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Influence of Humic Substances on Sorption and Methylation Processes of Inorganic- and Organo-tin Species

Jürgen Kuballa,* Madhukar V. M. Desai† and Rolf-Dieter Wilken
GKSS Research Centre, Institute of Chemistry, Max-Planck-Strasse, D-21502 Geesthacht, Germany

The influence of humic substances on sorption and methylation processes for inorganic- and organotin species is presented. Four sediment samples from different locations of the Rivers Elbe, Mulde and Spittelwasser, Germany, with different organotin and humic contents were selected to extract the humic and fulvic acids. The various fractions—the original sediment, the humic acid, the fulvic acid and the residual sediment—were analysed for their organotin content. The individual buyltin species show quite different distribution patterns. Monobutyltin is found mostly associated with humic acids. Dibutyltin shows a non-unique behaviour. At low total organotin content, dibutyltin is found bonded to humic and fulvic acids, whereas at high organotin content dibutyltin is distributed more with the residual sediment. Most of the tributyltin remains in the sediment unextracted; only small quantities of it are in the fulvic acid fraction. Tetrabutyltin is only in the humic acid fraction when it binds to humic matter; it mostly remains in the sediment. General observations indicate that ionic butyltin species bind to fulvic acids whereas the non-polar tetrabutyltin is not found in the fulvic acid fractions in any of the samples. The appearance of monomethyl- and dimethyl-tin species in the humic and fulvic acid fractions after the alkaline extraction was surprising. There is a correlation between the humic content of the sample and the formation of methyltin species. Evidence is provided by experiments that humic substances act as methylation agents.

Keywords: inorganic tin; organotin compounds; sediment; humic acid; fulvic acid; methylation; sorption

ABBREVIATIONS

OTC	organotin compounds
HA	humic acid
FA	fulvic acid
MBT, DBT, TBT, TTBT	mono-, di,- tri-, tetra-butyltin
MMT, DMT	mono-, di-methyltin
$NaBEt_4$	sodium tetraethylborate
GC–AAS	gas chromatograph coupled with atomic absorption spectrometer

INTRODUCTION

The River Elbe, Germany, is one of the most polluted rivers in Europe.[1-4] After the German reunification in 1989 the aim of many projects was to evaluate the current contamination of the river and to localize the anthropogenic sources. The IKSE (International Commission for Protection of the Elbe River) was established to coordinate the Elbe projects and to recommend measures for reducing the anthropogenic inputs and planning of new sewage treatment plants.

Organotin compounds (OTC) are contaminants of special concern in the River Elbe. The problematic nature of the use of the toxic tributyltin as an ingredient in many antifouling paints is well known.[5,6] The toxic effects of tributyltin on the entire aquatic life are well documented in the literature.[7-11] The Hamburg harbour area is a diffuse source of tributyltin and its degradation products, di- and mono-butyltin. Jantzen and Wilken first investigated the butyltin burden of different industrial and pleasureboat harbours.[6] Besides high tributyltin contents in the sediments, tetrabutyltin was found in all samples. The anthropogenic source for tetrabutyltin was localized later; it was a chemical plant in Bitterfeld. The highly contaminated run-off waters of this orga-

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* Author to whom correspondence should be addressed.
† Visiting scientist from Bhabha Atomic Research Centre, Bombay-40085, India.

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notin plant enter the Rivers Spittelwasser and Mulde, which enters the River Elbe. The Mulde and Spittelwasser are two of the world's rivers that are most highly polluted with butyltins.[4,10]

The possible sorption sites on sediment for butyltins are of various kinds.[12,13] The inorganic particles are coated with organic matter such as biofilm, humic substances and microorganisms. This paper focuses on the humic substances. Humic substances are ubiquitous in soil, sediment and water.[14,15] Their special role in the environment has been recognized. Humics are described in the literature as important substances for the complexation of tace elements.[16–18] Mobilization and subsequent transport of trace elements are influenced by humic matter. Humic materials also act as non-biological methylation agents for mercury and tin.[19,20]

This paper presents the influence of humic substances on sorption and methylation processes of inorganic- and organo-tin species. For this purpose four sediment samples were taken from low and highly contaminated sites of the Rivers Elbe, Mulde and Spittelwasser. Alkaline extraction was carried out to separate the humic and fulvic acids from the sediment. In all the fractions—original sample, humic and fulvic acid fractions, residual sediment—organotin contents were determined. The distribution of butyltins in the different fractions, as well as the formation of methyltin species during the extraction procedure, will be described.

