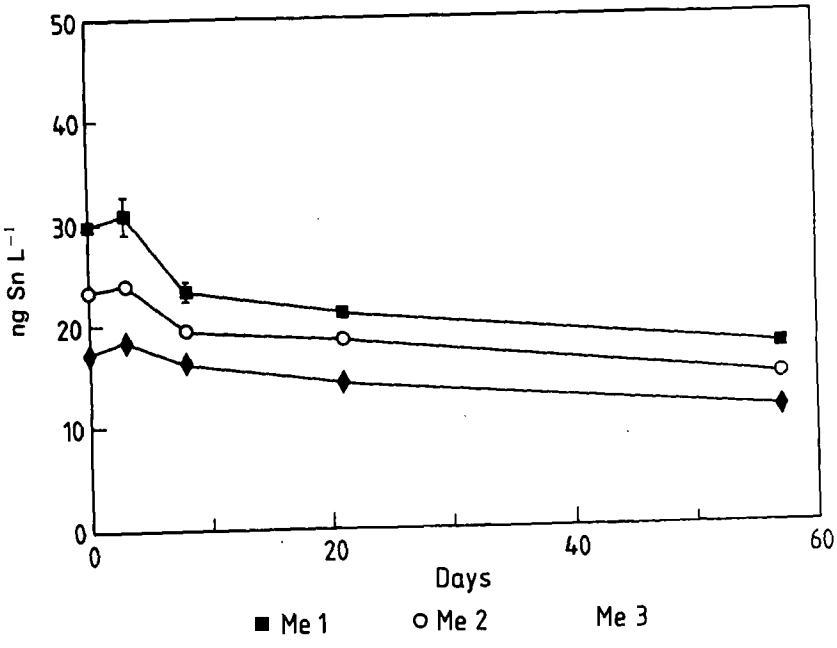


Figure 2 Changes in concentration of inorganic tin and organotin compounds in a river water sample stored at −20°C: (a) inorganic tin, (b) methyltin compounds, (c) butyltin compounds.



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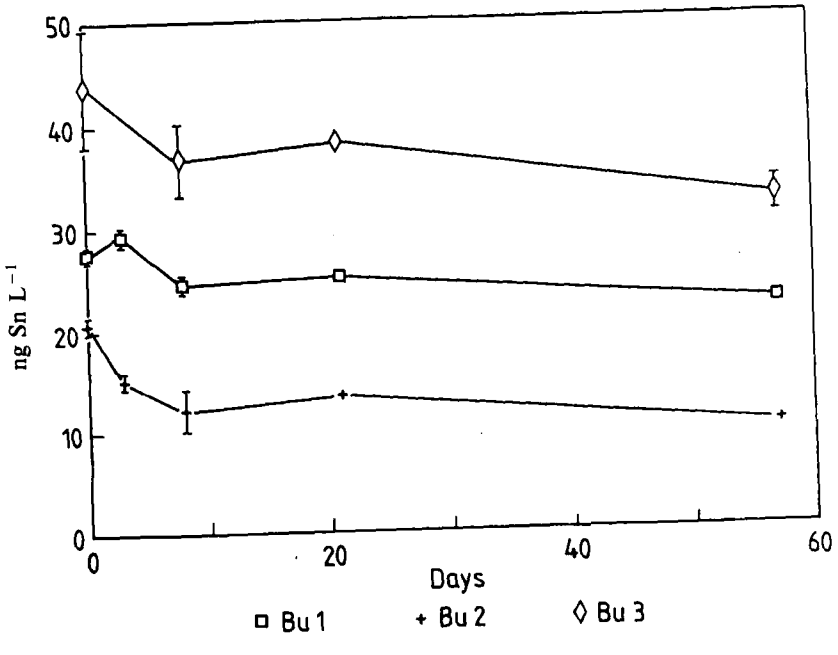


(c)

Table 2 Concentration of organotin compounds (ng Sn per g dry mass) in a sediment stored wet or freeze-dried at +10°C in the dark (duplicate analyses on extracts from two aliquots, means and standard deviations given).

Analyte	*Fresh*	3-*Months storage (freeze-dried)*	3-*Months storage (wet)*
$MeSn^{3+}$	2 ± 1	4 ± 1	4 ± 1
$BuSn^{3+}$	20 ± 2	17 ± 1	16 ± 1
Bu_2Sn^{3+}	17 ± 1	18 ± 2	24 ± 2
Bu_3Sn^{+}	22 ± 4	20 ± 6	25 ± 5

Table 3 Results of analysis of aliquots (ng Sn per g dry mass) of the same sediment as in Table 2, extracted freeze-dried or wet (duplicate analysis from duplicate extraction, means and standard deviations given).

