

Arsenic speciation in the River Zenne, Belgium

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Abstract

Arsenic species have been assessed in the Zenne River, a sewage contaminated tributary of the Scheldt estuary, in winter 2003. The highest total dissolved As concentrations were found in the middle part of the river with values up to $3.6 \mu\text{g L}^{-1}$. Particulate As concentrations increase towards the mouth of the River with highest levels of $2 \mu\text{g L}^{-1}$. A very good correlation between the % of dissolved As and % of dissolved Fe was observed. They both linearly decrease with the amount of dissolved oxygen.

In the middle part of the Zenne River where the oxygen levels were lowest, even below 1 mg L^{-1} , As(III) was the dominant species. In the other parts (upstream and downstream) of the river, As(V) was dominant. A linear relation between the measured redox values and those calculated via the As(III)/As(V) couple exists, but the range of measured Eh values is much larger than the calculated ones. No methylated dissolved As species were found during our survey.

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1. Introduction

Although a toxic element like arsenic has for a long time been regarded as only an accidental contaminant, it is widely distributed in the environment, both because of natural sources and through anthropogenic applications. The highest amounts of mineral As generally occur in sulphidic ores, indicating that As is chalcophilic. Arsenic can be associated to these ores as a minor compound, for example in pyrite (FeS_2) and sphalerite (ZnS), or to a larger extent, as a major compound, e.g. arsenopyrite (FeAsS), orpiment (As_2S_3) and realgar (As_4S_4). On the other hand, As has numerous applications in industry and agriculture; for example arsenic oxides are used in the glass industry, gallium arsenide in semiconductors, dimethylarsenic acid as pesticide and herbicide, nitrasone (phenyl arsonic acid) as growth promoter for swine and as food additive to combat

deceases in poultry or Chromated Copper Arsenate (CCA) as preservative for wooden structures such as pilings and docks.

As is the case for many environmental pollutants, extensive toxicity studies of As have shown that different forms exhibit different toxicities (Leermakers et al., 2006). Inorganic As species are more toxic than methylated compounds, arsenobetaine, arsenocholine (AsC^+) or arsenosugars. With the exception of tetramethylarsonium ion, acute toxicity generally decreases with increasing degree of methylation. Other organo-arsenic compounds such as the phenylarsenic warfare agents CLARK I, CLARK II, and ADAMSITE are strong irritants and very toxic. Fortunately in fish, arsenobetaine, a species with a relatively low toxicity, is dominating.

Arsenic is perhaps unique among the heavy metalloids and oxyanion-forming elements (e.g. arsenic, selenium, antimony, molybdenum, vanadium, chromium, uranium, rhenium) in its sensitivity to mobilization at the pH values typically found in surface and ground waters (pH 6.5–8.5)

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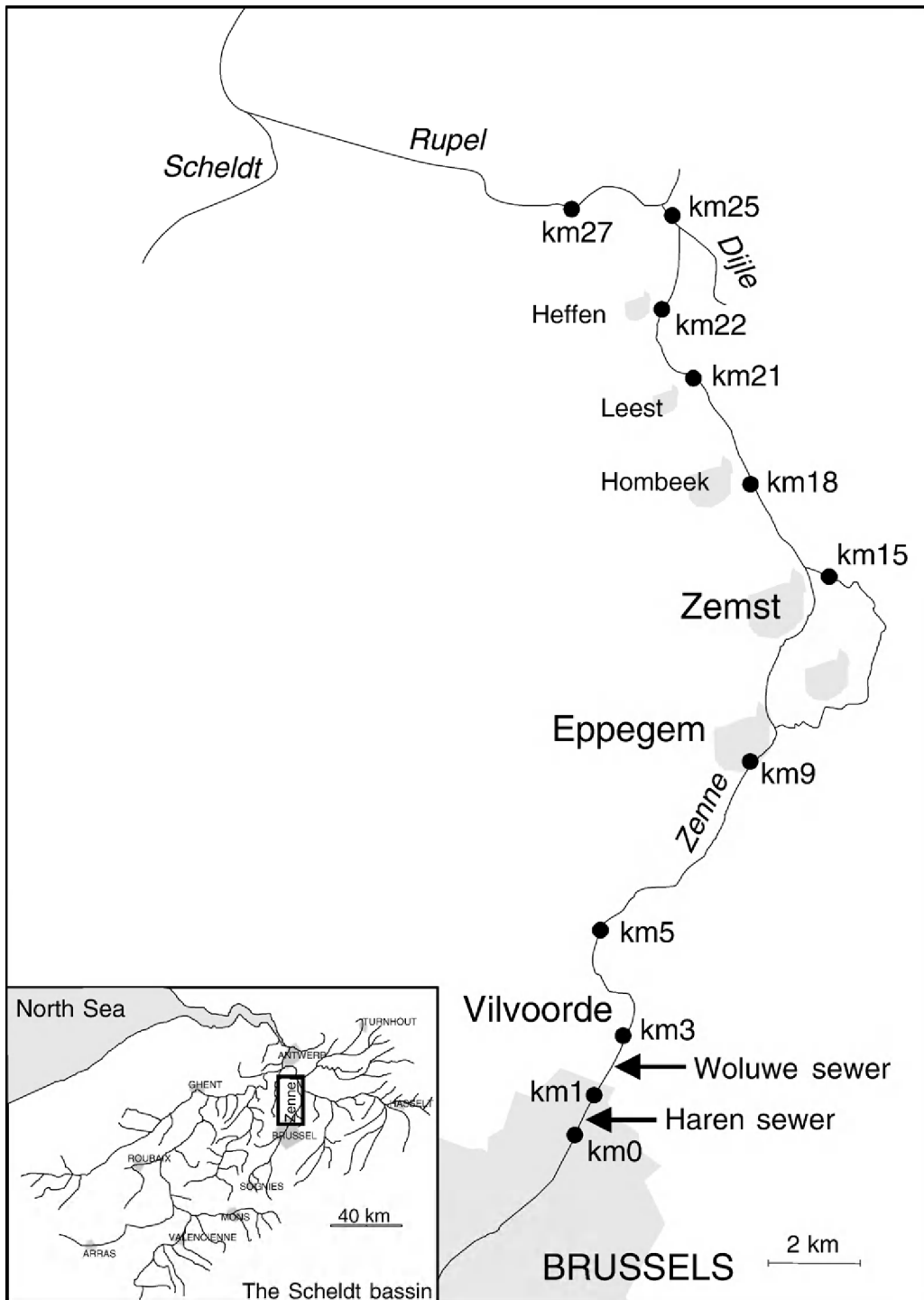


