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Methylated arsenic and antimony species in suspended matter of the river Ruhr, Germany

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Abstract

The methylated antimony and arsenic species content of sediments derived from a sedimentation bowl of the river Ruhr were monitored over a 12 month period. The most prevalent species detected were monomethylarsenic (MMAs) and monomethylantimony (MMSb). The methylantimony and methylarsenic species concentration was found to be directly correlated to the winter spate. As the biological activity in the water body is generally low at this time of the year, it may be concluded that the concentration maxima in winter originated from the translocation of soil- and sediment particles to the river by heavy rains and the melting of snow. A second maximum in Spring/early Summer was observed for the methylarsenic species, and specifically the dimethylarsenic species (DMAs); this occurred in parallel to the algal bloom. A change in the methylarsenic speciation pattern was observed between April, May and June, with DMAs replacing MMAs as the dominant methylarsenic species. For methylated antimony species no seasonal variation in the species pattern was detected. Taken together these data strongly indicate a higher degree of transformation of arsenic compared to antimony in the Ruhr river system in spring and can be taken as a record for a biogeochemical different behaviour of these two elements which are often treated as equivalent in environmental studies.

1 Introduction

From a hydrogeological viewpoint the Ruhr Area in North Rhine Westphalia, Germany is formed by the rivers Lippe, Emscher and Ruhr. As a result of the large scale industrialisation during the 17th–19th century, and the resulting migration of workers from other parts of Europe to the area, the Lippe and the Ruhr are used for the provision of drinking water and freshwater, and the Emscher for sewage disposal. This differentiation arose as a result of the spread of disease when populated areas became flooded and drinking water contaminated. Furthermore, the area has been subjected to a continuous deposition of combustion residues from industrial incineration processes, smelting and household fires. The soils and sediments of the Ruhr Area are witness to the contamination of both humans and environment in one of the largest urban centre in Europe. The aquifer system of the Ruhr is strongly regulated to assure the drinking and industrial water supply to one of the most populated areas of Europe. Five reservoirs are components of the Ruhr water course.

The origin of the suspended solids in the water can be attributed to three main sources:

1. Biological activity e.g. plankton.
2. Displacement of soil or sediment materials.
3. Municipal sources.

Suspended solids are confined to the <200 µm fraction except in flowing water with particularly strong flow regimes. The Ruhr possesses a moderate flow regime.

Organometal(loid) compounds are well known to occur in different environmental habitats (Craig, 2003) and can be formed in situ in sediments or the water column of flowing and still waters, or may be transported from soils in true soil/sediment pore water solution or by erosion of particulate matter. Organometal(loid) compounds display a strong tendency to accumulate in the <64 µm fraction (Duester et al., 2007a). Arsenic biomethylation by algae is well documented in both marine and fresh water environments (e.g. Santosa et al., 1996; Suhendrayatna et al., 1999, or Hellweger, 2005). Reports by Howard et al. (1995) are compatible with observations here regarding the association of organoarsenic and plankton yearly profiles: They reported that in a saline and in a semi-saline environment methylarsenic species were detected in the water phase in association with a rise in water temperature and algal bloom. Likewise, Millward et al. (1993) reported the formation of DMAs by the macroalga *Ascophyllum nodusum* in estuarine areas. For methylantimony species, environmental studies are rare and none of the studies deals with the in situ methylation of the metal in flowing water bodies.

The objectives of this study were (i) examination of the potential changes in the seasonal cycle of the methylarsenic und methylantimony species content in the suspended material in the river Ruhr water and (ii) comparison of the biogeochemical behaviour of arsenic and antimony within this specific environment.

2 Materials and methods

2.1 Sedimentary material derived from suspended solids

The sedimentation basin used in this study is part of the Ruhr-monitoring station located at the city of Hattingen. The station is run by the Ruhrverband and the North Rhine-Westphalia State Environment Agency (LANUV NRW). The basin is fed continuously throughout the year via a bypass from the Ruhr. Settling of suspended solids occurs as a result in the decrease in flow rate; these sediments are defined as "sedimentary material derived from suspended solids". The suspended solids were deposited on the floor of the basin over a period of two weeks, after which time the supernatant was removed and a 5 l sample of the suspended sedimentary deposit was taken. Aliquots of 0.5 l were subsequently centrifuged at 8000 rpm and 10°C for 30 min. The resulting sediment was analysed by inductively coupled plasma-mass spectrometry (ICP-MS) as described below.

