CORA Cork Open Research Archive
Cartlann Taighde Oscailte Chorcaí

Title	A procedure to identify natural arsenic sources, applied in an affected area in North Rhine-Westphalia, Germany
Authors	Banning, Andre;Coldewey, Wilhelm G.;Göbel, Patricia
Publication date	2008-05-10
Original Citation	Banning, A., Coldewey, W.G. and Göbel, P. (2009) 'A procedure to identify natural arsenic sources, applied in an affected area in North Rhine-Westphalia, Germany', Environmental Geology, 57(4), pp. 775-777. doi: 10.1007/s00254-008-1355-4
Type of publication	Article (peer-reviewed)
Link to publisher's version	https://link.springer.com/article/10.1007/s00254-008-1355-4 - 10.1007/s00254-008-1355-4
Rights	© Springer-Verlag Berlin Heidelberg 2008. This is a post-peer-review, pre-copyedit version of an article published in Environmental Geology. The final authenticated version is available online at: https://doi.org/10.1007/s00254-008-1355-4
Download date	2026-11-01 13:29:45
Item downloaded from	https://hdl.handle.net/10468/12333



UCC
University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

A procedure to identify natural arsenic sources, applied in an affected area in Northrhine-Westphalia, Germany

A. Banning, W.G. Coldewey, P. Göbel

Andre Banning (corresponding author)

Department of Engineering Geology and Hydrogeology, RWTH Aachen University, Aachen, Germany

Lochnerstraße 4-20, 52064 Aachen

e-mail: banning@hydro.rwth-aachen.de

Tel.: +49-241-8099775

Fax: +49-241-8092280

Wilhelm Georg Coldewey

Department of Applied Geology, Münster University (WWU), Münster, Germany

Corrensstraße 24, 48149 Münster

Patricia Göbel

Department of Applied Geology, Münster University (WWU), Münster, Germany

Corrensstraße 24, 48149 Münster

Abstract

The study´s aim was to identify the geogenic source for elevated arsenic (As) concentrations recently discovered in soils of the Heubach plain, Northrhine-Westphalia, Germany. Therefore, a catalogue of conditions that an As source has to fulfil to be considered as geogenic was formulated, including the source´s linkage to the sink, its mineralogy, As total content, As mobilization potential, groundwater redox conditions and As output. Accordingly, mineralogical, geo- and hydrochemical investigations were carried out, including X-ray diffractometry, microscopy, ICP-OES and AAS analysis and a sequential extraction procedure. Paleo bog iron ores (PBIOs) of Tertiary age, occurring within unconsolidated sands (Haltern-layers, Santonian-Lower Campanian), and glauconitic marlstones (Dülmen-layers, Lower Campanian) were examined. Results indicate that output from the PBIOs is responsible for the elevated As levels. Accounting their diverse mineralogy, five types of PBIOs were defined. Type-dependent, they at least partly fulfil all of the formulated requirements. The relations and behaviour of As sources and sinks in space and time could be clarified for the area of interest. The approach presented in this paper may offer a tool for identifying natural As sources worldwide.

Keywords

Arsenic source, Mobilization potential, Redox conditions, Bog iron ore, Haltern-layers, Germany

Introduction

Due to its toxicity, As in drinking water causes dramatic health problems worldwide. The most prominent example is Bangladesh. It is estimated that more than 25 million people there are supplied with drinking water exceeding the Bangladeshi As threshold value of 50 µg/l. Another 25 million people drink water containing 10-50 µg/l (Ravenscroft et al. 2005), thus exceeding WHO´s Guidelines for Drinking-Water Quality and US-EPA limitations (Smedley and Kinniburgh 2002). Also the German As threshold value was decreased from 40 to 10 µg/l in 1996 (Rott and Meyer 2000). Without any treatment, about 1.5 million people in Germany would consume water containing more than 10 µg/l As (Heinrichs and Udluft 1996). Considering developments like these, it is not surprising that scientists, as well as water suppliers and the public, show an increasing interest in As, especially its sources, behaviour and regional distribution in groundwater and soils. Thus, many problem areas showing elevated As concentrations – a review is given by Smedley and Kinniburgh (2002) – could be identified and described worldwide. Most of them receive their As from natural sources, i.e. geothermal waters (e.g. Aiuppa et al. 2003, Planer-Friedrich 2004, Rosenberg et al. 1999) and especially the weathering of As-bearing minerals (e.g. Acharyya et al. 2000, Armienta et al. 2001, García-Sanchez et al. 2005, Goldberg et al. 1995, Gómez et al. 2006, Heinrichs and Udluft 1996, Matschullat 1999, Ravenscroft et al. 2005, Schreiber et al. 2000, Smedley and Kinniburgh 2002, Wendland et al. 1999). The latter include primary, mainly sulfidic, As minerals like arsenopyrite (FeAsS) or realgar (AsS), but also many rock-forming minerals are able to incorporate As or bind it to their crystal structure. Important examples are pyrite (FeS_2) and goethite (FeOOH) which each can contain As concentrations in percent values (by weight). Certain clay minerals and Mn-(hydr)oxides are further potential host minerals (Smedley and Kinniburgh 2002), also glauconite may be an As sink, even though of minor importance (Mertens et al. 2001). Under certain hydrochemical conditions – reducing in the case of goe-

thite, oxidizing in the case of pyrite – the bound As can be remobilized and enter the groundwater and, finally, the drinking water (McGeehan 1996, Rochette et al. 1998).

In 2001, elevated As concentrations (> 50 mg/kg) were discovered in soils of the Heubach plain, Northrhine-Westphalia, Germany (Fig. 1). Peronne (2003) found that the As is predominantly occurring in soils influenced by groundwater, i.e. gleys and podsol gleys which are widespread in the area surrounding the Heubach river where the element is bound to Fe(III)-hydroxides. Most significant As enrichments (> 500 mg/kg) could be detected in bog iron ores, concretions from goethite and lepidocrocite which are formed within the zone of groundwater oscillation. While Peronne (2003) did not deal with the As source responsible for the elevated concentrations, he was able to exclude an anthropogenic input from mining, industrial emissions, wastewaters or agriculture.