Fig. 1. Map of the River Zenne.

and under both oxidizing and reducing conditions. Arsenic can occur in the environment in several oxidation states (-3 , 0 , $+3$ and $+5$) but in natural waters it is mostly found in inorganic form as oxyanions of trivalent arsenite

(As(III)) or pentavalent arsenate (As(V)). Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may, however, occur where waters are

Table 1
As species concentrations and related parameter values in the river Zenne

Station	Location	pH	Eh meas. mV	Eh calc. mV	Turbid. mg/L	Temp. °C	O ₂ mg/l	DAs µg/l	As (III) %	PAs µg/g	PAs µg/L	PFe µg/g	PMn µg/g	DFe µg/L
Scheldt (upstream Zenne)				162	179.8		7.0	1.82	7	20.6	3.70	40900	786	23.1
Zenne (km27)	Hamersdijk	7.28	224	132	35.7	7.4	5.0	1.01	44	43	1.54	76800	535	61.5
Zenne (km25)	Heindonk	7.65	168	110	26.7	6.2	4.2	0.97	45	35	0.93	78300	400	48.2
Zenne (km22)	Heffen	7.66	-32	97	83.5	7.9	1.0	2.74	69	23.4	1.95	18600	289	96.4
Zenne (km21)	Leest	7.7	-40	97	47.0	8.4	0.8	2.94	65	14.4	0.68	18700	236	97.0
Zenne (km18)	Hombeek	7.7	-64	94	60.0	9.1	1.4	3.60	70	9.0	0.54	15900	206	110.3
Zenne (km15)	Zemst	7.67	132	101	67.0	8.4	1.5	3.04	60	8.4	0.56	13800	207	66.6
Zenne (km9)	Eppegem	7.6	200	106	26.0	8.8	1.2	3.45	58	17	0.44	22500	316	30.8
Zenne (km5)	Vilvoorde	7.79	91	108	87.0	9.4	1.1	1.12	34	5.9	0.51	9150	170	46.1
Zenne (km3)	Vilvoorde	7.94	167	99	113.0	10.2	1.1	1.07	34	4.4	0.50	8080	174	51.3
Zenne (km1)	Vilvoorde	7.95	-11	99	105.0	9.2	2.0	1.06	33	5.88	0.62	12400	253	50.4
Zenne (km0)	Vilvoorde	7.84	160	104	56.0	8.4	3.0	1.1	36	12.4	0.69	21900	314	48.3

significantly impacted by industrial or agricultural pollution (Abdel-Moati, 1990).

Relative to other oxyanion-forming elements, arsenic is among the most problematic in the environment because of its relative mobility over a wide range of redox conditions. For example Se, Cr, Mo, V, ... appear to be less mobile under reducing conditions. Arsenic can be found at concentrations in the mg L⁻¹ range when all other oxyanion-forming metals are present in the µg L⁻¹ range (Smedley and Kinniburgh, 2002).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, H₂AsO₄⁻ is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO₄²⁻ becomes dominant (H₃AsO₄⁰ and AsO₄³⁻ may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H₃AsO₃⁰ will predominate (Brookins, 1988; Yan et al., 2000). Although As(V) is generally the dominant species in lake and river waters (e.g. Seyler and Martin, 1990; Pettine et al., 1992), significant seasonal variations in speciation as well as absolute concentration have been found. Concentrations and relative proportions of As(V) and As(III) vary according to changes in input sources, redox conditions and biological activity. The presence of As(III) may be maintained in oxic waters by biological reduction of As(V), particularly during summer months. Higher relative proportions of As(III) have been found in river stretches close to inputs of As(III)-dominated industrial effluent (Andreae and Andreae, 1989) and in waters with a component of geothermal water. In fact, in the Scheldt Andreae and Andreae (1989) found arsenic concentrations in the

range 0.75 to 3.75 µg L⁻¹ typical of European rivers. In the river Zenne, a fresh water tributary of the Scheldt river, they also sampled one station and found an As concentration of 27.8 µg L⁻¹ which is an order of magnitude higher than all their other measurements in the Scheldt River Basin. They assumed that either municipal or industrial discharges into that river are responsible for the elevated arsenic levels. In a preliminary survey we also found at one station a high As level of 17 µg L⁻¹. As a first objective, we therefore wanted to check those elevated As levels along the whole stretch of the Zenne River. In addition, because of the significant input of untreated sewage from Brussels agglomeration, the influence of redox conditions on the speciation of the As species was a second objective.