2.2 ICP-MS analysis

2.2.1 pH-gradient-ICP-MS

Organometal(loid) species present in the sediment samples were analysed by pH-gradient hydride generation GC-ICP-MS (Diaz-Bone et al., 2003; Duester et al., 2005). The system was designed such that whilst a sample was being analysed, the subsequent sample was being derivatised in parallel, thus significantly increasing the sample throughput in comparison to standard batch hydride generation systems.

Aliquots (solid samples 0.5–1 g; liquid samples 0.5–3 ml) were dispensed to a 4-neck round bottomed flask containing 10 ml citrate buffer (0.04 M, pH 7) and 0.5 ml antifoam 289 (Sigma Aldrich). The sample was continuously agitated by a magnetic stirrer and purged with helium (300 ml/min) for eight minutes. A pH gradient from pH 7 to pH 1 was initiated by the drop-wise addition of 1 M sodium borohydride ($NaBH_4$, Sigma Aldrich) and 2 M hydrochloric acid (Merck). The headspace of the flask and volatile species generated were continuously purged with helium and cryofocussed on the trap. Purging was continued for a further 2 min once derivatisation was complete. The traps and the GC column were packed with Supelcoport (10% SP-2100, 80/100 mesh, Sigma-Aldrich, Supelco, Germany). The transfer tubing was made of fluorinated ethylene propylene (FEP) (CS Chromatography Service, Germany) and maintained at a constant temperature of 120°C.

Following derivatisation and purging, volatile species were thermally desorbed from the traps and transferred via the GC column under a flow of helium (120 ml/min) to the ICP-MS (7500a, Agilent Technologies, Japan).

ICP-MS gas flow rates were as follows: carrier gas 0.74–0.8 l/min and makeup gas 0.36–0.4 l/min. Internal standards (Ga, In, Rh, Y, and Tl) were introduced via the microflow nebulizer to the Scott spray chamber via the peristaltic pump of the ICP-MS. The P/A factor (pulse to analogue factor) was determined anew on each day of analysis and the ICP-MS was tuned using a 10 μg/l Ce, Co, Li, Y und Tl solution. Quantification of volatile organometal(loid) species was performed using the inter-element calibration as described by Feldmann (1997) and validated by measuring monomethylarsonic acid, dimethylarsinic acid (both Strem, Germany), trimethylarsenic oxide (Tri-Chemical-Laboratories, Japan) and trimethylantimony bromide (Sigma Aldrich, Germany). Monomethyl- and dimethylantimony standards were not commercially available. Species identification was carried out as described previously at Duester et al. (2005). Recoveries of the hydride generated species were better than 73%.

2.2.2 Total metal(loid) analysis

Aqua regia digestion (ARD) and reverse aqua regia digestion (rARD) are generally referred to as delivering a pseudo-total metal concentration as the silicate fraction is not digested by this method. Silicate associated arsenic and antimony minerals however do not occur in the environment to any significant extent, and are furthermore of limited bio-availability. Consequently it is entirely reasonable to use ARD or rARD in studies such as these and the elemental concentrations obtained can be viewed as being total concentrations.

For the monoisotope arsenic, ArCl is the most significant interference during ICP-MS analysis, and the decision was made to use rARD, i.e. 1 HCl:3 HNO_3, rather than ARD (3 HCl:1 HNO_3) to reduce the chlorine input to the sample.

Digestion of the sediment samples was performed under elevated temperature and pressure conditions in a microwave digestion system (Duester et al., 2005). Total element content of microwave digests was performed using an Agilent 7500ce ICP-MS (Agilent Technologies, Japan). The use of the collision/reaction cell further reduces polyatomic interference.

ICP-MS gas flow rates were as follows: total argon 1.2 l/min as carrier gas 0.8–0.84 l/min and make-up gas 0.36–0.4 l/min; helium flow to collision cell 3–4 ml/min. The collision cell was tuned using a 1% HCl solution, which was introduced to the Scott spray chamber via a peristaltic pump (0.8 rpm) and microflow nebulizer. The P/A factor was determined anew on day of analysis.

Quantification was performed by external calibration and all data validated by comparison to the certified reference material CRM 610 (Trace Elements in Groundwater – high level, Community Bureau of References, Belgium). The efficiency for arsenic recovery was >92%.

2.2.3 Turbidity and chlorophyll-*a* content

Turbidity was measured as equivalent formazine nephelometric units (FNU). Measurements were performed by 90° infrared scattered light online method in accordance with EN ISO 7027. Measurements were conducted at 15 min intervals. Chlorophyll-*a* content was monitored fluorimetrically online at 15 min intervals in accordance to DIN 38412-16.