To identify the natural, i.e. geological, As source, a catalogue of conditions has been formulated (Table 1). A "candidate" rock should fulfil all of these requirements in order to be classified as a source for elevated soil As. The conditions which should be checked step by step are as follows:

Condition 1: Link between As source and sink

The As-bearing rocks (now referred to as "source") should be hydro(geo)logically linked with the problem area (in this case, the affected soils of the Heubach plain; now referred to as "sink") to make sure that As mobilized from the source can be found in the sink. Although this condition is intuitively agreeable, it should be checked carefully if the potential source is located upstream from the sink or if the sink can be reached by vertical groundwater flow that interacted with the source in advance. Thus, its As will be available in the sink through transport in groundwater or surface run-off. Besides the consultation of maps and own geological and hydro(geo)logical mapping, tracer tests offer a possibility to gather the information required to check this condition, especially in hard rock aquifers.

Condition 2: Mineralogy

To be a potential As source, a rock has to be an As sink as well. Ergo, it must contain minerals showing an affinity towards As and which are thus able to incorporate it into their crystal structure or bind it to their surfaces. As mentioned before, Fe-hydroxides and pyrite, for example, are able to do so. This way, a mineralogical analysis of the material of interest is crucial for the given task.

Condition 3: Total As concentration

The source should contain As concentrations significantly exceeding the geogenic background values. Since soils represent young, subrecent developments, a material with a low As content is unlikely to be the source because it would take a too long (geological) time span for mobilization and transport to create the high As concentrations in the sink. Thus, a highly-enriched As source will be expected.

Condition 4: Arsenic fractionation / Mobilization potential

A material enriched in As is not qualified to be a source if the As is bound so strongly to the host mineral that it cannot be mobilized under natural conditions. For that reason, it is highly recommended to investigate if there is potentially soluble As, and in what quantities. A possible method to determine As fractionation and mobilization potential will be described later.

Condition 5: Actual mobilizability / Redox conditions

Since As will only become mobile under certain hydrogeochemical conditions, it is worth having a look at the predominant Eh-pH-milieu. In particular, the groundwater redox potential should be analyzed carefully as it exerts the most important influence on As speciation and mobility.

Condition 6: As output

After identification of potentially soluble As in significant quantities and suitable hydrochemical conditions, the actual As output from the source should be estimated in a last step. An

assessment of stream sediments, as well as surface water and groundwater, will indicate if, and to what extent, there is an As output from the source.

After the successful identification of the As source, a simple model concerning As transport in time and space can be set up. The model can be valuable in understanding the development of sources and sinks over time and for predicting other existing and future problem areas.

Investigation area

The investigation area is located in the northwestern part of Northrhine-Westphalia in northwestern Germany (Fig. 1a). It is mainly an agricultural region with a few cities, each with less than 50.000 population (i.e. Coesfeld, Dülmen, Haltern). Morphologically, it is relatively flat with altitudes of about 50 m a.s.l. in the western part (around the river Heubach) and up to 90 m a.s.l. on a ridge between Coesfeld and Dülmen. The ground level in the southern part (between Dülmen and Haltern) is anthropologically influenced by the surface exploitation of quartz sands from the Haltern-layers (Santonian–Lower Campanian, up to 300 m in thickness). This stratigraphical unit covers the western and southern parts of the investigation area while in the northern and eastern parts it is overlain by sandy limestones of the Dülmen-layers (Lower Campanian, about 50 m in thickness) which build up the aforementioned morphological ridge. The Dülmen-layers are concordantly overlain by marly limestones, the Holtwick-layers, which drain into a different catchment and, therefore, are of no interest in this study (Fig. 1c). The Cretaceous rocks are mostly covered by a thin (<3 m) overlay of glacial sands and marly ground moraine deposited during the Pleistocene age. The whole area is part of a bigger syncline structure filled with Cretaceous sediments called the Münsterland Cretaceous Basin (Fig. 1b; Braun and Thiermann 1975, Grabert 1998).

Due to the shallow groundwater table around the receiving water courses (<2 m), gley and podsol gley soils, including close-to-surface bog iron ores, could develop from the sandy sub-

stratum, i.e. the Haltern-layers. In the Heubach plain itself, swampy areas arose during the Holocene. The area´s main receiving water course is the river Heubach which is supplied by smaller streams, like Kannebrooksbach and Sandbach, and a large number of agricultural drainage ditches. Both the Dülmen-layers and the Haltern-layers drain into the Heubach system whose main flow direction is southeastwards (Fig. 1c).

The quite unconsolidated sands of the Haltern-layers play an important role as a granular aquifer for a large section of western Northrhine-Westphalia. About 80 million m^3/a of water are extracted for public supply and, in addition, numerous private wells are used for self-supply with drinking water and agricultural requirements. The Dülmen-layers contain little fissure water which is hardly exploited with the majority pouring into the more permeable Haltern-layers (Hilden 1975, Michel 1995).

Materials and methods

Eight rock samples were taken from the Dülmen-layers, partly from stream beds, partly from artificial outcrops (excavations). The rocks are sandy limestones of greyish colour. They contain an average of 46.4 % (by weight) calcite (Table 3); darker greenish components were interpreted as glauconite. These marine limestones are very fossiliferous, containing molluscs and foraminifera.