2. Methods and materials

2.1. Description of the sampling area

The Zenne River is a small tributary, in terms of flow discharge, of the Scheldt Estuary (it accounts for about 10% of the Scheldt flow) through the Dijle and Rupel Rivers (Fig. 1). The Zenne river basin covers 1160 km² of land from which 64% is constituted of arable land while the rest of the basin is characterized by important urbanization. The total population living in the basin approximates 1.6 million inhabitants from which 1 million live in Brussels, capital of Belgium. Upstream the Brussels agglomeration, at 43 km from its source, the Zenne River has a flow rate of 6 m³ s⁻¹, but is already largely polluted (around 400,000 inhabitants are living in the basin upstream Brussels, with 50% of their sewage treated). The Zenne River crosses the city from

South to North over a distance of about 20 km and receives the sewage (in total about $4 \text{ m}^3 \text{ s}^{-1}$) from a combined sewer system draining a 238 km^2 urban area with a population of 1 million inhabitants. About 30% of the sewage is treated by a Waste Water Treatment Plant (Brussels-South WWTP using an activated sludge treatment) since August 2000 while the remaining 70% is discharged in the river without any treatment (Brion et al., submitted for publication). Downstream Brussels, the average annual river discharge thus increased to about $10 \text{ m}^3 \text{ s}^{-1}$. The last stretch of the river until the confluence with the Dijle and next the Scheldt, is about 20 km long.

2.2. Sampling procedure

All material used for collection or processing of samples was prior to sampling thoroughly cleaned (for more details see De Gieter, 2004). Collection of water samples was done on December 22, 2003 either by hand from a Zodiac, or from the river bank (Fig. 1 and Table 1). 1 L acid-cleaned HDPE bottles were thoroughly rinsed and filled with surface water. Immediately upon collection, the samples were transferred into PTFE filter devices and filtered under N_2 -pressure on $0.45 \mu\text{m}$ polycarbonate filters (Nuclepore), to separate dissolved from particulate substances. Dissolved phase samples were acidified with HCl (suprapur, Vel) in a 1:100 (v/v) ratio and refrigerated at 6°C . The best storage conditions according Hall et al. (1999) and Lagarde et al. (1999) is to keep the samples in the dark in a refrigerator at about 5°C . We also tested the storage conditions during several coastal surveys: a random sample was spiked with a known amount of As. Neither loss nor contamination was observed. All analyses on the dissolved phase were performed in the next 2 days following sampling. Samples of the particulate phase were rinsed with 20 mL milli-Q water and stored in their respective petrislides at -20°C . Of each decontaminated filter batch, one filter was kept aside as a blank check. At the very start and at the end of every sampling event, filtrates of milli-Q water and their respective filters served as blanks for potential filter device or milli-Q water contaminations.

2.2.1. Analysis of total dissolved As

Analysis of total dissolved As was performed with a Hydride Generation Atomic Fluorescence (HG-AFS) system from PS Analytical (Orpington, UK) according to the following HG settings: HCl (3.0 M) at 8 mL min^{-1} and NaBH_4 (1.5% (m/v)) at 4 mL min^{-1} . The gas flowrates were: Ar (purging) at 250 mL min^{-1} and Ar (drying) at 2.5 mL min^{-1} . Apart from pre-reduction of the As immediately before analysis, the samples did not

require any pretreatment. Detection and quantification limits were calculated according to their definitions of respectively 3 and 10 times the pooled standard deviation of several sets of blank determinations. As a result, the detection limit of the method was calculated as $0.013 \mu\text{g L}^{-1}$, its limit of quantification as $0.043 \mu\text{g L}^{-1}$.

The repeatability, reproducibility and accuracy of the method were checked by including a range of certified water reference materials (NASS-4 and AQUACHECK 105) in every analysis batch. The coefficient of variation for the repeatability ranged from 2.2 to 3.7%, for the reproducibility from 6.3 to 6.5%. Although the HG-AFS measurements appeared to be consistently lower than the assigned values of the references, all results still lie within the 95% confidence interval around the certified value.

Our laboratory also participated in several rounds of the laboratory performance-intercomparison exercises organized by Quasimeme (Quality Assurance of Information for Marine Environmental Monitoring in Europe). The results of our four participations provided z-scores (it is a measure of how many standard deviations a raw score is from the mean) between -1 and 1 (for details see De Gieter, 2004 thesis). Z-scores between -2 and 2 represent satisfactory results; it indicates that the result falls within the 95% confidence interval around the assigned value.

