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Particle size distribution of organometal(loid) compounds in freshwater sediments

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The aim of this study was to determine to what extent particle size determines the occurrence of organometal(loid) compounds of the elements As, Sb, Sn and Te in freshwater sediments. In addition, the anthropogenic impact upon the distribution through differing usage of freshwater habitats was examined *vis-à-vis* flowing water, fish farms and a maturation pond for the bio-treatment of wastewater. All habitats sampled were located in the basin of the river Ruhr, Germany. In addition to the detection of high concentrations of total metal(loid) content of As, Sb, Sn and Te in the maturation pond sediments, this habitat also possessed the highest concentration of organometal(loid) species. Interestingly, the concentration of monomethylated metal(loid)s was up to 100-fold higher than those of higher methylated species of the same element. A maximum of 28 $\mu g\ kg^{-1}$ MMAs, 18 $\mu g\ kg^{-1}$ MMSb and 8 $\mu g\ kg^{-1}$ MMSn per dry weight was detected. A similar tendency was noted for all other freshwater habitats tested. In contrast to methylated arsenic (arsenic containing pesticides are banned in Germany) and antimony species, there is no doubt that the alkyltin species detected, e.g. MBSn and DBSn, are of anthropogenic origin since biogenesis of these species does not occur. Alkyltins are, however, known to enter the environment in a continuous and diffuse manner via discharge to sewage and air. In samples from the maturation pond concentrations of up to 86 and 11 $\mu g\ kg^{-1}$ per dry weight were detected for MBSn and DBSn, respectively. The detection of methylated arsenic and antimony species indicates that biotransformation of these elements is occurring in freshwater habitats. Irrespective of the usage and (anthropogenic) demands on the freshwater habitats tested, the highest concentration of organometal(loid) species was always detected in the sediment fractions that contained the highest concentration of humic substances and comprised up to 40% clays and silt particles (<63 µm). Owing to their high surface area to volume ratios these particles possess a high binding capacity for metal(loid) ions and are attractive microhabitats for microorganisms. The resulting microcosmos therefore has a high potential for the biomethylation of metal(loid)s. At this point in time it is not fully clear whether the high concentrations of organometal(loid) species detected in the clay/silt fraction are produced *in situ* by microbial biotransformation of bound metal(loid) ions or whether, as is the case for inorganic ions, the organometal(loid) species are translocated to this fraction and bound. Regardless of the mechanism, the accumulation of organometal(loid) species in clay/silt fraction means that these species are held in contact with the interstitial water and are therefore highly bioavailable, with potentially toxic consequences for aquatic organisms. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: methylated species; particle size distribution; freshwater sediments; arsenic; antimony; tin; tellurium; biomethylation; organometal(loid); alkyltin species

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INTRODUCTION

Since the middle of the 1960s sediments and solids of water bodies have been studied with respect to their heavy metal burden, and in particular with a view to identifying the contaminant source. The top sediment layers of freshwater habitats are particularly useful in this respect as they provide significant information as to the history and development of the environmental pollution of the watercourse.[1]

Elevated metal(loid) concentrations in a watercourse can have various causes. Heavy metals and metalloids are not exclusively delivered from the catchment area by weathering of geogenic sources. Surface flooding of anthropogenically influenced sediments, in particular agricultural lands, also contributes to the contamination of water bodies. Over and above this, metal-emissions can arise from the metal-processing industry and from various burning processes via wet and dry deposition carried to water bodies directly, or indirectly by erosion of sediments. Direct discharge occurs mainly through leaching from waste sites and effluents.[2]

Following introduction to the water body, some pollutants bind to the suspended particulate matter, which possesses a high adsorption potential, and are subsequently deposited via sedimentation. For the ecology of a water body this process represents a decontamination of the water column and simultaneously the contamination of the sediments.

The ecosystems of the catchment area of the river Ruhr have been subjected to organic and inorganic pollutants for several centuries. Studies of sediments with respect to the mobility and bioavailability of metal(loid)s and their resulting entry and movement up the food chain indicate that these apparently immobilized metal(loid)s are subjected to biogeochemical transformations within the sediments.[3–9] In addition to redox processes, the physico-chemical properties of the metal(loid)s are subject to change by methylation. The addition of a methyl group sometimes results in increased mobility and toxicity. A particular danger with respect to organometal(loid) compounds is their ampiphilic nature, which increases their bioavailability over and above that of the respective inorganic species, thus resulting in increased accumulation in the food chain. Mok und Wai[9] reported that methylation of metal(loid)s promotes their movement from sediments to the water body.