EXPERIMENTAL

Sampling

For our investigations four sediment samples were freshly collected from the Rivers Elbe, Mulde (a tributary of the River Elbe) and Spittelwasser (a tributary of the River Mulde). The Elbe sediments were taken at Tangermünde (Elbe 1), and Magdeburg (Elbe 2); the Mulde sample was taken near Dessau and the Spittelwasser sample was collected at Jessnitz (2 km away from Bitterfeld). The sediments were taken with a VanVeen grab and stored in the cool (4 °C) and dark until sample preparation.

Isolation of humic acid (HA) and fulvic acid (FA) from sediments

The Elbe, Mulde and Spittelwasser sediments were taken for humic and fulvic acid extraction. About 20 g of the wet sediment sample (10 g dry weight) was shaken with 200 ml of sodium hydroxide solution (0.1 M) for 24 h. Subsequently the sample was centrifuged and the supernatant was collected. The residue was washed twice with 50 ml of NaOH (0.1 M). The combined alkaline solutions were acidified to pH 2 with hydrochloric acid (0.1 M). The precipitated humic acids were separated by centrifugation. The supernatant, which contained the fulvic acid, was stored at 4 °C in the dark.

The humic acid precipitate was dissolved in a minimum of alkali (0.1 M NaOH), filtered (0.45 μm) and made up to 50 ml with Millipore water. These prepared humic acid fractions were also stored at 4 °C in the dark. The humic and fulvic acids were taken out just before analysis.

The percentage of humic acid in the sample was determined by measuring the dry weight of an aliquot of the humic acid fraction.

Analysis of organotin compounds

Organotin analysis was carried out using the sodium tetraethylborate and gas chromatography–atomic absorption (GC–AA) technique.[4,10] Sodium tetraethylborate is an *in-situ* ethylation agent for organotin compounds. Methyl-, butyl-, octyl-, phenyl- and cyclohexyl-tin compounds can be derivatized and extracted in a single step. Hexane is used as an extractant.

Inorganic tin in sediment appears in different chemical forms, e.g. SnO_2, $Sn(O)(OH)_2$, $Sn^{2+/4+}Cl^-$, OH^-. Part of the total inorganic tin can also be determined by the sodium tetraethylborate method. We call this the 'mobile reactable tin', which is less strongly complexed tin (eg. $Sn^{2+/4+}Cl^-$, OH^-). SnO_2 cannot be determined by this method.

The following fractions of each of the sediments were analysed for their organotin content:

(a) the untreated original sample;
(b) the humic acid fraction;
(c) the fulvic acid fraction;
(d) the residual sediment after alkaline extraction.

Apparatus

The GC–AAS consists of a Perkin–Elmer (Überlingen, Germany) GC 8400 and a Perkin–Elmer AAS 3030. The chromatographic data were processed with a Perkin–Elmer Nelson 2600 software package. A column from ICT

Table 1. Butyltin concentrations and content of humic acid (HA) in sediment samples from the Rivers Elbe, Mulde and Spittelwasser (original sample)

Location	HA content (%)[a]	Butyltin concentration (μg Sn kg^{-1}, dry wt)[a] MBT	DBT	TBT	TTBT
Elbe 1	0.67 ± 0.6	18 ± 3	5 ± 1	5 ± 1	12 ± 3
Elbe 2	1.10 ± 0.11	7 ± 3	8 ± 2	4 ± 1	40 ± 5
Spittelwasser	1.52 ± 0.15	158 ± 20	1810 ± 110	150 ± 12	756 ± 48
Mulde	6.49 ± 0.15	3660 ± 180	1560 ± 90	1080 ± 80	12700 ± 800

[a] Mean ± standard deviation of two samples.

(Frankfurt, Germany) was used (DB 1701, length 30 m, i.d. 0.32 mm, 0.24 μm film thickness). The GC–AAS parameter are given by Jantzen and Wilken.[6]

RESULTS AND DISCUSSION

Two River Elbe sediments, one River Mulde and one Spittelwasser sediment were selected to investigate the influence and sorption properties of humic substances on the fate of organotin compounds in sediments. The various sediments are characterized by different organotin contents (Table 1) and different humic acid contents (0.67–6.49%). The Mulde and Spittelwasser samples are more contaminated with butyltin compounds than the Elbe samples. The high contamination was mainly caused by run-off waters of an organotin plant in Bitterfeld. The Spittelwasser sample was collected from a location about 2 km away from this plant.