2.2.2. Analysis of total particulate As

2.3. Digestion optimisation

The following digestion procedure was chosen: the particulate matter was transferred to 50 mL Teflon digestion bombs (Savillex, US) and heated on a hot plate to 60°C in 3 mL of H_2O_2 (32%, VEL), during 45 mins. 5 mL of sub-boiled HNO_3 was added, the vessels were firmly closed and the mixture was heated to 105°C for 22 h in a regular oven. After cooling down, the digests were transferred to 30 mL HDPE bottles. Digestion bombs were rinsed twice with 10 mL milli-Q water and this water was added to the digests. Analysis was done on an ICP-MS instrument (VG PlasmaQuad II).

Blank digestions as well as certified reference materials BCSS-1, 1646a and CRM414 were included in every digestion batch. Upon digestion and analysis of several sets of samples an average recovery of 92 to 105% and an average reproducibility of 8.4 to 9.6% were observed.

2.4. Speciation

The optimization of HPLC and HG-AFS coupling provided chromatograms of the four 'anionic' arsenicals,

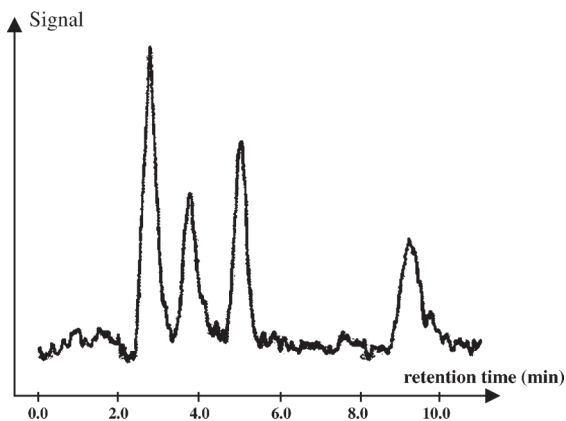


Fig. 2. Chromatogram of a 0.5 $\mu\text{g As L}^{-1}$ mixed standard of As(III), As(V), MMA and DMA, using HPLC-HG-AFS. Order of elution: As(III)–DMA–MMA–As(V).

similar to that in Fig. 2, for a mixed standard of 0.5 $\mu\text{g As L}^{-1}$ of each of the compounds. The chromatographic conditions are the following: column (Hamilton PRP-X100 (250 \times 4.1 mm; 10 μm); mobile phase ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ buffer; 20 mM, pH 6.0 (HCl)); flowrate (1 mL min^{-1}); injection volume (200 μL). For the Hydride Generation system the Ar gas flowrates are the same as for the total As determinations but they are modified for HCl (1.5 M; 1 mL min^{-1}) and NaBH_4 (2.5% (m/v); 1 mL min^{-1}). Detection limits respectively are: As(III) (0.030 $\mu\text{g As L}^{-1}$), DMA (0.043 $\mu\text{g As L}^{-1}$), MMA (0.041 $\mu\text{g As L}^{-1}$) and As(V) (0.067 $\mu\text{g As L}^{-1}$). Repeatability and accuracy on the lowest sensitivity scale were calculated from 10 consecutive measurements of an artificial standard containing 0.4 $\mu\text{g As L}^{-1}$ of each of the four compounds of interest. The repeatability varied between 7 and 13% while the accuracy, expressed as 100*result/standard value, was within 2 to 8%, except for As(V) which was 19% higher. Accuracy measurements could not be made from measurements of reference material, since there was no liquid reference material, which is certified for the separate As compounds, available.

For a general discussion of analytical speciation methods for As in environmental samples see Leermakers et al. (2006).

2.4.1. Analysis of other parameters

Redox measurements were realized with a combined platinum electrode (Mettler Toledo/Pt4800) those of pH with a combined glass electrode (Mettler Toledo). In both cases, the reference electrode is Ag/AgCl ([KCl]=3 M), having a potential of 220 mV versus the SHE (Standard Hydrogen Electrode). Dissolved Fe was measured by ICP-MS ((VG PlasmaQuad II) in the

sample filtrates also used for total dissolved As determination, while particulate Fe and Mn were measured by the same instrument in the digested particulate matter serving also for the determination of total particulate As.

3. Results and discussion

3.1. Concentration profiles of dissolved and particulate As

In 2003 a complete profile of total dissolved and particulate As concentrations in the Zenne river was assessed (Fig. 3). The highest total dissolved As levels were found in the middle part of the river with values above 3 $\mu\text{g L}^{-1}$. The particulate concentrations increase towards the mouth of the Zenne, with the highest level of 2 $\mu\text{g L}^{-1}$. The same tendency is found for the particulate As concentrations when expressed in $\mu\text{g g}^{-1}$ (Table 1). The station in the Scheldt river, upstream the mouth of the Rupel and hence the Zenne river, shows a relative high total dissolved As concentration (1.8 $\mu\text{g L}^{-1}$) and particulate As concentration (20.6 $\mu\text{g g}^{-1}$). However, the suspended matter content in the Scheldt station is very high (180 mg L^{-1}) compared to the Zenne stations (they mostly show suspended matter levels below 100 mg L^{-1}). Comparing these levels with the single dissolved As concentration reported by Andreae and Andreae (1989) in the Zenne (27.8 $\mu\text{g L}^{-1}$), all our values appear to be much lower. However, we also observed in a previous, preliminary campaign a value of 17 $\mu\text{g L}^{-1}$ of total dissolved As. This also points in the sense that the origin of the As contamination in the Zenne is of an anthropogenic (industrial) kind, resulting in an irregular discharge pattern