With respect to the biomagnification of organometal(loid) species, organotin species are more significant in ecotoxicological terms. As a result of their wide and varied anthropogenic usage, organotin compounds are found in terrestrial, limnic and marine environments. Tri-organotin compounds (R_3Sn^+, $R =$ alkyl) are particularly toxic,[10–12] e.g. trimethyltin is a potent insecticide and triethyltin has a high mammalian toxicity. Bacteria, yeasts and molluscs are highly sensitive to tributlytin, and triphenyltin is highly phytotoxic and is often used as a fungicide. Mono- and diorganotin compounds, in comparison, elicit lower toxicity and the toxicity is strongly dependent upon the nature of the alkyl group, e.g. methyl, ethyl, butyl, etc.

In this work, the association and distribution of organometallic compounds of arsenic, antimony, tellurium and tin with sediment particles in fresh water was investigated. Sediments from the Ruhr catchment area subjected to various usages and pollutant burdens were studied. The obtained information should enable an improved understanding of the occurrence and biogeochemical cycling of organometal(loid)s in sediments.

MATERIALS AND METHODS

Chemicals

All chemicals, unless otherwise stated, were purchased from Fluka (Buchs, St Gallen, CH), Gerbu (Gaiberg), Merck (Darmstadt) or Sigma (Deisenhofen), and were of PA quality or higher. Seralpur water was obtained from a Seralpur filtration $<0.18\ \mu\Omega$ (Seral pro 90 CN, Elga-Seral, Ransbach-Baumbach).

Sampling and sample treatments

Sampling was performed using a Russian peat borer (ARI, USA) or an Ekman-sampler depending on the water depth. Samples were sieved using a stainless steel sieve (particle size <2 mm) and were stored at −80 °C until analysis. All results are based on the dry weight. The dry weight was determined following DIN EN 12880.[13]

Total content determination

Total metal analysis (e.g. $As_{tot.}$ or $Sb_{tot.}$) of trace elements was performed by microwave digestion using reverse aqua-regia. As hydrofluoric acid was not used for the digestion it should be noted that a certain small proportion of total metal(loid)s will remain associated with the undigested silicates. Since these will not be bio-available under normal circumstances they do not need to be further considered with respect to methylation.

Aliquots (0.5 g) of sediment were weighed into PTFE reaction vessels. Nitric acid, 65% (9 ml) and hydrochloric acid, 37% (3 ml) were added. The digestion broadly followed that specified by DIN EN 13346.[14]

Following a 10 min equilibration period, the reaction vessels were placed in the microwave (Mars5, CEM, Germany) and the samples digested according to the following program: 10 min ramp to 80 °C; 5 min hold; 10 min ramp to 130 °C; 5 min hold; 10 min ramp to 180 °C; 20 min hold. The reaction pressure of the digestion vessels was not allowed to exceed 25 bar.

The extracts were transferred to a glass round-bottomed flask, and diluted to a final volume of 250 ml with Seralpur water, to which 20 μg each of Y, Rh, and Ho were added as the internal standard. Samples were filtered using 0.45 μm PTFE filters prior to ICP-MS analysis. Samples were introduced to the ICP-MS (Agilent 7500 a) via an auto sampler (AsX-510, Cetac). The ICP-MS was operated at 1 W Rf-power, with argon flows of 1.2 l min^{-1} (plasma gas), 0.86 l min^{-1}

(carrier gas) and 0.34 l min^{-1} (auxiliary gas). Solutions were delivered at 0.8 ml min^{-1} to a micro flow nebuliser and routed through a double-pass Scott-type spray chamber maintained at 2 °C. The following signals were monitored: As 75, Sb 121, Sn 118, Te 126, Y 89, Rh 103 and Ho 165. To control the interference of Cl on the determination of As, m/z 77 was additionally monitored. Quantitation was performed by external calibration and validated using PACS-2, marine sediment reference material, NRC-CNRC.

Particle size determination

To establish the distribution of metal(loid)s and organometal(loid)s within a sediment, samples were sieved according to DIN 4220,[15] i.e. wet samples (equivalent to a sample dry weight of 200 g) were filtered through decreasing sized sieves (2000, 630, 180, 63 and 20 µm) using a mechanical shaker bed (Vibrotronic Typ VE 1, Retsch). Water from the water body from which the sediment sample was taken was used as eluent. To monitor the artifactual effects arising as a result of sample preparation, and in particular the effect of particle size upon hydride generation efficiency, samples were additionally frozen and ground to a uniform particle size prior to derivatisation.