The relatively unconsolidated sands of the Haltern-layers contain concretions from Fe minerals in their uppermost parts (Fig. 2) which originate from chemical weathering processes during the Tertiary age. Initially, the Haltern-layers were present as hard rocks, rich in calcite and glauconite but the region became continental at the end of the Cretaceous age and thus got exposed to surface weathering. During most of the Tertiary age, the climate was tropical-warm and wet (Braun 1969, Skupin 1995). Under these conditions, a deep chemical weathering of the rocks could take place, leading to the alteration of glauconite into Fe-hydroxides

which are responsible for the sands´ brownish and yellowish colours that can be observed nowadays. In late Miocene period, a drainage system developed with large swampy valleys and acid, reducing waters were produced which infiltrated the ground. These dissolved the calcite and the Fe-hydroxides – the loss of its carbonatic binder agent caused the present unconsolidated status of the sands to a depth of 60-70 m (Braun 1969). The dissolved Fe^{2+} was carried away through broad valleys where, in their marginal parts, it was partly oxidized to Fe^{3+}. Thus, it could be accumulated within the groundwater oscillation zone, leading to the formation of layers rich in (amorphous) Fe-hydroxides that illustrate paleo groundwater tables (Skupin 1995). Taking these genetic processes into consideration, the authors suggest these iron concretions be entitled "paleo bog iron ores" (PBIOs). With successive oxidation, the primarily amorphous hydroxides were partly transformed into crystalline phases like goethite. This differentiation process allowed the PBIOs´ classification into five different types (four of which are shown in Figure 2, all of them are described in the Results chapter).

Eighteen samples of PBIOs were collected in the western and southern parts of the investigation area, most of which were taken from active or shut-down sand pits. As a reference material, a sample of the pure, unconsolidated sands was also obtained.

Stream sediments were sampled at 13 locations, from the area of both the Haltern-layers and the Dülmen-layers. Surface water samples were taken from eleven of those locations and seven groundwater samples were collected from private water supplies (all water samples were obtained in February 2006).

The mineralogy of all solid samples was examined using X-ray diffractometry after grinding the samples down to powder grain size. A Siemens D 500 diffractometer (operation adjustments: 35 kV, 30 mA) was applied. Additionally, thin sections were produced from seven limestone samples and six samples of PBIOs. These were studied and photographed using the polarization microscope Leica DMRX. Calcite contents were determined using a CO_2-

gasometer whereby the volume of CO_2 produced by the digestion of the fine-ground sample by HCl (10%) is measured (Scheibler procedure).

For elemental analysis, the solid samples (à 3 g) were digested in aqua regia (21 ml HCl 37%, 7 ml HNO_3 65%). Additionally, a few samples were digested using hydrofluoric acid (HF/HNO_3 5:1) so as to dissolve the very stable silicate minerals that could also carry an As load. Thus, the total As concentrations could be measured. On the other hand, highly volatile AsF_3 and AsF_5 might be produced during digestion and lead to a loss of As from the sample. This phenomenon is described in the literature (e.g. Krachler and Emons 2000) but could not be generally quantified so far. For all solid samples, concentrations of As, Fe and Mn were determined using ICP-OES (SPECTRO Analytical Instruments SpectroFlame-EOP). For the sake of quality control, the As content of most solid samples was additionally measured by AAS (THGA furnace, Perkin Elmer AAnalyst 800). It was also used for determining As concentrations in the water samples while other cations were measured by ICP-OES, anions by IC (METROHM Compact IC 761). Redox potential and pH values of surface water and groundwater were determined on site at the time of sampling. The redox behaviour over time was studied by analyzing Eh data for selected wells in the range of both the Dülmen-layers and the Haltern-layers for the period from February 2000 to February 2006 (own sampling in 02/2006, previous data was provided by the *Abteilung für Abfallwirtschaft und Umweltkoordination, Kreis Coesfeld (Department of waste management and environmental coordination, Coesfeld district)*).

To examine the fractionation and mobilization potential of As, a sequential extraction procedure (SEP), consisting of six steps, was applied for eleven solid samples (two from the Dülmen-layers, six PBIOs and three stream sediments). The principle is to expose the pulverized sample to different solvents, each of which is able to extract mainly one specific As fraction. Wenzel et al. (2001) describe a SEP for As that was applied in this study but which was modi-

fied according to sample composition: because of the Dülmen-layers´ high calcite content, it seemed rational to include an extraction step targeting the As fraction bound to carbonates (fraction 3a, sensu Han and Banin 1995). Furthermore, a step aiming for the As fraction bound to Mn-(hydr)oxides (fraction 3b) was adopted from Zeien and Brümmer (1989). It was implemented because of very high Mn concentrations in some PBIOs, with a maximum as high as 20.9 % (Table 3). Table 2 illustrates the full procedure. The sample (2 g) was placed in 100 ml centrifugation tubes and 50 ml of the extraction reagents were added sequentially. After applying the extractant procedure for each step (Table 2), the tube was centrifuged for 15 minutes at 3000 rotations/min. Afterwards, the solution was filtered through 0.45 µm cellulose acetate filters into PE-bottles and was then prepared for As concentration measurement by AAS. Subsequent wash steps were implemented to gather As entrapped in or re-adsorbed by the remaining solid sample. The residual material was then used for the subsequent extraction step (Wenzel et al. 2001).

Fraction 1 represents the water-soluble and unspecifically bound portion of As in the sample, as well as easily soluble organic complexes. It is the most mobile fraction and corresponds approximately to the bioavailable As portion.

Fraction 2 includes the As specifically adsorbed to mineral surfaces. The extraction is based upon strong competition between arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}). The latter can replace the arsenate on the mineral surfaces and thus lead to As solution (Driehaus 2005).

Fraction 1 and *2* procedures were applied to all samples. Together, these make up the readily mobilizable share of As and are therefore of highest ecological relevance.

Fraction 3a was utilized only for the limestone samples from the Dülmen-layers. The As fraction bound to carbonates is targeted in this step. It must be considered a relatively mobile fraction since the bound As will be mobilized during calcite dissolution.

Fraction 3b was determined for all samples except the limestones. It represents the As bound to Mn-(hydr)oxides.