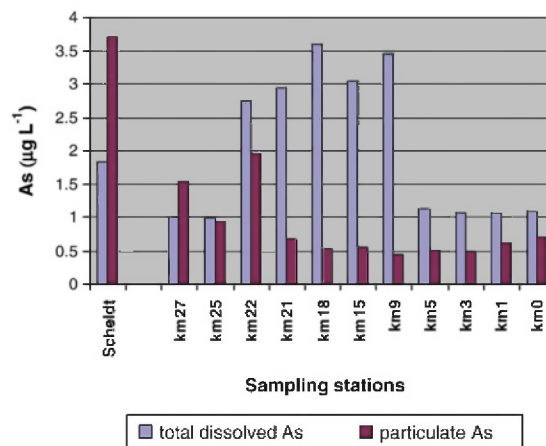


Fig. 3. Dissolved and particulate As concentrations in the River Zenne (km0 is at the border of Brussels Region, see Fig. 1).

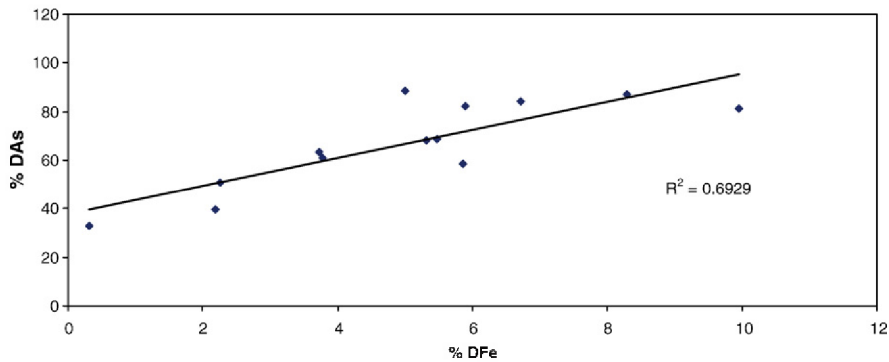


Fig. 4. % of Dissolved As versus % of Dissolved Fe in the River Zenne.

and patches of higher and lower concentration in the Zenne river and further downstream in the Scheldt. This makes it also difficult to estimate the impact of the Zenne discharge on the As fluxes in the Scheldt river and estuary. [Andreae and Andreae \(1989\)](#) found between 1 and 3 $\mu\text{g L}^{-1}$ of total dissolved As in the river Scheldt in November 1984, while [De Gieter et al. \(2005\)](#) deduced an effective riverine As concentration (dissolved phase) between 1.92 and 2.76 $\mu\text{g L}^{-1}$. All these values are similar to the concentrations found at the mouth of the river Zenne in the present campaign. Also the average particulate As concentration (40 $\mu\text{g g}^{-1}$) at the riverine/estuarine interface reported by [De Gieter et al. \(2005\)](#) corresponds to the particulate As concentrations at the Zenne mouth.

3.2. Mobilization processes

According to [Smedley and Kinniburgh \(2002\)](#), there is not much known about the reduction rate of As(V) to As(III) in the water column, but there have been some studies with soils and sediments. The evidence from soils is that under moderately reducing conditions ($E_h < 100$ mV) induced by flooding, As(V) is reduced to As

(III) in a matter of days or several weeks and adsorbed As(V) is released as As(III) ([Masscheleyn et al., 1991](#); [Reynolds et al., 1999](#)). [Masscheleyn et al. \(1991\)](#) found from laboratory experiments that some of the As was released before Fe, implying reductive desorption from iron oxides rather than reductive dissolution. Up to 10% of the total As in the soil eventually became soluble. [Smith and Jaffé \(1998\)](#) modeled As(V) reduction in benthic sediments as a first order reaction with respect to arsenate with a rate coefficient of 125 year^{-1} .

Our results show a good correlation between % of dissolved As and % of dissolved Fe ([Fig. 4](#)). In addition, both parameters linearly decrease with the amount of dissolved oxygen ([Fig. 5](#)), while the KDs (distribution coefficient = particulate metal ($\mu\text{g kg}^{-1}$)/dissolved metal ($\mu\text{g L}^{-1}$)) linearly increase with the amount of dissolved oxygen. It seems thus that dissolution of Fe from the particulate phase at decreased dissolved oxygen levels is associated with a release of As from that particulate phase and vice versa. If the release of As precedes that of Fe (reductive desorption) or goes together (reductive dissolution) can not be deduced from our observations. Since we did not measure the dissolved Mn

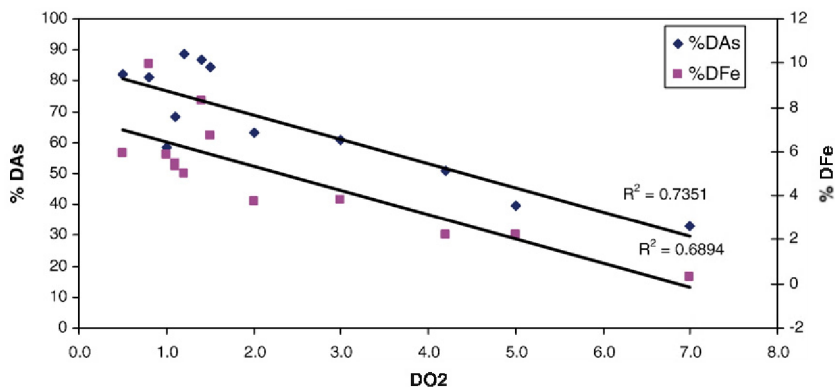


Fig. 5. % of Dissolved As and Dissolved Fe versus Dissolved Oxygen Concentration in the River Zenne.