Hydride generation technique

Detection of methylated metalloid species was performed by HG-PT-GC/ICP-MS as described by Feldmann.[16] Quantification was performed by interelement calibration and validated by measuring mono-, di-, trimethylarsenic and trimethylantimony as well as mono-, di-, trimethyltin, monobuthyl and dibuthyltin standards. Non-volatile methylmetalloid species were volatilised by derivatisation according to the pH-gradient hydride generation method of Diaz-Bone *et al.*,[17] additionally described by Duester *et al.*[18]

RESULTS AND DISCUSSION

Influence of particle size on hydride generation efficiency

No statistically significant difference in hydride generation efficiency was noted for sieved, sieved and milled or untreated samples (Fig. 1). Despite this, the reproducibility of derivatisation was higher for samples prepared by sieving with subsequent cryomilling of the sample. Consequently this method was applied to prepare all samples.

Screening

Fifteen samples from still water bodies and 12 samples from flowing waters were screened for organoarsenic, -antimony, -tin and -tellurium species. Water bodies tested included flowing water, fish farms, maturation pond for the bio treatment of wastewater to enable an ecological risk assessment and identify potential links between on-site load and the organometal(loid) profile.

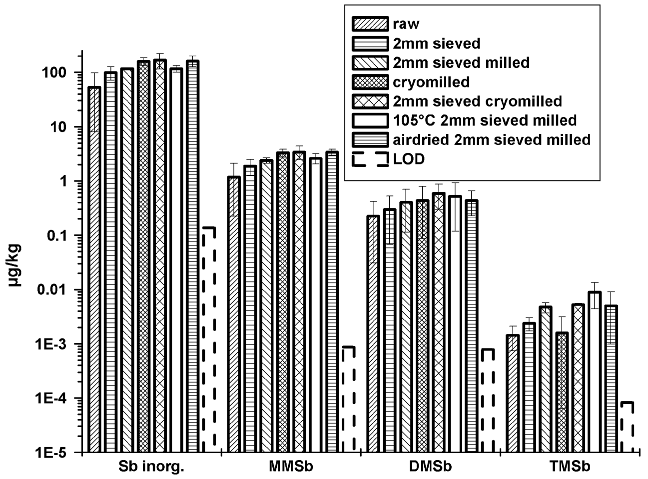

Figure 1. Influence of the preparation of a soil sample on extraction efficiency (concentrations per dry weight).

Table 1. Concentration range of methylated and butylated species in sediments of flowing water bodies and standing water bodies

	Concentration range of organometal(loid) species in sediments (µg kg^{-1} dry weight)		
Species	Standing water (15 samples)	Flowing water (12 samples)	LOD (µg kg^{-1})
MMAs	0.6–28	0.1–8	0.1
DMAs	0.02–3	0.01–2	0.01
TMAs	<LOD–0.6	<LOD–0.4	0.02
MMSb	0.8–11	0.2–18	0.01
DMSb	0.02–6	0.04–8	0.01
TMSb	<LOD–0.3	<LOD–0.2	0.001
MMSn	0.2–8	<LOD–2	0.1
DMSn	<LOD–5	<LOD	0.1
TMSn	<LOD–0.2	<LOD	0.01
MBSn	<LOD–26	<LOD–2	0.4
DBSn	<LOD–13	<LOD	0.2
DMTe	0.02–0.7	0.02–0.2	0.001

Monomethylarsenic (MMAs) was the most prevalent species originating from methylation detected in still water sediment (up to 28 µg kg^{-1} per dry weight, Table 1). This compares with 10-fold lower concentrations of the species in flowing sediments. Similar observations were made for monoalkylated tin species with up to 8 µg kg^{-1} monomethyltin (MMSn) and 26 µg kg^{-1} monobutyltin (MBSn) being detected in still water sediments, whilst no tin species could be detected in sediments from flowing water bodies. The highest MMSn and MBSn concentrations were detected in sediment samples taken from a maturation pond of a sewage treatment plant, for which the source of these species is most likely domestic wastewater.

As still waters are less dynamic and therefore sedimentation of fine particulate matter is higher compared with flowing waters, it was anticipated that organometal(loid) species would be present in higher concentrations in such sediments. This postulate could not be conclusively demonstrated. For methylated and alkyltin species as well as for MMAs, higher concentrations were detected in sediments taken from still water bodies. For tin species this is a result of human impact on the still-water habitats (maturation pond, oil retention basin, oxbows suffering from high anthropogenic impact), as these species are predominantly man-made and persistent.