Fractions 4 and *5* include the As bound to amorphous and crystalline Fe-(hydr)oxides, respectively. Under oxidizing conditions, these represent the most important As sinks. This is because of their strong binding affinity towards As and their great abundance (Smedley and Kinniburgh 2002). The oxalate utilized as an extraction agent leads to complexation and, thus, solution of Fe whereby the bound As is also mobilized. Because of the stronger binding forces in crystalline mineral phases, a more powerful extractant has to be used to win *Fraction 5*. This can be achieved by adding ascorbic acid to the NH_4-oxalate. Ascorbic acid is a very effective dissolution agent for Fe-(hydr)oxides as it rapidly saturates the (hydr)oxide´s surface, leading to Fe^{2+} release to solution (Banwart et al. 1989, Postma 1993). *Fraction 4* and *5* procedures were applied for all samples.

Between *Fraction 4* and *Fraction 5*, the authors placed the important borderline between "potentially mobilizable" and "firmly bound" As. This is because of the different binding geometries of the arsenate to the host minerals. In crystalline Fe-(hydr)oxides like goethite, there are mainly bidentate arsenate complexes on the surfaces which, due to shorter Fe-As ion distances, are far more stable than the monodentate complexes dominating in amorphous phases like ferrihydrite. During the aging processes of amorphous Fe-(hydr)oxides, one can observe an increasing polimerization in the mineral structure whereby ferrihydrite changes slowly into goethite, leading to a greater stability of the arsenate complexes (Waychunas et al. 1993, Gautier et al. 2006).

The size of *Fraction 6*, i.e. residual As, was calculated from the difference between the total As concentration (after digestion with HF/HNO_3) and the sum of As extracted from the samples in *Fractions 1* to *5*. For the stream sediments, none of which were digested with hydro-

fluoric acid, the total As concentrations measured after aqua regia digestion were taken as a basis. The residual fraction is estimated to mainly include As bound to silicate minerals.

Results

Dülmen-layers

XRD results are quite homogenous for the rock samples. In all of them, quartz and calcite are the main mineral phases. Nevertheless, clay minerals (kaolinite, montmorillonite), goethite and glauconite could also be identified. Also, some samples contain small quantities of heavy minerals like rutile and titanite. These findings were fully confirmed by microscopical investigations (Fig. 3a).

All thin sections show mainly sub-angular quartz grains in calcitic binder agent. Moreover, fresh green glauconite grains, as well as light brownish goethite grains (probably originating from the oxidative alteration of glauconite), are to be observed. Areas of darker brown coloration within the goethite grains indicate the presence of amorphous Fe-hydroxides like ferrihydrite (Schwertmann & Cornell 2000). Such amorphous mineral phases cannot be detected using XRD. Furthermore, a rich foraminifera and mollusca fauna was revealed under the microscope (Fig. 3a). The stream sediments consist of hardly anything but quartz. Traces of rutile and, in some cases, calcite and clay minerals could be found while Fe-hydroxides were totally absent. Arsenic, Fe and Mn concentrations are shown in Table 3.

The sandy limestones of the Dülmen-layers have an average Fe content of 0.73 % (min. 0.47, max. 1.1 %) and an average As content of 4.5 ppm (min. 1.5, max. 8.4 ppm), measured after aqua regia digestion. After digestion with HF/HNO_3, considerable additional As could be determined, leading to an average concentration of 7.4 ppm. Thus, the total As content (including the silicate-bound share which is not dissolved by aqua regia and therefore referred to as "residual") can be calculated for every sample which is possible through a very close regres-

sion (correlation coefficient R^2=0.93) between As extracted by HCl/HNO_3 and by HF/HNO_3 (Hornburg 2003). The coefficient needed to calculate the total As content is obtained by dividing the average c(As-HF/HNO_3) by the average c(As-HCl/HNO_3). This is done for the samples digested with both acids, the result is then multiplied by every other sample´s c(As-HCl/HNO_3).

Soil and rock samples often show a narrow correlation between As and Fe concentrations (e.g. Mertens et al. 2001, Peronne 2003) but this could not be observed for the rock samples in this study. Besides, there does not seem to be any spatial tendency for the distribution of elevated As concentrations which appear, rather coincidently, among lower values.

Looking at the results of the SEP (Fig. 4), it becomes obvious that no exchangeable As (*Fraction 1*) is present in the samples and that only the stream sediment sample contains a significant proportion of surface-bound As (*Fraction 2*). In spite of the high calcite content of the hard rocks (Table 3), only an average of 9 % of the total As is bound to carbonates (*Fraction 3*) which is consistent with the finding that As concentrations show a slightly negative (R^2=0.50) correlation with calcite concentrations. In all samples, *Fraction 4* (stream sediment: 51 %, hard rocks: 29 % the average) is more important than *Fraction 5* (11 % and 15 %, respectively). Residual As (*Fraction 6*) occurs most significantly in the rock samples with a maximum of 60 %. A mobilization potential could be calculated since the borderline between "potentially mobilizable" and "firmly bound" As was placed between *Fractions 4* and *5*. An amount of 43 % of the total As in the Dülmen-layers can be potentially mobilized on average. But in spite of this quite high proportion, an absolute As amount of not more than 3.2 ppm (i.e. calculated average for all rock samples) would be extractable under natural conditions. However, to properly quantify the absolute amount of As in the Dülmen-layers, one would have to multiply the mass of rock by its As concentration (see Conclusions). For the stream sediments, the relative share of 77 % converts to an absolute amount of 1.6 ppm As on aver-

age. Surface water and groundwater in the area are slightly basic with a pH value of about 8; the groundwater was oxidizing in 02/2006 (Eh value: 366 mV on an average). Checking the Eh development over time (years 2000-2005) for wells within the Dülmen-layers, only very few single values <200 mV were found and none <120 mV, which is in contrast to the range of the Haltern-layers (see next chapter). No As was found exceeding the detection limit in any water sample.

Haltern-layers

The sands of the Haltern-layers are barely anything but quartz. Nevertheless, their PBIOs show important differences in mineralogy and consolidation and were therefore subdivided into five types.

Type 1 PBIOs are rather unconsolidated concretions of darker brownish colours which occur bulb-like within the pure sands (Fig. 2). XRD results show quartz to be the only mineral detected. However, it is important to keep in mind XRD´s inability to reveal amorphous mineral phases. Under the microscope, it becomes clear that the quartz grains (sub-angular to well-rounded) are bound by an Fe-rich binder agent dominated by rather amorphous Fe-hydroxides.