3 Results and discussion

Figure 1 depicts the yearly profile of chlorophyll-*a* and the turbidity of the Ruhr between April 2004 and May 2005 at Hattingen. Chlorophyll-*a* concentration is known to be directly correlated to the concentration of phototrophic eukaryotes and cyanobacteria in waters of which Diatomeae and Chlorphyceae are the major species in the waters of the Ruhr (Ruhrverband, 2003). Turbidity is an indicator of the suspended matter concentration and other components such as humic acids which can cause turbidity. In this study, peak concentrations of chlorophyll-*a* were clearly associated with phytoplankton development between April and August, whereas two distinct maxima were seen for turbidity measurements (November/December and February); the February peak was associated with the peak flow rate of the Ruhr (Fig. 2a).

The flow at Hattingen tide gauge and the monthly mass balance for organometal(loid)s in suspended particulate matter are shown in Fig. 2. General sampling parameters utilised during sampling of the sedimentation basin at the Hattingen control station are given in Table 1 and raw data of methylated antimony and arsenic species content per dry weight is presented in Tables 2 and 3.

When the mean monthly flow, suspended particulate matter concentration, and the dry weight are compared, it can be seen that the methylarsenic and methylantimony concentrations of suspended particulate matter show different maxima during the year. For both elements monomethyl species are the dominant species throughout the year, with the exception of species pattern shift (from MMAs to DMAs as dominant methylated species) from April to June. For dimethylarsenic species the highest concentration was observed in May. A maximum concentration of 24.05 μg/kg per dry weight was observed. Interestingly, this was associated with the maximal chlorophyll-*a* concentrations and therefore by inference the algal concentrations.

We noted a strong correlation between the chlorophyll-*a* concentration and the 8.6 g/month methylarsenic species load, which suggests that the formation of methylated species occurs in the water bodies of the stream and/or the storage lakes. The absence of a methylantimony species and especially of a DMSb peak concentration in spring indicates that in contrast to arsenic, little methylation of antimony occurs within the water body.

The turbidity measurements provide an explanation for the occurrence of the methylantimony species concentration maximum and the second methylarsenic maximum in the 12-month period (23 g/month for methylantimony, Fig. 2b) both in February 2005 when the biological activity is at its winter minimum. These concentration maxima are identical with the turbidity and flow maxima during the analysis period (Fig. 1).

The composition of particulate matter is highly dependent upon the flow rate. When the flow rate is less than 100 m^3/s, mineral material comprises between 50–70% of the particulate matter. This proportion increases as the flow rate increases, such that it represents 60–90% of the particulate matter at flow rates of 500–600 m^3/s. According to the Ruhrverband, the highest suspended particulate matter concentrations occur just before a spate event maximum. In mid-February flow rates of up to 548 m^3/s were noted and hence the hypothesis of the methylated species bound to mineral particulate matter dislocated from soils/sediments is supported.

It may therefore be concluded that organometal(loid) methylation in the current, which was observed for arsenic in the spring and early summer months, does not play a significant role during the winter period. During the winter, the majority of the methylated antimony and arsenic species therefore likely arise as a result of previous methylation in soils and sediments; the translocation being particularly associated with rainfall and thaw water. Hence the graphs for methylantimony and methylarsenic concentrations presented in Fig. 2e and f show a strong degree of affinity, with the notable exception of the Spring period when methylarsenic, and particularly DMAs, concentrations are significantly higher than those observed for methylantimony species. We postulate that the increase in methlyarsenic species during this period is due to the increased bioactivity and specifically the algae bloom. This hypothesis is supported by the observation of a linear correlation between methylarsenic and chlorophyll-*a* concentrations (r^2=0.87, $p \ll 0.05$). No such correlation is observed for methylantimony concentrations and turbidity (r^2=0.35, $p \ll 0.05$). It should also be noted that no change in the ratio of MMAs:DMAs:TMAs occurs in the winter during the second methylated arsenic species concentration maximum. The translocation of methylated arsenic and antimony species either bound by particulate matter or the pore water pathway has been described before (Duester et al., 2005, 2007b).

The concentrations of methylarsenic and methylantimony as a percentage of total suspended particulate matter were at their highest in May and June (methylarsenic 0.38% and methylantimony 2.15%, Table 4). This coincides with the lowest flow rates (when strong rainfall events are ignored), when generally lower total metal(loid) concentrations in the water and particulate matter of flowing waters occur.

A definitive source for the particulate matter collected in the sedimentation bowl in winter cannot be deduced via indicator elements monitored in this study since as an example Pb and Fe both occur in the natural environment and because they are major components of industrial and domestic waste waters, can arise through anthropogenic input. Future studies therefore require that the analysis incorporates elements that are little used industrially, e.g. of scandium, or through analysis of isotope ratios, to conclusively prove that the source of the methylated antimony species is indeed originating from their translocation from soils.