Monobutyltin

The distribution of monobutyltin in the various fractions of the different samples is shown in Fig. 1. A clear trend can be observed. In all the samples most of the monobutyltin is found to be associated with HA (82–96%); only small amounts are with FA (1–5%) and residual sediment (4–13%). The distribution of MBT is lar-

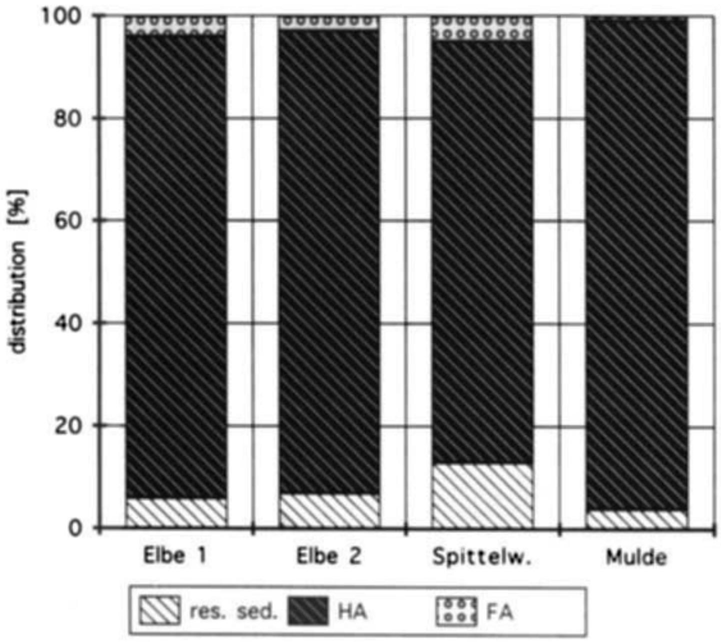

Figure 1 Distribution of monobutyltin species in various fractions (residual sediment, humic and fulvic acid fractions) after alkaline extraction.

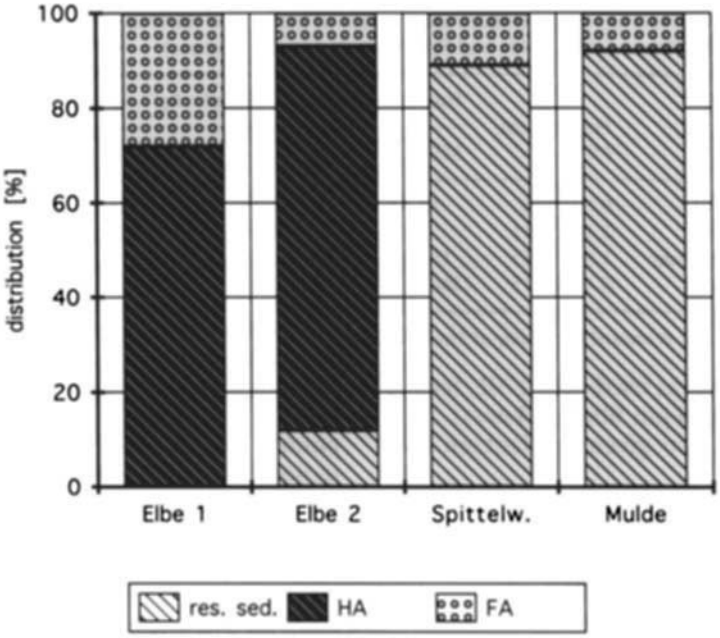

Figure 2 Distribution of dibutyltin species in various fractions (residual sediment, humic and fulvic acid fractions) after alkaline extraction.

gely independent of the contents of humic acid and organotin in the samples.

Dibutyltin

Quite different behaviour is seen in the case of dibutyltin. As shown in Fig. 2, the samples can be divided into two groups:

Group A Elbe-1 and Elbe-2 sediment:
low HA content; low organotin content
Group B Spittelwasser and Mulde sediment:
high HA content; high organotin content

Dibutyltin in group A sediments is mainly associated with humic acids (72–81%). The amount of DBT in the fulvic acid fraction is 7–28% and is generally higher than that observed for monobutyltin species, which is only 1–4%.