Type 2 PBIOs are significantly harder and manually hard to break. In outcrops, they appear as reddish-brown to black ribbons and dykes within the sands (Fig. 2). Again, quartz is the dominating mineral but XRD also reveals some goethite which could be confirmed in the thin sections as part of the Fe-rich binder agent.

Still harder iron concretions (hardly breakable even with a hammer) are those of *Type 3* PBIOs. They are of darker brown and black colours, with polished, shining surfaces (Fig. 2). Besides quartz, goethite is clearly detectable by XRD. Microscopically, goethite is recognizable in the samples by its partly oolithic structures (Pichler and Schmitt-Riegraf 1993, Fig. 3b).

They also occur, but less frequently, in *Type 2* PBIOs, while they are missing completely in *Type 1*.

The authors suggest PBIO *Types 1 to 3* to be representative of different iron ore oxidation ("aging") stages. This aging process (i.e. the oxidative transformation of amorphous Fe-phases like Ferrihydrite) leads to a successively better crystallinity and thus greater stability of the Fe-hydroxides (Waychunas et al. 1993, Gautier et al. 2006).

Type 4 PBIOs are red-coloured sandstones with a hardness comparable to *Type 2* PBIOs. However, they do not appear as ribbons but rather bulb-like in the outcrops. The Fe mineral within this type is siderite ($FeCO_3$) and neither goethite nor amorphous Fe-hydroxides could be observed in XRD or thin sections. Nevertheless, they are partly covered by an oxidation crust that can be described as *Type 2* PBIO, regarding its consolidation and mineralogy (Fig. 2).

Another somewhat exotic PBIO is *Type 0*. This occurs as reddish to black and ribbon-like in the outcrops but the material is far softer than *Type 2* PBIOs. XRD merely showed quartz but in some parts, the binder agent is rich in oolithic structures, indicating goethite presence. In the thin sections, grains of calcite and glauconite (within the alteration process into goethite) and even foraminifera shells also turned up. These phenomena are unique within all PBIOs.

Stream sediments from the range of the Haltern-layers are very similar to those from the Dülmen-layers. Apart from quartz, only traces of rutile were found by XRD and there seem to be no calcite, clay minerals or Fe-hydroxides in the samples.

Table 3 data make it clear that the pure, unconsolidated sands are very poor in As and heavy metals, whereas the PBIOs show an average As concentration (43.9 ppm) ten times higher than the one found in the Dülmen-layers. However, As concentrations within the PBIOs are extremely variable, even within one PBIO type. Exceptions from this are *Type 4* (generally low As) and *Type 0* (generally high As). In contrast, Fe concentrations are more stable and

show a clear dependence upon PBIO type (Fig. 2, Table 3) with the overall average (type-independent) being 14.9 % (3.0-29.5 %) Fe.

Iron concentrations increase with rising degree of crystallinity of the Fe-hydroxides (PBIO *Types 1* to *3*). Like in the Dülmen-layers, a regression between As and Fe cannot be observed (not even within the different PBIO types), and tendencies in spatial distribution are also missing. Neighbouring high and low As concentrations, even in the same outcrop, seem to be the rule rather than the exception. The missing correlation between Fe and As within the Dülmen-layers as well as the PBIOs might be explained by irregular mobilization during chemical weathering, taking into account the incongruent release of As with Fe^{2+} during the reductive dissolution of Fe-hydroxides (Pedersen et al. 2006).

However, PBIOs can be considered quite effective As and metal sinks, compared to the pure sands they appear in. HF/HNO_3 digestion extracted an additional 29 % As from the samples, leading to a total average As content of 56.6 ppm in the PBIOs. Yet, due to the low number of samples extracted and the evident heterogeneity of the material, this figure must be regarded a rough estimate. With an average of 3.9 ppm, the stream sediments contain almost twice as much As as their pendants from the area of the Dülmen-layers. Checking the covariation of Fe and As within the stream sediments from both ranges (Dülmen- and Haltern-layers), a narrow correlation with R^2=0.88 could be observed.

Akin to the SEP results from the Dülmen-layers, *Fraction 1* could not be detected in any sample from the Haltern-layers (Fig. 5). The finding that surface-bound As (*Fraction 2*) is present in significant quantities only in the stream sediments (17 % the average) is also analogous. In spite of partly high Mn concentrations within the PBIOs (up to 20.9 % in sample #11, *Type 0*, Table 3), As bound to Mn-(hydr)oxides (*Fraction* 3) was not found at all. Therefore, the Mn concentration was measured in the extracted fraction of sample #11 in order to control the applicability of the method. Nearly 75 % of the total Mn were recovered, hence the selec-

tive extraction was successful. Further results for the PBIOs were type-dependent: while the main part of As in *Type 1* (65 %) is bound to amorphous Fe-hydroxides (*Fraction 4*), *Type 2* is dominated by As attached to crystalline Fe-hydoxides (*Fraction 5*; 57 % the average). Residual As (*Fraction 6*) is most important (64 % the average) in *Type 3* PBIOs. *Type 0* shows an As fractionation similar to *Type 2*, but is dominated even more by *Fraction 5* (83 %).

The calculated average mobilization potential for all PBIOs is 24 % of the total As. Nevertheless, there are important variations between the different types. *Type 1* PBIOs have the most prominent share (68 %) of potentially mobilizable As; it is much smaller in *Type 2* (12 %), and especially *Type 3* (3 %), due to the higher percentage of the "firmly bound" *Fractions 5* and *6*. *Type 0* PBIO shows a relatively small mobilization potential (13 %). However, because of its high absolute As concentrations, it must be considered an important As source. An amount of 86 % of the total As found in the stream sediments can be mobilized, meaning an absolute amount of 3.4 ppm As on average which is more than twice as much as in the range of the Dülmen-layers.