Analyte	*Freeze-dried*	*Wet*
$MeSn^{3+}$	4 ± 1	6 ± 3
$BuSn^{3+}$	17 ± 2	9 ± 2
Bu_2Sn^{2+}	15 ± 2	12 ± 2
Bu_3Sn^{+}	23 ± 5	19 ± 2

are strictly valid only for the concentration levels investigated, and that storage effects should be examined by each investigator with the materials and samples actually used in his work.

Stability of sediment samples during storage. A sediment which had been analysed immediately after procurement was stored wet in the refrigerator at +4°C for three months and then re-analysed; an aliquot was freeze-dried before storage and also re-analysed after three months. Results are shown in Table 2. In the case of the freeze-dried sediment, statistical evaluation showed differences only for monobutyltin, where a decrease in concentration of 14% was seen. However, it has to be noted that this lies within the range of the relative standard deviation for the extraction step (10–20% for monobutyltin, Table 1). In the wet sediment, the concentration of monobutyltin decreased by 19%. Additionally, in this sediment an apparent rise in dibutyltin concentration of 40% was seen, for which no explanation could be found. Clearly, fewer changes in concentration take place in freeze-dried than in wet sediments over an extended storage period.

Freeze-drying of sediment samples. To evaluate the effects of freeze-drying separate from storage effects on organotin compounds in sediments, aliquots of a fresh sediment sample were extracted wet and freeze-dried. Results are shown in Table 3.

Table 4 Recovery of organotin compounds (ng Sn per g dry weight) extracted from spiked Main river sediment (duplicate analyses from duplicate extractions, means and standard deviations given).

Analyte	*Spiked concentration*	*Amount found*	*Recovery (%)*
$MeSn^{3+}$	64	29 ± 3	45
Me_2Sn^{2+}	46	39 ± 9	83
Me_3Sn^{+}	35	33 ± 8	95
$BuSn^{3+}$	66	36 ± 4	55
Bu_2Sn^{2+}	52	52 ± 5	101
Bu_3Sn^{+}	119	170 ± 21	142

No losses of tin species result from freeze-drying. Concentrations of butyltin compounds appear to be slightly higher in the freeze-dried sediment, although a statistically significant difference can only be confirmed for monobutyltin. Further experiments (see below) indicate that this may be the result of a higher extraction efficiency for freeze-dried sediments.

Extraction of sediments

Extraction efficiency. We first determined the recovery of several tin compounds by spiking a sediment with known amounts of organotins and re-extracting. For this experiment, a sediment from the river Main was chosen which had been analyzed before and found to have a low content of organotin compounds. To 3 g of the freeze-dried sediment, 50 μl of a solution of organotin compounds in methanol and 50 ml of clean methanol were added. The suspension was stirred overnight to allow equilibration and extracted the following day by adding 1 ml of hydrochloric acid and refluxing as usual. The experiment was carried out in duplicate. Results (mean values) are given in Table 4. Clearly, recovery varies considerably for different tin species: while tri-substituted compounds seem to be re-extracted quantitatively, only about 50% of the mono-substituted compounds are recovered. Furthermore, recovery seems to be slightly better for butyltin than for methyltin compounds. These findings indicate that recovery cannot correctly be determined for all organotin compounds by the use of a single compound as an internal standard.

The method of spiking and re-extracting a sediment, although commonly used, may not be reliable in determining extraction efficiency and, thus, the real content of tin compounds in a sample: we do not know whether the compounds added to a sediment are adsorbed in the same way as those adsorbed 'naturally', i.e. in an aquatic ecosystem over long periods of time. If adsorption modes differ, extraction efficiencies may differ as well. To evaluate this problem further, a method was sought to ascertain the true content of organotin compounds in a sediment. We used a procedure suggested by Hellmann[19] which has been applied to the extraction of some organic compounds from clay and sludge[20].