With regard to sources of antimony and arsenic, currently, the most significant sources of inorganic antimony are the particulate release from brake linings and from the incineration of plastics (e.g. Haus et al., 2007; Gomez et al., 2005; Furuta et al., 2005, or Shotyk et al., 2005). The impact and the biological transformation of the diffuse antimony release from brake linings dislocated in the urban dust to freshwater environments has not been examined and quantified in detail so far. The release of methylated species from direct anthropogenic sources can be dismissed for the Ruhr catchment as no semiconductor industry is located here and the use of arsenic based pesticides has been banned for more than 10 years.

In conclusion, this study demonstrates that (i) methylarsenic concentration in suspended particulate matter is correlated with the algal bloom, and that a speciation shift towards DMAs as the dominant methylated arsenic species occurs in the Spring and early Summer, (ii) methylantimony and methylarsenic concentrations are influenced by the dislocation of particulate matter from soils and/ or sediments of the catchment area via heavy rain and spate events. Hence a significant difference in spring and summer in the biogeochemical cycling of these two elements which are often treated the same, is presented.

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Table 1. Drain and sedimentation data (April 2004–May 2005) Hattingen river Ruhr.

Month	Mean discharge m^3/s	Discharge of the sedimentation bowl during sampling time m^3	Sedimentary material wet g	Dry matter %	Mean monthly temperature °C
05.04	63.33	53.60	573.5	13.53	14.59
06.04	28.34	55.50	703.0	9.49	18.95
07.04	35.43	46.15	422.5	12.97	19.19
08.04	36.12	48.10	293.0	14.35	21.03
09.04	54.40	49.45	251.5	12.78	15.64
10.04	33.59	55.45	133.0	10.69	12.39
11.04	123.1	44.15	274.0	12.48	8.82
12.04	65.88	48.60	130.0	17.28	4.73
01.05	150.3	43.20	154.0	17.45	6.13
02.05	185.3	36.60	283.0	20.74	4.68
03.05	108.5	36.55	153.5	23.14	6.92
04.05	81.73	39.85	183.0	19.15	11.16

Table 2. Methylated arsenic species concentrations of the sedimentary material derived from suspended particulate matter sedimentation bowl Hattingen, river Ruhr (April 2004–May 2005) in μg/kg per dry weight (n=4).

Month	MMAs	DMAs	TMAs
05.04	12.06±0.357	24.05±2.705	0.230±0.006
06.04	13.18±3.000	18.13±10.35	0.170±0.017
07.04	9.755±1.816	6.588±1.009	0.103±0.038
08.04	5.957±0.713	0.903±0.525	0.093±0.021
09.04	8.308±1.014	0.615±0.352	0.093±0.032
10.04	7.674±1.274	0.849±0.331	0.101±0.054
11.04	4.316±0.732	0.418±0.161	0.056±0.011
12.04	5.804±1.091	0.670±0.316	0.089±0.022
01.05	7.478±1.038	1.091±0.920	0.148±0.062
02.05	7.685±0.806	3.860±1.149	0.237±0.035
03.05	5.708±1.395	1.902±1.355	0.140±0.053
04.05	8.044±0.501	8.974±1.771	0.172±0.018

Table 3. Methylated arntimony species concentrations of the sedimentary material derived from suspended particulate matter sedimentation bowl Hattingen, river Ruhr (April 2004–May 2005) in μg/kg per dry weight (n=4).

Month	MMSb	DMSb	TMSb
05.04	10.51±0.554	4.686±1.176	0.172±0.038
06.04	11.03±2.108	3.731±1.739	0.182±0.078
07.04	9.514±0.655	1.017±0.313	0.062±0.023
08.04	11.64±1.359	1.540±0.047	0.072±0.019
09.04	9.776±1.254	1.276±0.269	0.043±0.009
10.04	14.81±2.214	2.160±0.625	0.030±0.020
11.04	10.43±2.372	0.709±0.253	0.029±0.007
12.04	19.60±2.184	6.369±0.450	0.091±0.008
01.05	16.76±1.950	3.433±0.332	0.086±0.037
02.05	21.43±1.007	10.84±1.582	0.268±0.131
03.05	13.30±3.505	3.051±1.626	0.081±0.048
04.05	12.45±1.840	4.665±1.562	0.200±0.054

Table 4. Percentage of methylated arsenic and antimony species to total metalloid content of the sedimentary material derived from suspended particulate matter sedimentation bowl Hattingen, river Ruhr (April 2004–May 2005).