Near-neutral pH values were found for surface water (pH=7.2) and groundwater (pH=7.3), with most samples showing oxidizing conditions (average Eh value for surface water: 474 mV, for groundwater: 345 mV). Nonetheless, strongly reducing conditions (Eh=-219 mV) were detected in one groundwater sample which also contains an elevated Fe concentration of 8.07 mg/l. Arsenic above the detection limit could only be measured in one groundwater sample (8 µg/l). Thus, no excess over the German As threshold value for drinking water (10 µg/l) could be found.

Analyzing the behaviour of the groundwater redox potential over time, striking fluctuations were pointed out. As an example, Figure 6 shows the temporal changes of Eh in one well within the Haltern-layers during a time span of six years (own sampling in 02/2006, previous data was provided by the *Abteilung für Abfallwirtschaft und Umweltkoordination, Kreis*

Coesfeld (Department of waste management and environmental coordination, Coesfeld district)).

In 2002, the Eh curve dropped below the line of As species transition: As(V) was then reduced to the far more mobile As(III) – this reduction starts rapidly under anaerobic conditions (Stollenwerk 2002, McGeehan 1996) – suggesting that As mobilization was possible during that time span. Taking into consideration the process of Fe-hydroxide dissolution (a procedure that also leads to mobilization of possibly bound As), the perception is even more striking: for 30 % of the overall time, the curve is below the "dissolution line". Ergo, between 2000 and 2006, it was possible to mobilize As for almost two years altogether, thus probably leading to As output from the host minerals and, hence, input into groundwater. This Eh development is characteristic for the examined wells within the Haltern-layers, all of which are showing at least temporarily values <120 mV.

In consequence, it could be proved that reducing conditions (concerning As behaviour) occur at least locally and temporarily within the Haltern-layers that contain the PBIOs. Additionally, the swampy areas around the river Heubach might also be sources for reducing waters that could enter the subsurface and extract Fe and As from host minerals.

Conclusions

Following the conditions catalogue for a natural As source formulated earlier, it is now possible to compare the examined "candidate rocks".

Condition 1: Link between As source and sink

The Dülmen-layers (dewatering into the affected area) as well as the PBIOs in the uppermost part of the Haltern-layers (Heubach river bed and plain lying within this unit) fulfil the condition. They are both hydro(geo)logically linked with the As sink, thus potentially mobilized As may be found in the soils of the Heubach plain.

Condition 2: Mineralogy

Goethite, amorphous Fe-hydroxides, glauconite and clay minerals as potential As sinks are components of the Dülmen-layers. Nevertheless, an average Fe content of not more than 0.73 % indicates that those minerals might not appear in large quantities. The PBIOs contain goethite (*Types 2, 3* and *0*) and amorphous Fe-hydroxides (*Types 1, 2, 3* and *0*). Microscopic analysis and Fe concentrations of nearly 15 % on average suggest that these mineral phases should be present in significant amounts. The condition can be considered fulfilled by both candidates.

Condition 3: Total As concentration

Arsenic concentrations within the Dülmen-layers (4.5 ppm after HCl/HNO_3 digestion) cannot be considered an important enrichment because the average As content is even lower than the background concentration for Cretaceous marlstones in Northrhine-Westphalia (7.5 ppm As) determined by Hornburg (1999). Moreover, they approximately coincide with the lower limit of the span of natural background As values in sedimentary rocks (5-10 ppm) sensu Smedley and Kinniburgh (2002). Since *Condition 3* requires As concentrations significantly in excess of the geogenic background levels, the Dülmen-layers do not match this requirement. It cannot be excluded that a small share of the As pool in the Heubach plain derives from the Dülmen-layers. Nevertheless, the authors consider that only a very small fraction of the total As in the Dülmen-layers was available for mobilization and transport during the development of the sink. It will not be enough to explain the high As contents in the affected subrecent soils. However, one should keep in mind that in general, a large mass of rock, even with low concentrations, might be an effective source if connected with a sink of small volume. This might especially be important in cases where a high-As "candidate rock", that also matches the other conditions, could not be identified.

In contrast to the Dülmen-layers, the PBIOs can be declared to be partly enriched in As, considering an average concentration (all PBIO types) of 43.9 ppm (after HCl/HNO_3 digestion). In spite of the high variability of As content and the lack of distributive tendencies, one can generally expect significantly elevated values, in view of some samples exceeding 100 ppm As (Table 3). This is not valid for *Type 4* (siderite PBIOs, 1.6 ppm As on average) which is certainly not an As source.

Condition 4: Arsenic fractionation and mobilization potential

An amount of 43 % of the total As within the Dülmen-layers could potentially become mobile, most of which is bound to amorphous Fe-hydroxides deriving from glauconite alteration. Nevertheless, this impressive proportion corresponds to only small absolute As amounts (3.2 ppm on average). Nearly half of the total As is bound in the residual portion which, therefore, is the most important fraction within the Dülmen-layers. It could be argued that this As proportion is bound firmly to glauconite and might become potentially mobile through oxidative alteration of the minerals into Fe-hydroxides in the (geological) future.

Arsenic fractionation and mobilization potential within the PBIOs is heavily type-dependent. While as much as 68 % of the total As is potentially mobile in *Type 1* PBIOs, *Types 2* and especially *3* show by far lower potentials. As mentioned before, *Type 0* PBIO, despite its relatively low mobilization potential (13 %), is an effective As source due to its high concentrations.

Conditions 5 and 6: Redox conditions and As output

SEP results clearly show that amorphous Fe-hydroxides are the most important host minerals for potentially mobile As in the examined rocks. To really mobilize this As share, reducing groundwater conditions will be needed. In the area of the Dülmen-layers, redox circumstances are oxidizing extensively, thus preventing As mobilization. Consequently, no significant As

concentrations were found in stream sediments, surface water and groundwater. Arsenic output from the Dülmen-layers could not be detected.