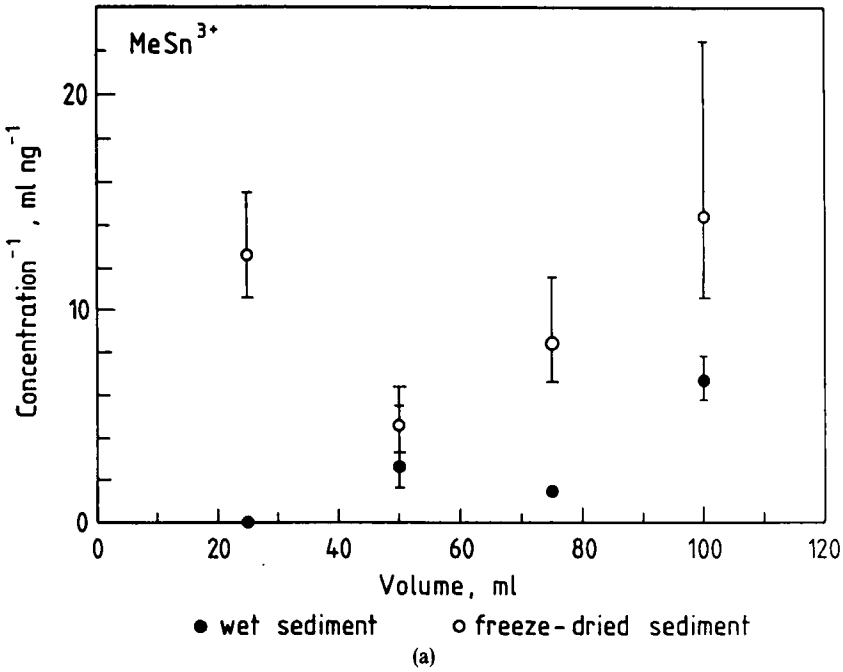
The following equation applies to an extraction:

$$c_M \cdot M = c_{Mi} \cdot Mi + c_L \cdot V_L \tag{1}$$

where c_M = true concentration of the extracted compound in the sediment; c_{Mi} = remaining concentration of the extracted compound in the sediment; c_L = concentration of the extracted compound in the solvent; M = weight of the sediment; Mi = weight of the sediment after extraction; V_L = volume of the extraction solvent.

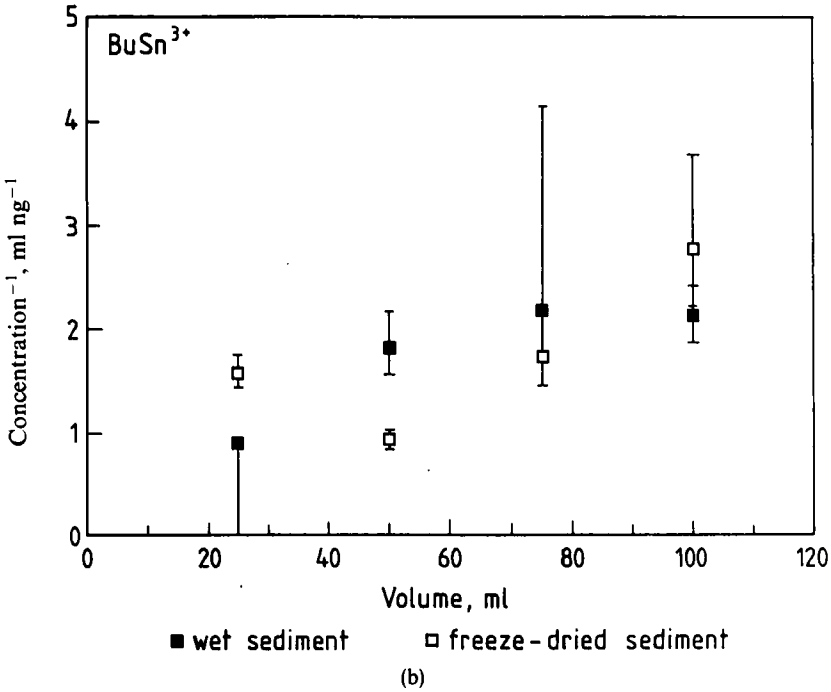
Assuming a linear adsorption isotherm,

$$c_{Mi} = C_L \cdot k \tag{2}$$



(a)

Figure 3 Results of extraction experiments on sediment from the river Rhine (wet and freeze-dried, respectively): (a) monomethyltin, (b) monobutyltin, (c) dibutyltin, (d) tributyltin.