The concentration of polymethylated species did not appear to be dependent upon whether the water body was flowing or not. For both still and flowing waters the sediment concentration of polymethylated As, Sb, Sn and Te species was around 5 μg kg^{-1} per dry weight.

Taken together these data demonstrate that there is no significant difference in the concentrations of those methylated species, which do not predominantly originate from anthropogenic sources, in the sediments of standing and flowing water bodies. This may be explained by the fact that the flowing water bodies studied contain meso habitats with low stream velocity. These are suitable as a habitat for methylating microorganisms and are similar to the habitats of standing water bodies.

Distribution of organometal(loid) species

The distribution of organometal(loid) species in fractionated sediment samples is presented in Tables 2 and 3 for all six samples tested in this study. A direct correlation between particle size and distribution of organometal(loid) species can clearly be seen, with the concentration of organometal(loid) species increasing as particle size decreases and therefore volume-to-size ratio increases. This constitutes the first report of particle size distribution of several of the mentioned methylated species and complements the existing literature reports for the distribution of inorganic metal(loid)s in sediments.

Many environmental studies of sediments are confined solely to the <63 μm[5] and <20 μm[19,20] fractions on the basis that the majority of inorganic species are associated with the silt- and clay-rich fractions, and that these fractions have the closest similarity to the suspended particulate matter of the water column. Although data obtained from such studies are easily comparable, a skewed impression of an environmental sample and parent habitat is obtained: it is possible that detection of organo- and inorganic metal(loid) species in these fractions without analysis and reference to other fractions could exaggerate the risk for a water body or aquatic organisms.

Furthermore the data obtained viewed in the context of fine particulate matter <63 μm and in particular <20 μm, the fractions are very important in terms of ecotoxicological relevance. These small particulate matters have likewise a large adsorption potential and are constantly and readily supplied to the water phase, e.g. through erosion; likewise they remain suspended in the water phase for long periods of time. This suspended particulate matter in aquatic ecosystems therefore possesses enhanced uptake potential via mucous

Table 2. Mean, minimum and maximum concentrations of As and Sb species of six fractionated sediment samples

		Concentration of inorganic and organometal(loid) species in sediments (μg kg^{-1} dry weight)							
Fraction		$As_{tot.}$	MMAs	DMAs	TMAs	$Sb_{tot.}$	MMSb	DMSb	TMSb
>2000	Mean	6 600	3.56	0.66	0.08	900	2.92	0.33	0.02
	Minimum	4 000	2.14	0.37	0.03	500	1.27	0.05	0.004
	Maximum	12 300	4.09	4.04	0.17	5.90	6.37	2.76	0.12
2000–630	Mean	5 400	3.90	0.23	0.07	1.80	2.62	0.35	0.01
	Minimum	2 500	0.34	0.11	0.01	400	0.58	0.01	0.004
	Maximum	8 100	19.9	3.05	0.41	23.6	52.6	1.89	0.25
630–180	Mean	3 200	2.18	0.24	0.09	700	1.53	0.14	0.01
	Minimum	1 700	0.91	0.10	0.02	300	0.84	0.01	0.004
	Maximum	7 700	8.58	2.35	0.44	34 400	22.5	6.89	0.10
180–63	Mean	3 600	4.74	0.36	0.07	800	4.86	0.13	0.01
	Minimum	30 000	0.45	0.05	0.02	500	0.86	0.02	0.00
	Maximum	7 100	6.76	1.62	0.86	29 500	47.43	15.9	0.24
63–20	Mean	4 100	4.32	0.28	0.12	1 000	6.72	0.24	0.01
	Minimum	2 400	2.37	0.06	0.02	400	3.65	0.04	0.004
	Maximum	8 100	7.58	0.73	0.38	38 800	16.1	0.78	0.10
<20	Mean	9 300	8.86	1.65	0.32	2 500	12.02	0.40	0.06
	Minimum	40 000	5.13	0.18	0.05	600	9.92	0.12	0.004
	Maximum	12 600	20.1	3.09	0.56	66 500	19.8	7.26	0.13

Table 3. Mean, minimum and maximum concentrations of Sn and Te species of six fractionated sediment samples