In contrast, at least temporarily and locally, reducing groundwater conditions were verified within the Haltern-layers containing the PBIOs. Therefore, As(V) bound to amorphous hydroxides could be mobilized by reduction to As(III) or reductive dissolution of the minerals themselves. As a result, higher As concentrations were found in the area´s stream sediments and, at least, in detectable levels in its groundwater. Due to fluctuations in the redox conditions (Fig. 6), it is probable that As output from the PBIOs varies heavily over time. However, it is likely to be able to reach significant quantities.

Unlike the sandy limestones of the Dülmen-layers, the PBIOs within the Haltern-layers fulfil all formulated conditions for classification as an As source. The authors therefore suggest that As output from the PBIOs is the cause for the elevated As concentrations in the affected soils of the investigation area. However, for a proper quantification of this phenomenon, it would be crucial to know the geographic distribution and the amount of the PBIOs in the area. Dahm-Arens (1972) tried to map the iron ores from a morphological point of view, i.e. she used the fact that due to their greater hardness, the iron ores form a positive relief within the otherwise rather flat area covered by the Haltern-layers. Using this technique, she may well have registered PBIO *Types 2* and *3* (and maybe *4*) but surely not *Types 0* and *1* which are nearly as unconsolidated as the sands in which they are found. To reiterate, it is precisely these PBIO types that must be considered as effective As sources because of their high As concentrations and mobilization potential, respectively. Theoretically, they might be widespread at shallow depths all over the area. The construction of a map showing the distribution of the different types of PBIOs suggested in this study might be an object of future research.

Finally, it must be said that the examined PBIOs are not the primary As sources. They are, rather, As sinks having received their As from a primary source (which is presumed to be the

Haltern-layers in their original development, preserved in an altered form as *Type 0* PBIOs) and now acting as secondary sources. Also the subrecent bog iron ores occurring in soils around the river Heubach are supposed to have this double function (i.e. secondary sink/tertiary source). Thus, As fixed in the soils will be remobilized and flushed out in the future, generating a tertiary sink elsewhere. Figure 7 illustrates schematically the investigation area´s As flow in space and time.

Modified according to the respective geological and hydrological conditions in the region of interest, the approach introduced in this study could be a helpful tool for identifying natural As sources in problem areas worldwide.

Acknowledgements

The authors wish to thank the *Abteilung für Abfallwirtschaft und Umweltkoordination (Department of waste management and environmental coordination), Kreis Coesfeld* for financial support, the contribution of spatial and most of the hydrochemical data and for general participation in this study. To the *Department of Mineralogy* (Prof. Dr. Klaus Mezger and his team) and the *Laboratory for Environmental Analytics* (Alexandra Reschka and her team), both Münster University, as well as to Andrea Müller, Stephan König and Ralf Orzol, we are thankful for advice and support during laboratory work. Our gratitude to David Barry (*DLB Environmental*, Surrey, UK) for critical editorial review of the manuscript.

References

Acharyya SK, Lahiri S, Raymahashay BC, Bhowmik A (2000) Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. Environmental Geology 39: 1127-1137

Aiuppa A, D´Alessandro W, Federico C, Palumbo B, Valenza M (2003) The aquatic geochemistry of arsenic in volcanic groundwaters from southern Italy. Applied Geochemistry 18: 1283-1296

Armienta MA, Villaseñor G, Rodriguez R, Ongley LK, Mango H (2001) The role of arsenic-bearing rocks in groundwater pollution at Zimapán Valley, México. Environmental Geology 40: 571-581

Banwart S, Davies S, Stumm W (1989) The role of oxalate in accelerating the reductive dissolution of hematite (α-Fe_2O_3) by ascorbate. Colloids Surfaces 39: 303-309

Braun FJ (1969) Bericht über die Vorkommen reiner Quarzsande (SiO_2-Gehalt über 99 %) im Gebiet von Haltern i. Westf. (Comment on the occurence of pure quartz sands (content of SiO_2 above 99 %) in the area of Haltern/Westphalia, Germany). Geologisches Landesamt Nordrhein-Westfalen, Krefeld, Germany [in German]

Braun FJ, Thiermann A (1975) Erläuterungen zu Blatt C 4306 Recklinghausen – Geologische Karte von Nordrhein-Westfalen 1:100000 (Comments on the geological map C 4306 Recklinghausen – Geological map of Northrhine-Westphalia 1:100000). Geologisches Landesamt Nordrhein-Westfalen, Krefeld, Germany [in German]

Dahm-Arens H (1972) Entstehung der Eisenschwarten in den Kreidesanden Westfalens (Formation of iron crusts within Cretaceous sands in Westphalia, Germany). Fortschritte in der Geologie von Rheinland und Westfalen 21, 133-142 [in German]

Driehaus W (2005) Adsorption von Arsen aus Trink- und Grundwasser: Bedeutung von Konkurrenzeffekten (Arsenic adsorption from drinking water and groundwater: the importance of ion competition). Paper presented at the conference „Arsen 2005“, Leipzig, 19-20 April 2005 [in German]

García-Sanchez A, Moyano A, Mayorga P (2005) High arsenic contents in groundwater of central Spain. Environmental Geology 47: 847-854

Gautier J, Grosbois C, Courtin-Nomade A, Floc´h JP, Martin F (2006) Transformation of natural As-associated ferrihydrite downstream of a remediated mining site. European Journal of Mineralogy 18: 187-195

Goldberg G, Lepper J, Röhling HG (1995) Geogene Arsengehalte in Gesteinen und Grundwässern des Buntsandsteins in Südniedersachsen (Geogenic arsenic contents in rocks and groundwater of the Buntsandstein formation in southern Lower Saxony, Germany). Zeitschrift für Angewandte Geologie 41: 118-124 [in German]

Gómez JJ, Lillo J, Sahún B (2006) Naturally occuring arsenic in groundwater and identification of the geochemical sources in the Duero Cenozoic Basin, Spain. Environmental Geology 50: 1151-1170

Grabert H (1998) Abriß der Geologie von Nordrhein-Westfalen (The Geology of the State of Northrhine-Westphalia, Germany). Stuttgart: Schweizerbart [in German]