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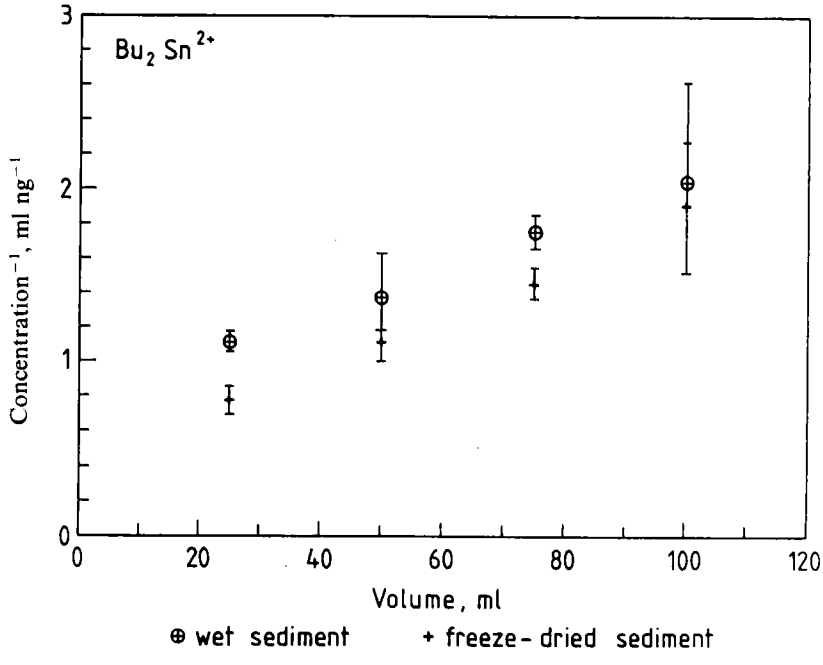

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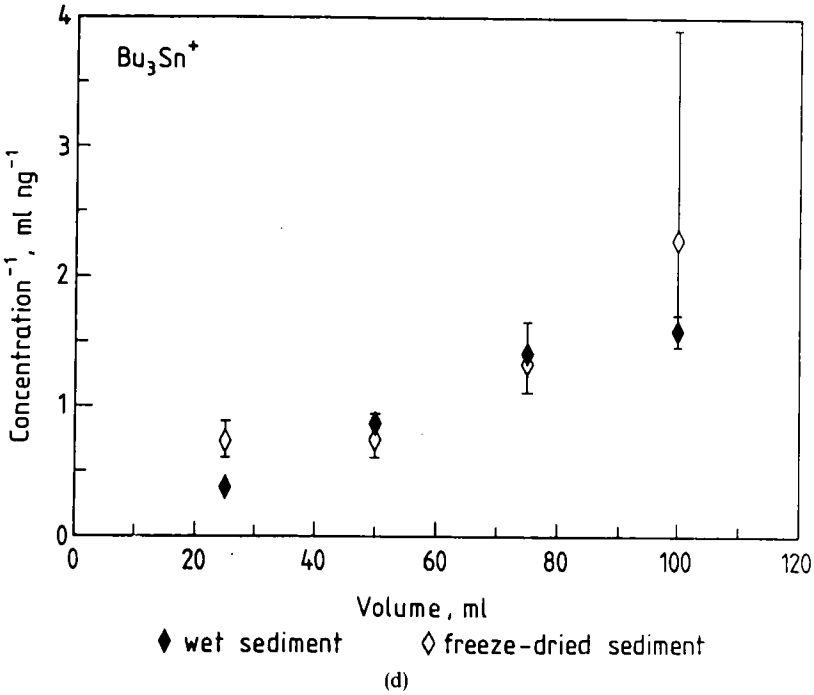