Group B sediments show the opposite behaviour. Most of the dibuyltin is found in the residual sediment. The DBT content in FA of group B is similar to the content in group A FA fraction (8–11%). It is interesting to observe that in Spittelwasser and Mulde sediments, although the humic content is higher, no DBT is found associated with the humic acid fraction.

This non-uniform behaviour cannot be explained adequately. Despite the fact that Elbe sediments contain less humic substances, most DBT is bound to HA, whereas Spittelwasser and Mulde sediments with high humic content bind DBT with FA and most DBT remains in the residual sediment. This may indicate that DBT is generally attached to sediments and, when it moves along the water course, it slowly interacts with humic substances and becomes bound to HA. There is also a possibility that DBT is first bound to FA and then is slowly transferred to HA.

Tributyltin

In three of the samples (Elbe 1, Elbe 2 and Spittelwasser), tributyltin is found mainly in the residual sediment (88–96%); no tributyltin was observed in the humic fraction (Fig. 3). The tributyltin content in the fulvic fraction is between 4 and 12%. Only in the Mulde sample was TBT also found associated with humic acids (28%). This effect is presumably caused by the very high HA content in this sample. The TBT content in the FA fraction (17%) of the Mulde sample is slightly higher than in samples Elbe 1 and 2 and Spittelwasser (12, 6 and 4% respectively).

Tributyltin preferentially stays bound with the redidual sediment. Whatever small amount is bound with organic matter is preferably bound to fulvic acids. Only when there is excess of humic acids available (e.g. in the Mulde), does it find its place with HA also.

Tetrabutyltin

Tetrabutyltin is the only butyltin species that is not found in the fulvic acid fraction in all the samples (Fig. 4). In samples Elbe 1 and 2 and Mulde, tetrabutyltin is associated with humic acids (15–28%). TTBT prefers to be with the residual sediment and it is associated only with HA whenever it is bound to organic matter. It does not seem to interact with the FA fraction at all. This behaviour is presumably caused by the non-polar character of tetrabutyltin.

Distribution of butyltin species between HA, FA and residual sediment

The distribution of butyltin species between humic substances (humic + fulvic acid) and particulates (residual sediment) indicates a clear trend. It is observed that as the number of butyl groups increases, their affinity to particulates increases (Table 2). For example, for monobutyltin species, only 4–13% was associated with particulates, whereas it was 0–92% for DBT, 55–96% for TBT and 85–100% for TTBT.

Exactly the reverse trend was observed for their affinity to humic substances, whereas as butyl groups increase, their association with humic substances decreases from 93% for MBT to 52% for DBT, 17% for TBT and 16% for TTBT. It can be seen that the greater the charge on the species, the more of it is associated with humic substances. As the charge decreases, butyltin species tend to be associated more with the residual sediment.

Table 3 compares the distribution of butyltin species between FA and HA fractions only, without reference to the butyltin content in the residual sediment. The ratios of butyltin concentrations in FA to those in HA fractions are given for the various samples.

The values in Table 3 reveal one important point. MBT, DBT and TBT, the ionic butyltin species have values of ratios in the range from 0.008 ± 0.004 to ≫1. The ratios for TTBT are all zero. That is the ionic species have a behavioral trend: the more ionic the species, the more is it found in the HA fraction, and the less ionic the species, the more of it is found in the FA fraction. The non-ionic non-polar tetrabutyltin is not found in FA at all.

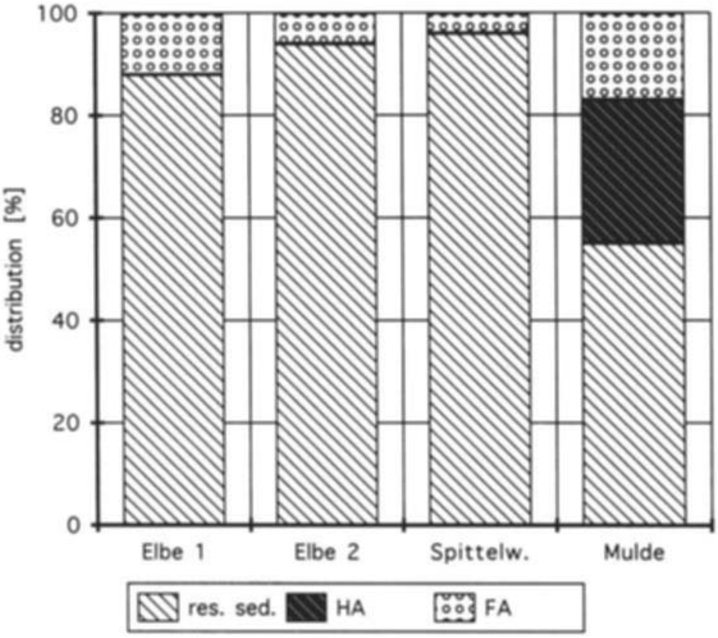

Figure 3 Distribution of tributyltin species in various fractions (residual sediment, humic and fulvic acid fractions) after alkaline extraction.