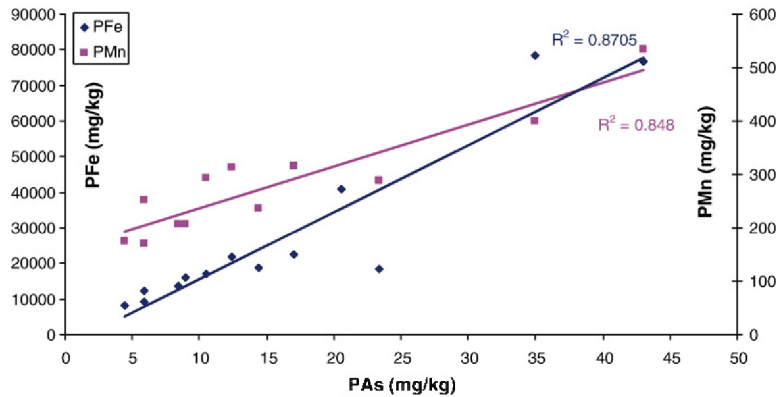


Fig. 6. Particulate Fe and Mn concentrations versus Particulate As concentration in the River Zenne.

concentrations a similar exercise can not be carried out for As and Mn. However, particulate Fe and particulate Mn correlate both very well with particulate As (Fig. 6).

3.3. Speciation of As compounds and kinetic aspects

Redox reactions are important for controlling the behavior of many major and minor species in natural waters, including that of arsenic (for a detailed discussion see Smedley and Kinniburgh, 2002). In practice, redox equilibrium is often achieved very slowly. For example, Wersin et al. (1991) estimated that the complete reductive dissolution of Fe(III) oxides in an anoxic Swiss lake sediment would take more than 1000 years. Oxidation of As(III) by dissolved oxygen, is a particularly slow reaction. Johnson and Pilson (1975) gave half-lives for the oxydation of As(III) in seawater ranging from several months to a year.

Cherry et al. (1979) found from experimental studies that the As(V)/As(III) ratios were stable in anoxic solutions for up to 3 weeks but that gradual changes occurred over longer timescales. They also suggested that the measured As(V)/As(III) ratios in natural waters might be used as an indicator of the ambient redox (Eh) conditions, particularly in groundwater where equilibration times are long. Yan et al. (2000) have also concluded that the As(V)/As(III) ratio may be used as a reliable redox indicator for groundwater systems. However, this optimism may be unfounded since Welch et al. (1988) found that the Eh calculated from the As(V)–As(III) couple neither agreed with that from the Fe(II)–Fe(III) and other redox couples nor with the measured Eh. Therefore, the reliability of the arsenic redox couple as a redox indicator remains to be seen. Redox values in the Zenne were measured with a combined platinum electrode on the one hand and were

calculated via the As(III)/As(V) couple on the other hand:



$$E^0 = +559\text{mV}$$

$$\text{Eh} = 559 - 59\text{pH} - 29.5 \text{Log} (\text{As(III)}/\text{As(V)}) \quad (2)$$

A linear relation between the measured and calculated redox values exists (Fig. 7), but the range of measured Eh values (−64 to +224 mV) is much larger than the calculated ones (+94 to +132 mV). This also suggests that the As(III)/As(V) ratio is not in thermodynamic equilibrium, due to the slow oxidation-reduction rates.

The As(V) species was dominating in the upstream sampling stations of the Zenne where the oxygen levels were 2 to 3 mg L^{−1}. In the middle part of the river where the oxygen levels were lowest (even below 1 mg L^{−1}) As(III) became the dominant species. Close to the

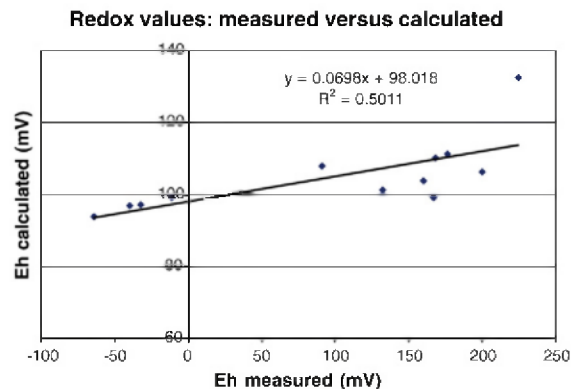


Fig. 7. Measured versus calculated redox values in the River Zenne.