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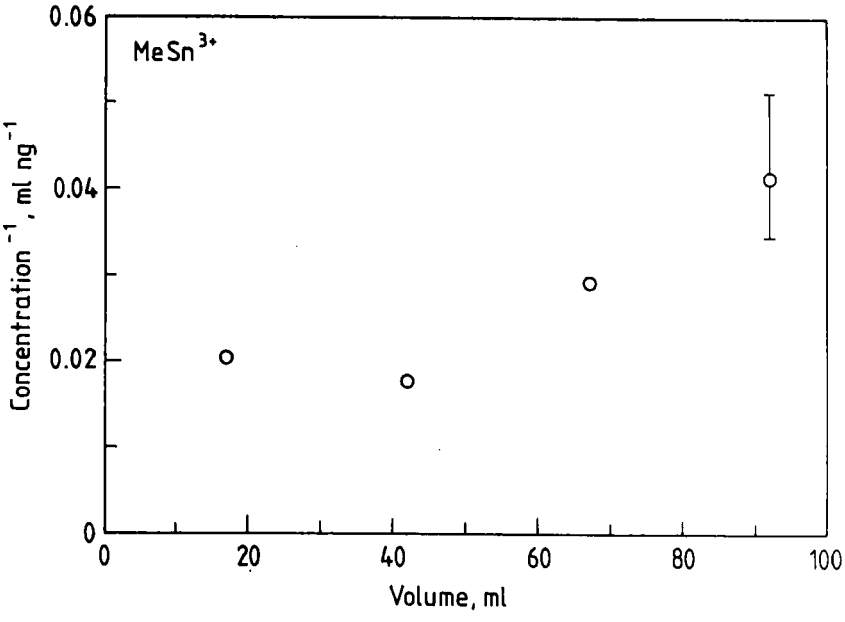
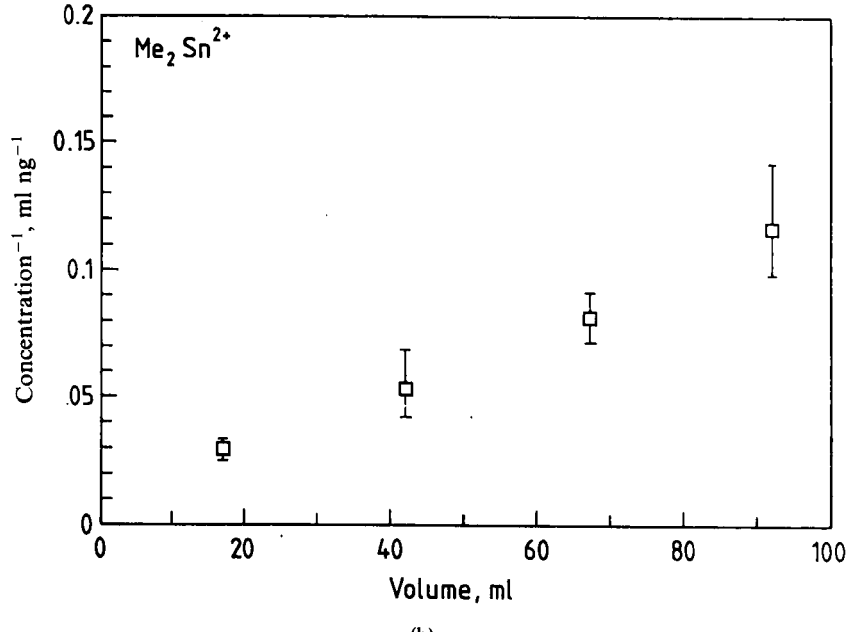


(a)

Figure 4 Results of extraction experiments on a lake sediment: (a) monothyltin, (b) dimethyltin, (c) monobutyltin, (d) dibutyltin, (e) tributyltin.



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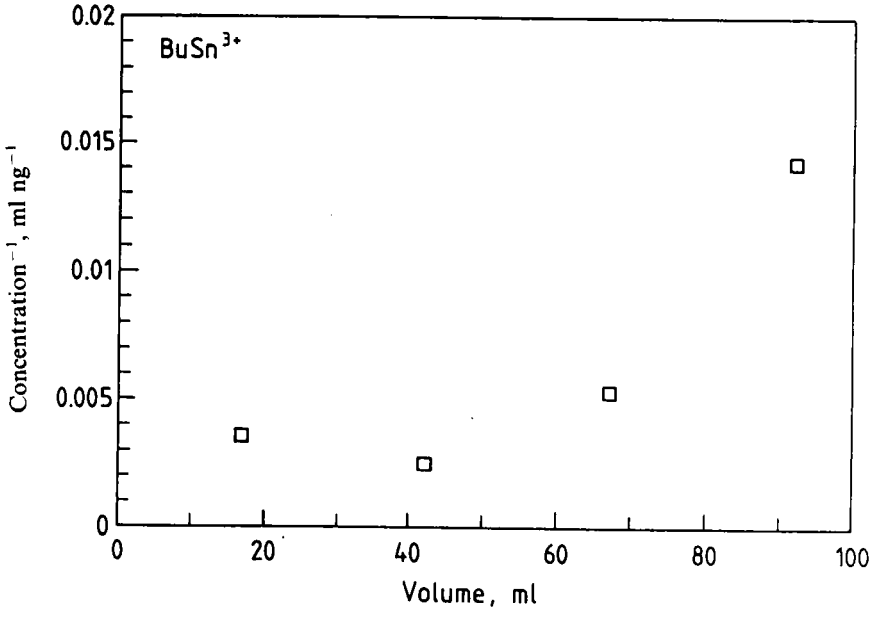