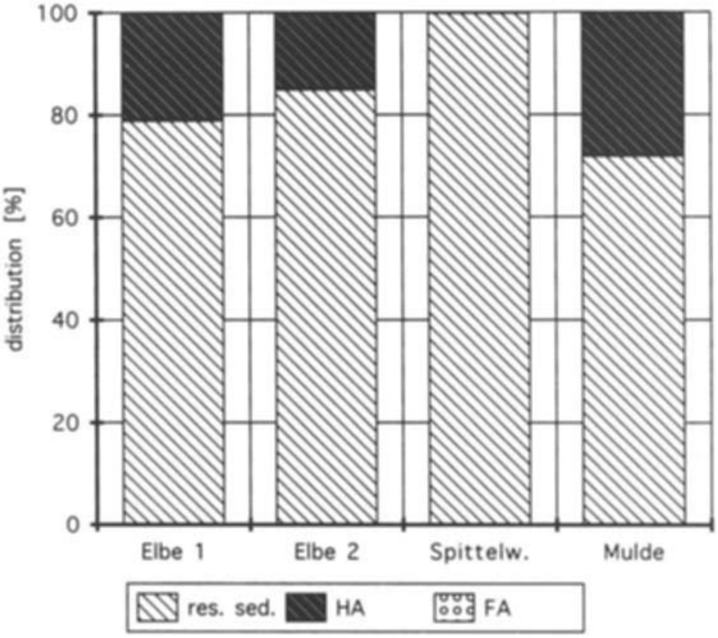

Figure 4 Distribution of tetrabutyltin species in various fractions (residual sediment, humic and fulvic acid fractions) after alkaline extraction.

Methylation of inorganic tin by humic substances

Table 4 shows the methyltin concentrations in the river sediment samples investigated. Methyltins were not detected in Elbe 1 and 2 and Swittelwasser sediments; only in the Mulde sample was monomethyltin (MMT) found in the original sample (256 ± 24 μg Sn kg^{-1}). Dimethyltin (DMT) species were not found in any of the original samples.

Monomethyltin was found in the HA fractions of all the samples. MMT was also found in most of the fulvic acid fractions; however, concentrations are lower compared with the HA fractions. Dimethyltin species were found only in FA fractions.

Figure 5 shows the dependence of the formation of monomethyltin during the extraction on the humic acid content of the sample. It can be observed that the higher the humic content, the more is monomethyltin found in the HA fraction. In the diagram the value for MMT of the HA fraction of the Mulde sample (714 ± 70 μg Sn kg^{-1}) is subtracted from the MMT concentration of the original Mulde sample (256 ± 24 μg Sn kg^{-1}) to show the effect of the extraction above (458 ± 46 μg Sn kg^{-1}) (see Table 4).

Table 2 Distribution of butyltin species between humic matter and particulates

	Butyltin species (%)			
Fraction	MBT	DBT	TBT	TTBT
Residual sediment	4–13	0–92	55–95	85–100
HA + FA	87–96	8–100	4–45	0–15

The monomethyl- and dimethyl-tin species appear after the alkaline extraction. This behaviour is an indication of methylation of inorganic tin by humic substances during the extraction procedure. In other words, humic substances may act as methylating agents here.

An open question is the chemical form of the inorganic tin which can be methylated. As indicated before, inorganic tin occurs in different chemical forms in the sediment. It can be said that SnO_2 occurs in an immobile form that cannot be methylated by any environmentally relevant agents. However, di- and tetra-valent tin species complexed with chloride or hydroxide ions are water-soluble and can genrally be methylated.

In the environment there are many more chemical forms of inorganic tin, and it is not within the scope of this paper to discuss them here. However, their role in methylation processes is still not known.