Month	Methylated arsenic species content to total As content	Methylated antimony species content to total Sb content
05.04	0.34%	2.15%
06.04	0.38%	1.45%
07.04	0.11%	0.91%
08.04	0.03%	0.71%
09.04	0.09%	0.84%
10.04	0.14%	1.00%
11.04	0.03%	0.60%
12.04	0.05%	0.70%
01.05	0.05%	0.66%
02.05	0.05%	0.79%
03.05	0.04%	0.75%
04.05	0.10%	0.97%

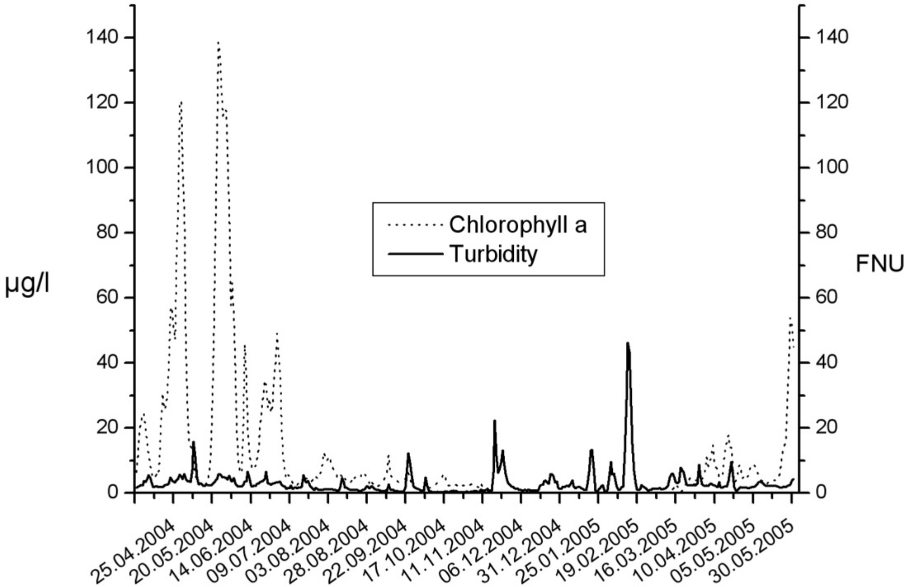

Fig. 1. Day mean value of chlorophyll-*a* content in μg/l and turbidity in FNU of water of the river Ruhr between April 2004 and May 2005 at Hattingen.

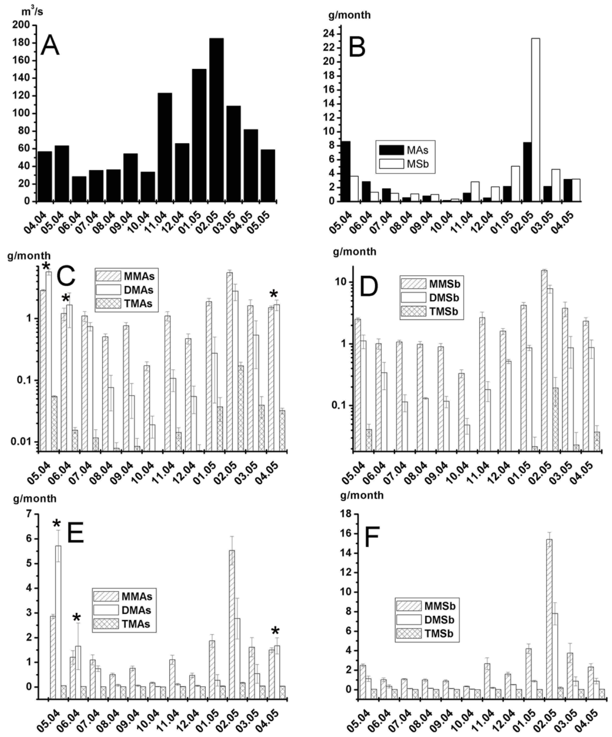

Fig. 2. (A) Water amount at Hattingen tide gauge; **(B)** sum of methylated- antimony- (MSb) and arsenic (MAs) species content of the sedimentary material in g/month per dry weight (calculated including the discharge of the Ruhr, the discharge of the sedimentation bowl and amount of sedimentary material); **(C)** logarithmic diagram and E linear graph of monomethyl-, dimethyl- and trimethyl arsenic species content (MMAs, DMAs, TMAs) of the sedimentary material derived from suspended particulate matter in g/month; **(D)** logarithmic and **(F)** linear graph of monomethyl-, dimethyl- and trimethylantimony species content (MMSb, DMSb, TMSb) of sedimentary material derived from suspended particulate matter in g/month. *Arsenic species pattern shift occurring with algae bloom.