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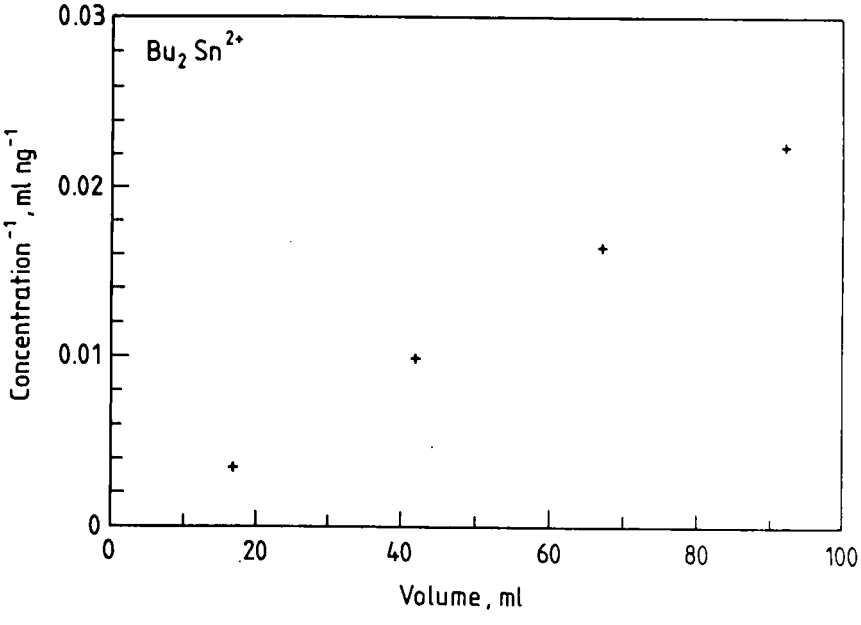

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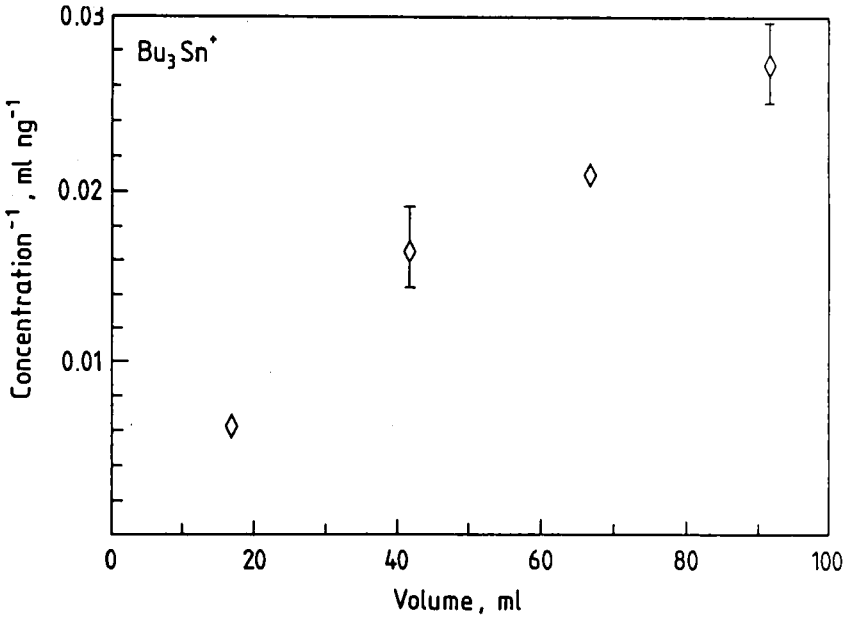

(e)

it follows that

$$c_L = \frac{c_M \cdot M}{V_L + k \cdot Mi} \tag{3}$$

With small concentrations of the extracted compound one can neglect the difference between M and Mi and this results in

$$\frac{1}{c_L} = \frac{V_L}{c_M \cdot M} + \frac{k}{c_M} \tag{4}$$

As V_L and M are known, the 'true' concentration of the analyte in the sediment can be calculated from the slope of the straight line obtained by plotting $1/c_L$ versus V_L. Obviously, a linear relationship is only obtained in this plot if the assumption of a linear adsorption isotherm is valid. If a sufficient number of different extraction solvent volumes are used in the experiment, any possible deviation from linearity becomes readily apparent.

We extracted aliquots of a sediment from the river Rhine with 25, 50, 75 and 100 ml methanol containing 2 vol.% of 30% hydrochloric acid. The sediment was extracted wet and freeze-dried. Results are given in Figure 3a–d. Results for the wet and the freeze-dried sediment agree fairly well: the assumption of a linear adsorption isotherm is valid only for dibutyltin and—with slight deviations—for tributyltin.