Table 3. Distribution of butyltin species between humic and fulvic acid fractions

	c_{FA}/c_{HA} (ng Sn g^{-1}/ng Sn g^{-1})[a]			
Sample	MBT	DBT	TBT	TTBT
Elbe 1	0.039 ± 0.005	0.364 ± 0.018	$\gg 1^b$	0^b
Elbe 2	0.037 ± 0.005	0.078 ± 0.004	$\gg 1^b$	0^b
Spittelwasser	0.067 ± 0.003	$\gg 1^b$	$\gg 1^b$	—[b]
Mulde	0.008 ± 0.004	$\gg 1^b$	0.618 ± 0.032	0^b

[a] Mean ± standard deviation of two samples.
[b] Concentrations of < 1 ng Sn g^{-1} were set to zero.

One more observation can be made. In samples containing mobile inorganic tin up to about 14 ± 5 µg Sn kg^{-1} (dry wt), there is no MMT in the residual sediment (Elbe 1 and 2). However, those with more than 219 ± 50 µg Sn kg^{-1} (dry wt) show the presence of MMT in the residual sediment (Spittelwasser and Mulde). But MMT in residual sediment cannot be correlated with MMT in the FA and HA fractions. Most probably, the MMT observed in residual sediment is essentially the MMT that was partially removed from the sediment during the extraction. Perhaps the MMT remaining in the residual sediment may be that associated with the humic fraction which is immobile. This may also indicate that inorganic tin is first methylated by the humic materials and then extracted. But for dimethyltin no such comments can be made. In all probability small amounts of

Table 4. Methyltin, mixed butylmethyltin and 'mobile inorganic tin' concentrations in the untreated original sample, in the humic and fulvic acid fractions and in the residual sediment

	Tin species (µg Sn kg^{-1}, dw)[a]			
Sample and fraction	MMT	DMT	$Me_xBu_y^{4-x-y}$	Mobile inorganic tin
Elbe 1				
Original sample	< 1	< 1	< 1	9 ± 5
Residual sediment	< 1	< 1	< 1	n.a.
HA fraction	2 ± 1	< 1	< 1	n.a.
FA fraction	< 1	< 1	< 1	n.a.
Elbe 2				
Original sample	< 1	< 1	< 1	14 ± 5
Residual sediment	< 1	< 1	< 1	n.a.
HA fraction	13 ± 2	< 1	< 1	n.a.
FA fraction	1 ± 1	1 ± 1	< 1	n.a.
Spittelwasser				
Original sample	< 1	< 1	< 1	219 ± 50
Residual sediment	44 ± 4	< 1	< 1	n.a.
HA fraction	62 ± 5	< 1	< 1	n.a.
FA fraction	40 ± 4	11 ± 1	< 1	n.a.
Mulde				
Original sample	256 ± 24	< 1	< 1	2540 ± 350
Residual sediment	28 ± 3	< 1	< 1	n.a.
HA fraction	714 ± 70	< 1	< 1	n.a.
FA fraction	3 ± 1	10 ± 1	< 1	n.a.

[a] Mean ± standard deviation of two samples.
[b] n.a., not analysed.

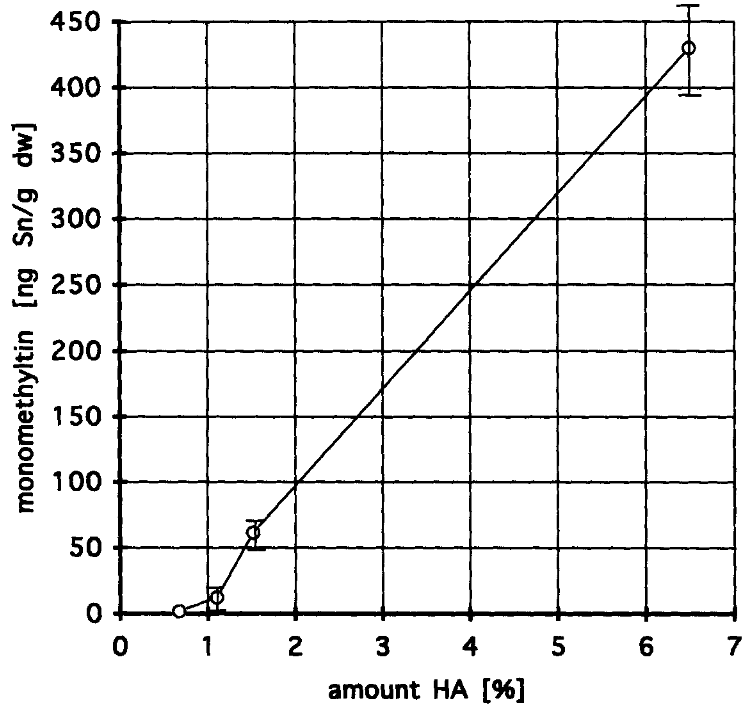

Figure 5 Methylation of inorganic tin by humic acids during alkaline digestion. The concentration of monomethyltin on the ordinate is given by $c_{\mathrm{MMT}} = c_{\mathrm{HA}} - c_{\mathrm{orig.\,sample}}$ (ng Sg g^{-1}).