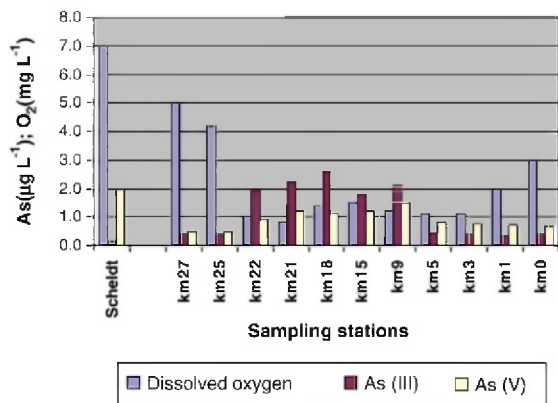


Fig. 8. As(III), As(V) and Dissolved Oxygen Concentrations in the River Zenne (km0 is at the border of Brussels Region, see Fig. 1).

mouth and at the Scheldt station oxygen levels again increase up to 7 mg L^{-1} restoring the dominance of the As(V) species (Fig. 8). The percentages of As(III) we observed in the Zenne vary between 33 and 70% while *Andreae and Andreae* (1989) found 30% at their Zenne station. In the Scheldt river they observed a range of 18 to 59%. An inverse relation between % As(III) and % dissolved oxygen is noticed (Fig. 9) but it does not mean that the main constituent controlling the ratio of As(III)/As(V) is dissolved oxygen. *Eary and Schramke* (1990) suggested that the half-life for As(III) in natural waters is 1–3 years although the rate may be greater because of the presence of ‘unknown aqueous species’ or oxide particles, especially manganese oxides. Certainly, there is considerable evidence that manganese oxides can increase the rate of As(III) oxidation with half-lives being reduced to as little as 10–20 min in the presence of manganese-oxide particles (*Oscarson et al.*, 1981; *Scott and Morgan*, 1995). Less is known about the role of iron oxides in altering the oxygenation kinetics. In the natural environment, the rates of both As(III) oxidation and As(V) reduction reactions are controlled by micro-organisms and can be orders of magnitude greater than under abiotic conditions. For example, sterile water samples have been noted to be less susceptible to speciation changes than non-sterile samples (*Cullen and Reimer*, 1989). *Wilkie and Hering* (1998) found that As(III) in geothermal waters input to streams in south-west USA oxidized rapidly downstream (pseudo first-order half-life calculated at as little as 0.3 h) and attributed the fast rate to bacterial mediation. The reduction of As(V) to As(III) in Mono Lake was also rapidly catalyzed by bacteria with rate constants ranging from 0.02 to 0.3 days (*Oremland et al.*, 2000). The literature also reports that microbiological activity, especially that of chemolithotrophic

micro-organisms, can derive energy from the oxidation of arsenite to arsenate (*Ehrlich*, 2002) and its incorporation into sediments (*Morin et al.*, 2003), as proposed for the Carnoulès mine site (France).

Methylated As species were not found in our samples, at least at levels comparable to those of the inorganic species, although they are well identifiable in our standard solutions (see Fig. 2). This is not exceptional in river water; for example *Andreae and Andreae* (1989) neither found them in their survey of the Scheldt watershed, just like *Zheng et al.* (2003) in their recent arsenic speciation study in the Moira watershed, Canada. At least 2 biological species may be involved in the methylation process of inorganic As compounds: (1) algae and more particularly marine or estuarine algae. In the Patuxent River Estuary (*Riedel*, 1993) DMA may occur two or more times per year, in winter and late spring, and appears to be highly linked to dense dinoflagellate and perhaps other algal blooms, and resulting phosphate limitation. *Howard et al.* (1988) observed differences in arsenic metabolism between marine and freshwater phytoplankton living at similar arsenic and phosphate concentrations, suggesting that biomethylation in the Tamar estuary is governed by marine biological processes; (2) bacteria. According to *Bentley and Chasteen* (2002), the microbial conversion of sodium arsenate to trimethylarsine proceeds by alternate reduction and methylation steps, with S-adenosylmethionine as the usual methyl donor. In anaerobic bacteria, methylcobalamin may be the donor.

The first mentioned methylation mechanism is without any doubt of no importance, since in winter period there is no phytoplankton present in the River Zenne. In addition, according to *Howard et al.* (1982), MMA and DMA are only found in warmer water (most often at temperature of 12°C and above), while in our Zenne campaign, the water temperature did not exceed 10°C .

The second mentioned methylation mechanism may be more important in the River Zenne because the

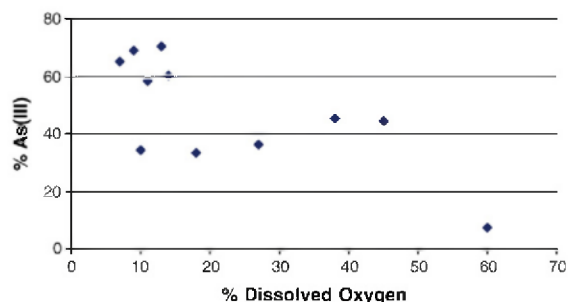


Fig. 9. % As(III) versus % Dissolved Oxygen in the River Zenne.