Mono-substituted compounds do not fit a linear equation. Experiments were also conducted with lake sediment from Lago Maggiore which had been prepared by the Community Bureau of Reference (BCR) of the Commission of the European Community for a round robin exercise on the determination of tributyltin (see below). Results are given in Figure 4a–e. Essentially, they confirm the finding that a linear correlation is found only for di- and tri-substituted tin compounds, but not for mono-substituted tin compounds.

The full reason for the above behaviour is not known. However, it should be noted that a methanolic extract of a sediment contains a large number of substances, many of them in far higher concentrations than the organotin compounds themselves, so that complexation of organotin compounds is possible. Mutually different behaviour of butyltin species with regard to adsorption on solids was also observed by other researchers[21]. The factors that affected adsorption of the different species to particulate matter were related to polarity (decreasing from monobutyl to tributyl tin) and hydrophobicity (increasing from monobutyl to tributyl tin). Variable partition coefficients were observed in these model experiments and in a study concerned with octanol/water partitioning of TBT[22]. Partition coefficients were found to depend on salinity and, at low salinities, on ionic strength. Since, in our experiments, we added variable amounts of extraction solvent to a fixed amount of sediment, the concentration of complexing agents and ionic solutes extracted from the sample into the extraction solvent varied with the amount of solvent added. The resulting differences in the ionic strength and complexing ability of the liquid phase may produce a shift in the equilibrium distribution of complexed species, which could result in different adsorption behaviour.

Table 5 gives the extraction efficiencies for the wet and freeze-dried Rhine sediments and the lake sediment. Data are presented only for those species (di- and trialkyl tins) where the linearity of the adsorption isotherms (Figures 3 and 4) validates the assumption that the true organotin species content can be obtained by using the variable-extractant-volume method. The values given in Table 5 were derived by calculating the true content of the compound from the slope of the straight line from the appropriate graph and comparing it with the amount extracted with 50 ml methanol/1 ml HCl. Data from the wet and freeze-dried sediment agree in that extraction efficiency is greater for tributyltin than for dibutyltin; extraction seems to

Table 5 Extraction efficiencies (%) for a river Rhine sediment (wet and freeze-dried) and a lake sediment (based on extraction of 3.0 g dry mass by 50 ml methanol/1 ml 30% HCl) (duplicate analyses from duplicate extractions, means and standard deviations given).

Analyte	*Rhine sediment (wet)*	*Rhine sediment (freeze-dried)*	*Lake sediment*
Me_2Sn^{2+}	—	—	112 ± 9
Bu_2Sn^{2+}	46 ± 8	68 ± 8	127 ± 5
Bu_3Sn^{+}	94 ± 18	142 ± 62	67 ± 12

be more efficient for the freeze-dried sediment. In contrast, data from the lake sediment show a better extraction for dibutyltin (and dimethyltin) than for tributyltin. It appears that extraction efficiency may vary significantly with different sediment materials. If this were confirmed by further investigation, the use of a single multi-species standard material would have limited value.

Results of the BCR round robin excercise on the determination of tributyltin in sediment are given in Table 6. The amount of TBT spike added to the sediment before its distribution to the participating laboratories was 3.3 μg/g; therefore a concentration of at least this level should be present in the sample when distributed. [This information was not given to the participants prior to submission of the results.] Using extraction with 50 ml methanol/HCl, we measured a TBT concentration of (2.6 ± 0.3) μg/g. Using the variable-volume method (Figure 4e), we found a concentration of (3.9 ± 0.4) μg/g, corresponding to an extraction efficiency of ($67 \pm 12\%$). This result is close to the expected value based on the amount of spike added and the fact that lake sediments contain, at most, a few tenths of μg/g of TBT.

Our result lies well above the mean concentration calculated from the data from all participating laboratories (2.8 ± 0.9 μg/g). This may be due to the fact that some laboratories did not correct their data for extraction efficiency at all and those who did mostly determined the extraction efficiency by spiking and re-extracting the sediment within 24 h. When we repeated this experiment, we also found a quantitative recovery of the added tributyltin, in strong contrast with the results from our variable-volume extraction experiments. This discrepancy is probably due to an increasingly strong binding of the organotins to the sediment over prolonged interaction of the spike with the particle surfaces. This is probably the result of the formation of kinetically inert surface complexes. These findings suggest that simple, short-term recovery experiments may not yield valid results with respect to the efficiency of organotin species extraction from sediments.

Table 6 Round robin exercise on determination of tributyltin in a lake sediment (duplicate analyses from duplicate extractions, means and standard deviations given).