dimethyltin are formed during methylation and presumably they are attached to the fulvic acid fraction.

Sodium tetraethylborate partially ethylates the inorganic tin in a sample. This part is presumably comparable with the amount of inorganic tin that is freely available and can be methylated under environmental conditions. Table 4 summarizes the 'mobile inorganic tin' values for the sediment samples investigated. In all cases it can be observed that the amount of methyltin species is equal to or lower than the values for inorganic tin. A correlation between the amount of mobile inorganic tin and the methyltin content in the humic fractions cannot be made; however it seems that high amounts of inorganic tin lead to enhanced appearance of methyltin species in the samples.

Mixed butylmethyltin species were not found in any of the sample fractions (Table 4). The environmental pathways and the circumstances for their formation are not described in detail in the literature. Jantzen[21] found butylmethyltin species in harbour sediments only in summer, indicating that methylation of butyltin species is presumably enhanced by microbial activity of the sediment. Butyltin compounds are presumably too strongly bonded to organic matter or particles to be methylated by the humic substances.

It is significant to note that butyltin species and humic substances are present in all the samples and that they interact or associate with each other. It is also interesting that methyltin species are produced by the humic substances. These factors and the absence of mixed butylmethyltin species indicate that butyltins are not methylated. This leads us to the conclusion that the human substances methylate only the mobile inorganic tin species.

Humic substances are described as possible abiotic methylating agents for mercury and tin in the environment. Shugui *et al.*[19] observed methylation of inorganic tin by humic substances isolated from harbour sediments. In laboratory experiments it has been shown that the degree of methylation of inorganic tin is affected by pH and salinity. Both humic acids and fulvic acids are able to methylate inorganic tin. However, only monomethyltin species have been detected.

The abiotic methylation of inorganic tin by humic substances can be confirmed by our investigations. It is worth noting here that we detected dimethyltin species associated with the fulvic acid fraction.

Shugui *et al.*[19] observed higher methylation activity by fulvic acids. Nagase *et al.*[22] found that lower-molecular-weight compounds, such as fulvic acids, have a higher methylation activity for inorganic mercury. Our results indicate higher methylation activity of the FA by formation of dimethyltin species, which are only observed in the FA fraction. The pH effect may also be responsible for the higher MMT concentration in the HA fraction. The influence of the amount of inorganic tin has not been investigated by Shugui *et al.*[19]

However, the role of humic acids in non-biomethylation pathways of inorganic tin and organotin compounds has to be discussed critically. It has to be considered for further experiments whether MMT and DMT compounds can be formed during sample preparation, in particular when alkaline extractions are performed. The mechanism of methylation and the compounds responsible for methylation are still not known.

The importance of the presence of methyltin compounds and of the abiotic methylation of inorganic tin species by humic substances in the environment needs careful consideration with reference to the possibility of transmethylation reactions of methyltin compounds with inorganic mercury. Methylmercury is one of the most toxic compounds in the environment and is known to be formed.[23,24]

CONCLUSIONS

In general, the increase in the number of butyl groups seems to decrease the affinity of butyltin species towards humic substances, the association of these being in the order:

MBT (87–96%) < DBT 8–100%)

< TBT (4–45%)

< TTBT (0–15%)

The ionic butyltins were found both in the humic and in the fulvic acid fractions, whereas tetrabutyltin was associatiated only with humic acids whenever it was bound to organic matter.

There is evidence of methylation of inorganic tin by humics during the alkaline extaction procedure. Humic and fulvic substances act as non-biological methylation agents for inorganic tin. The amount of monomethyltin in the HA fraction correlates with the humic acid content in the sample. Only the fulvic acids form dimethyltin species as well as monomethyltin; however, the concentrations of the methyltin species in the fulvic acid fraction are lower than in the humic acid fraction.

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