Table 2
Riverine arsenic concentrations ($\mu\text{g L}^{-1}$), adapted from Smedley and Kinniburgh (2002)

<i>Baseline</i>		
Various	0.83 (0.13–2.1)	Seyler and Martin (1991)
Norway	0.25 (<0.02–1.1)	Lenvik et al. (1978)
South-east USA	0.15–0.45	Waslenchuk (1979)
Dordogne, France	0.7	Seyler and Martin (1990)
Po River, Italy	1.3	Pettine et al. (1992)
Schelde catchment, Belgium	0.75–3.8 (1 result up to 30)	Andreae and Andreae (1989)
Zenne River (Schelde catchment, Belgium)	0.97–3.6	This study
High-As groundwater influenced		
Northern Chile (Loa River Basin)	190–21800	Cáceres et al. (1992)
<i>Geothermal influenced</i>		
Waikato, New Zealand	32 (28–36)	McLaren and Kim (1995)
Madison and Missouri Rivers, USA	44 (19–67)	Robinson et al. (1995)
	10–370	Nimick et al. (1998)
<i>Mining influenced</i>		
Ashanti, Ghana	284 (<2–7900)	Smedley et al. (1996)
Tinto River, Spain	3–800	Sánchez-Rodas et al. (2005)
Odiel River, Spain	0.5–95	idem

abundant wastewater discharge in the Brussels agglomeration can also bring high amounts of micro-organisms to the river that can influence the processing of pollutants. For example, it was shown that wastewater discharges constitute important sources for nitrifying bacteria (Briand and Billen, 2000), large heterotrophic bacteria (Garnier et al., 1992a,b) and protozoans (Menon, 1993) and that these organisms continue to be active once in the river system. It is thus not surprising to observe oxygen depleted stretches in the Zenne river downstream the Brussels agglomeration. However, the bacterial activity is also temperature dependent and probably not high enough in winter to observe methylation of As species. Moreover, the short residence times in this small river, especially in winter, are neither in favor of methylation.

Methylated As species are readily oxidized chemically and biologically (Abdullah et al., 1995), although other studies indicate resistance of dimethylarsenate to oxydation (Vogels and Johnson, 1998).

3.4. Comparison with other riverine systems

Baseline concentrations of arsenic in river waters are low (in the region of $0.1\text{--}0.8\ \mu\text{g L}^{-1}$ but up to ca. $2\ \mu\text{g L}^{-1}$; Table 2). They vary according to the composition of the surface recharge, the contribution from baseflow and the bedrock lithology. Concentrations at the low end of the range have been found in rivers draining As-poor bedrocks. Seyler and Martin (1991) found average river concentrations as low as $0.13\ \mu\text{g L}^{-1}$ in the Krka region of Yugoslavia where the bedrock is As-poor karstic limestone (Table 2). Lenvik et al. (1978) also found low average concentrations of about $0.25\ \mu\text{g L}^{-1}$ in rivers

draining basement rocks in Norway, the lowest being in catchments on Precambrian rocks. Waslenchuk (1979) found concentrations in river waters from the south-eastern USA in the range $0.15\text{--}0.45\ \mu\text{g L}^{-1}$ (Table 2).

Relatively high concentrations of naturally-occurring arsenic can occur in some areas as a result of inputs from geothermal sources or high-arsenic groundwaters. Arsenic concentrations in river waters from geothermal areas have been reported typically at around $10\text{--}70\ \mu\text{g L}^{-1}$ (e.g. western USA and New Zealand; McLaren and Kim, 1995; Robinson et al., 1995; Nimick et al., 1998; Table 2), although higher concentrations have been found.

Increased concentrations are also reported in some river waters from arid areas where the surface water is dominated by river baseflow, i.e. by water flowing into the surface water from the surrounding rocks. The resulting surface waters often have a high pH and alkalinity. For example, in surface waters from the Loa River Basin of northern Chile (Antofagasta area, Atacama desert), Cáceres et al. (1992) found concentrations of naturally-occurring arsenic ranging between $190\text{--}21,800\ \mu\text{g L}^{-1}$.

Smedley et al. (1996) observed high As concentrations in the Ashanti River (Ghana). Those mining influenced levels could attain concentrations up to $5\text{--}10\ \text{mg L}^{-1}$, with an average of $0.3\ \text{mg L}^{-1}$. Mining also influenced the As levels in the Tinto and Odiel Rivers in Spain (Sánchez-Rodas et al., 2005) but compared to the Ashanti River they were 1 to 2 orders of magnitude lower.

Significant increases in arsenic concentrations of river waters may also occur as a result of pollution from industrial or sewage effluents. Andreae and Andreae (1989) studied As concentrations and speciation in the Scheldt River Basin. The highest concentrations, up to

30 $\mu\text{g L}^{-1}$, were found in water from the River Zenne, which is affected by inputs from urban and industrial sources, particularly sewage. However, the As concentrations in most of the catchment area rivers, were in the range 0.75–3.8 $\mu\text{g L}^{-1}$ and thus not significantly different from baseline concentrations. We therefore organized a preliminary study in the River Zenne and found 17 $\mu\text{g L}^{-1}$ as the highest total dissolved As concentration. During our December 2003 survey, the total As (dissolved+particulate) in the River Zenne ranged from 1.5 to about 5 $\mu\text{g L}^{-1}$, and the % As(III) from 30 to 70%. Although the As(III)/As(V) ratio does not agree with the measured redox potential value, there is strong evidence that it is directly and/or indirectly controlled by the dissolved oxygen level.

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