		Concentration of inorganic and organometal(loid) species in sediments (μg kg^{-1} dry weight)							
Fraction		$Sn_{tot.}$	MMSn	DMSn	TMSn	MBSn	DBSn	$Te_{tot.}$	DMTe
>2000	Mean	1,600	0.14		0.02	0.53		26.1	0.03
	Minimum	1,500	0.10	n.d.	0.01	0.59	n.d.	15.5	0.01
	Maximum	7,000	4.99	n.d.	0.21	17.7	n.d.	83.7	0.04
2000–630	Mean	3,500	0.41	16.5	0.15	0.95	13.9	21.8	0.01
	Minimum	1,400	0.03	1.34	0.00	0.53	1.51	14.5	0.004
	Maximum	35,500	23.9	30.4	1.51	210	24.8	114	0.49
630–180	Mean	1,700	0.50	9.02	0.05	1.91	6.71	16.7	0.01
	Minimum	900	0.03	1.22	0.01	0.53	1.13	11.1	0.001
	Maximum	35,600	13.1	15.6	0.92	117.31	11.15	111.0	0.61
180–63	Mean	3,000	0.89	6.39	0.09	3.57	5.66	20.6	0.03
	Minimum	2,100	0.13	0.59	0.01	0.53	1.02	13.9	0.002
	Maximum	32,100	11.9	11.6	0.76	107	10.3	76.6	0.46
63–20	Mean	4,700	0.38	12.08	0.36	1.06	13.0	25.3	0.04
	Minimum	1,400	0.28	5.43	0.00	0.53	12.8	13.6	0.00
	Maximum	47,100	15.8	13.3	1.01	145	13.2	112.0	0.50
<20	Mean	11,100	1.17	11.4	0.78	2.14	17.3	53.6	0.10
	Minimum	2,800	0.31	9.74	0.01	0.53	15.3	22.3	0.02
	Maximum	80,700	36.6	13.1	1.69	155	19.2	197.0	0.61

n.d., not detected.

Table 4. Relative proportion of MMAs and MMSb content of the fractions with respect to whole samples; calculated for the samples of Table 2 (product of the relative proportion of the species concentration with respect to the non-fractionated sample and the relative proportion of the fraction mass with respect to the whole sample)

	MMAs					MMSb				
Site	2000–630 μm	630–180 μm	180–63 μm	63–20 μm	<20 μm	2000–630 μm	630–180 μm	180–63 μm	63–20 μm	<20 μm
Oxbow 1	11.7%	8.0%	17.4%	24.9%	38.0%	9.9%	6.6%	16.8%	22.7%	44.0%
Oxbow 2	18.4%	28.8%	4.0%	20.8%	28.1%	15.8%	19.6%	6.7%	30.9%	26.9%
Fishpond 1	4.7%	13.2%	27.5%	33.4%	21.2%	2.8%	14.8%	38.2%	34.1%	10.1%
Fishpond 2	8.1%	16.9%	27.6%	42.1%	5.2%	2.0%	10.2%	24.3%	57.1%	6.4%
Maturation pond 1	18.8%	19.4%	15.1%	22.4%	24.3%	28.1%	25.1%	15.3%	16.3%	15.2%
Maturation pond 2	9.2%	58.1%	7.5%	18.9%	6.2%	15.4%	53.8%	7.5%	16.4%	6.9%

membranes, e.g. those of the gills, as well as the skin of aquatic invertebrates both free-living in the water and those in the sediments. This adds particular weight to the results of Vink,[8] who demonstrated the almost exclusive dermal uptake of heavy metals for *Limnodrilus*.

Relative proportion of the organometal(loid) species content of the fractions with respect to whole samples

In order to describe the distribution of metalloid species in the sediments in the best possible way, it is sometimes useful to relate percentage of (i) the specie concentration of the sub-samples/the concentration of the non-fractionated, and (ii) the percentage of the mass of the sub-samples/the mass of the non-fractionated sample (data not presented). As an example a particle size fraction can be over-estimated in its relevance with respect to the biotope if it contains a high amount of metalloids, but represents only a small amount of the total mass of the non-fractionated sample. In order to avoid this and similar phenomena, it is useful to correct the results by relating the species concentration percentage and mass percentage of the particle size fractions as follows: the relative proportion of the organometal(loid) species content of the fraction with respect to the whole sample = product of the relative proportion of the species concentration with respect to the non-fractionated sample and the relative proportion of the

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fraction mass with respect to the mass of whole sample. The corrected results for the dominant species MMAs and MMSb of the six fractionated samples from Table 2 are presented in Table 4. In general, applying the mass balance correction had in our case three main consequences: (i) there are no drastic pattern changes; (ii) in most cases a slightly stronger emphasis of the fractions 180–63 and 63–20 μm was obtained; and (iii) in cases of a polarization of the concentration and the proportion of the unfractionated sample represented by the sub-fraction, a more site-equitable picture needed to be drawn for the assessment. This effect was particularly noticable when a fraction contained a high burden of organic material.

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