Parameter	*Concentration (µg TBT acetate per g dry mass)*	*Recovery [%]*
Amount of spike added	3.3	
Amount found by extraction of 3 g dry mass with 50 ml methanol/1 ml HCl	2.6 ± 0.3	
Extraction efficiency		67 ± 12
Corrected concentration	3.9 ± 0.4	
Mean of all laboratories	2.8 ± 0.9	

CONCLUSIONS

Results of storage experiments with water samples show that with tin species at concentrations in the ng/l range, significant losses may occur within several days. This is true even when samples are kept frozen at −20°C. If samples are stored for a prolonged period prior to analysis, losses in concentration should be evaluated and considered when interpreting analytical data. Sediment samples are less subject to changes in concentration during storage than water samples. For storage times of a few months, however, freeze-drying appears to result in better preservation than the equivalent periods for wet sample storage. Evaluation of freeze-drying showed that no losses of organotin compounds occurred during the drying process.

Investigation of the efficiency of organotin compound extraction from sediment using methanol/HCl indicated the following. Firstly, recovery may vary considerably for different tin compounds. The use of only one compound as an internal standard is therefore not justified. Secondly, determination of extraction efficiency by spiking and re-extraction within a short time very likely leads to an overestimate of extraction efficiency. For di- and tri-substituted compounds, more accurate results can be achieved by extracting with different volumes of solvent and calculating the true content of a compound from the slope of the reciprocal concentration against the volume of solvent. Thirdly, extraction efficiency may vary with the type of sediment. The use of a single standard material to determine extraction efficiency may well lead to erroneous results for some of the sediments analysed.

References

1. E. A. Clark, R. M. Sterritt and J. N. Lester, *Environ. Sci. Technol.*, **22**, 600 (1988).
2. S. J. Blunden and A. Chapman, in P. J. Craig (ed.) *Organometallic Compounds in the Environment.* Longman, 1986, Ch. 3.
3. J. R. Ashby and P. J. Craig, in R. M. Harrison (ed.) *Pollution Causes, Effects and Control* 2nd ed., Royal Society of Chemistry, UK, 1990.
4. M. D. Müller, L. Reuberg and G. Rippen, *Chemosphere*, **18**, 2015 (1989).
5. M. O. Andreae and J. T. Byrd, *Anal. Chim. Acta*, **156**, 147 (1984).
6. Y. Hattori, A. Kobayashi, S. Takemoto, K. Takami, Y. Kuge, A. Sugimae and M. Nakamoto, *J. Chromatogr.*, **315**, 341 (1984).
7. C. L. Matthias, J. M. Bellama, G. J. Olson and F. E. Brinckman, *Environ. Sci. Technol.*, **20**, 609 (1986).
8. L. Randall, O. F. X. Donard and J. H. Weber, *Anal. Chim. Acta*, **184**, 197 (1984).
9. M. D. Müller, *Anal. Chem.*, **59**, 617 (1987).
10. S. Rapsomanikis and R. M. Harrison, *Appl. Organomet. Chem.* **2**, 151–157 (1988).
11. C. L. Matthias, J. M. Bellama, G. T. Olson and F. E. Brinckman, *Intern. J. Environ. Anal. Chem.*, **35**, 61 (1989).
12. M. O. Stallard, S. Y. Cola and C. A. Dooley, *Appl. Organomet. Chem.*, **3**, 469 (1989).
13. V. Desauziers, F. Leguille, R. Lavigne, M. Astruc and R. Pinel, *Appl. Organomet. Chem.*, **3**, 469 (1989).
14. W. R. Blair, G. J. Olson, F. E. Brinckman, R. C. Paule and D. A. Becker, *NBSIR* 86-3321, February 1986.
15. R. J. Carter, N. J. Turoczy and A. M. Bond, *Environ. Sci. Technol.*, **25**, 489 (1989).
16. K. Fent and M. D. Müller, *Environ. Sci. Technol.*, **25**, 489 (1991).
17. L. Schebek, M. O. Andreae and H. J. Tobschall, *Environ. Sci. Technol.*, **25**, 871–878 (1991).
18. J. J. Cooney, A. T. Kronick, S. J. Olson, W. R. Blair and F. E. Brinckman, *Chemosphere*, **17**, 1795 (1988).
19. H. Hellman, *Fresenius Z. Anal. Chem.*, **319**, 267 (1984).
20. J. Alberti, E. Plöger and A. Poppe, *Wasser und Boden*, 392 (1987).
21. L. Randall and J. H. Weber, *Sci. Tot. Environ.*, **57**, 191 (1986).
22. R. B. Laughlin, Jr., H. E. Guard and W. M. Coleman III, *Environ. Sci. Technol.*, **20**, 201 (1986).