Han F, Banin A (1995) Selective sequential dissolution techniques for trace metals in arid-zone soils: the carbonate dissolution step. Communications in Soil Science and Plant Analysis 26: 553-576

Heinrichs G, Udluft P (1996) Geogenes Arsen in Grundwässern Deutschlands unter Berücksichtigung der Aquifergeologie (Geogenic arsenic in German groundwater allowing for the aquifer´s geology). Zeitschrift der Deutschen Geologischen Gesellschaft 147: 519-530 [in German]

Hilden HD (1975) Erläuterungen zu Blatt C 4306 Recklinghausen – Hydrogeologische Karte von Nordrhein-Westfalen 1:100000 (Comments on the hydrogeological map C 4306 Recklinghausen – Hydrogeological map of Northrhine-Westphalia 1:100000). Geologisches Landesamt Nordrhein-Westfalen, Krefeld, Germany [in German]

Hornburg V (1999) Arsen in der Geosphäre (Arsenic in the geosphere). In: Rosenberg F and Röhling HG (eds) Arsen in der Geosphäre. Schriftenreihe der Deutschen Geologischen Gesellschaft 6: 73-80 [in German]

Hornburg V (2003) Vergleich von Methoden zur Bestimmung der Gesamtgehalte von Haupt- und Spurenelementen in Böden (Königswasser-Extrakt : Flusssäure-Aufschluss) (Comparison of total contents of principal elements and trace elements in soils (aqua regia vs. hydrofluoric acid)). Mitteilungen der Deutschen Bodenkundlichen Gesellschaft 102, 731-732 [in German]

Krachler M, Emons H (2000) Extraction of antimony and arsenic from fresh and freeze-dried plant samples as determined by HG-AAS. Fresenius Journal of Analytical Chemistry 368: 702-707

Matschullat J (1999) Arsen in der Geosphäre (Arsenic in the geosphere). In: Rosenberg F and Röhling HG (eds) Arsen in der Geosphäre. Schriftenreihe der Deutschen Geologischen Gesellschaft 6: 5-20 [in German]

McGeehan SL (1996) Arsenic sorption and redox reactions: Relevance to transport and remediation. Journal of Environmental Science and Health 31: 2319-2336

Mertens J, Klinger C, Schreiber U, Wiegand J (2001) Geogene Arsen- und Schwermetallanreicherungen im Essener Grünsand des mittleren Ruhrgebietes (Geogenic enrichments of arsenic and heavy metals within the Essen greensand in the central Ruhr area, Germany). Paper presented at the 153rd annual conference of the Deutsche Geologische Gesellschaft, Kiel, 2-6 October 2001 [in German]

Michel G (1995) Grundwasser – Dargebot, Nutzung und Gefährdung (Groundwater – resources, use and endangerment). In: Geologisches Landesamt Nordrhein-Westfalen (ed.) Geologie im Münsterland: 118-127 [in German]

Pedersen HD, Postma D, Jakobsen R (2006) Release of arsenic associated with the reduction and transformation of iron oxides. Geochimica et Cosmochimica Acta 70: 4116-4129

Peronne O (2003) Pedogene Arsenanreicherungen in grundwasserbeeinflussten Böden in der Heubachniederung, Kreis Recklinghausen (Pedogenic enrichments of arsenic in soils influenced by groundwater in the Heubach plain, Recklinghausen district, Germany). Master thesis, University of Bochum, Germany [in German]

Pichler H, Schmitt-Riegraf C (1993) Gesteinsbildende Minerale im Dünnschliff (Rock-forming minerals in thin sections). 2nd ed., Stuttgart: Enke [in German]

Planer-Friedrich B (2004) Volatile Arsenic in Aquatic Environments. Freiberger Forschungshefte C 503: 1-172

Postma D (1993) The reactivity of iron oxides in sediments: a kinetic approach. Geochimica et Cosmochimica Acta 57: 5027-5034

Ravenscroft P, Burgess WG, Ahmed K, Burren M, Perrin J (2005) Arsenic in groundwater of the Bengal Basin, Bangladesh: Distribution, field relations, and hydrogeological setting. Hydrogeology Journal 13: 727-751

Rochette EA, Li GC, Fendorf SE (1998) Stability of Arsenate Minerals in Soils under Biotically Generated Reducing Conditions. Soil Science Society of America Journal 62: 1530-1537

Rosenberg F, Mittelbach G, Kirnbauer T (1999) Geogene Arsengehalte im Bereich der Wiesbadener Thermalquellen (Geogenic arsenic concentrations in the area of the thermal springs in Wiesbaden, Germany). In: Rosenberg F and Röhling HG (eds) Arsen in der Geosphäre. Schriftenreihe der Deutschen Geologischen Gesellschaft 6: 101-106 [in German]

Rott U, Meyer C (2000) Die unterirdische Trinkwasseraufbereitung – ein Verfahren zur rückstandsfreien Entfernung von Arsen (Subterranean treatment of drinking water – a

procedure for the residue-free removal of arsenic). Wasser und Abfall 10: 36-43 [in German]

Schreiber ME, Simo JA, Freiberg PG (2000) Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. Hydrogeology Journal 8: 161-176

Schwertmann U, Cornell RM (2000) Iron Oxides in the Laboratory – Preparation and Characterization. 2nd ed., Weinheim: Wiley

Skupin K (1995) Tertiär (The Tertiary). In: Geologisches Landesamt Nordrhein-Westfalen (ed.) Geologie im Münsterland: 66-70 [in German]

Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry 17: 517-568

Stollenwerk KG (2002) Geochemical Processes Controlling Transport of Arsenic in Groundwater: A Review of Adsorption. In: Welch AH, Stollenwerk KG (eds) Arsenic in Ground Water – Geochemistry and Occurrence: 67-100, New York: Springer

Waychunas GA, Rea BA, Fuller CC, Davis JA (1993) Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochimica et Cosmochimica Acta 57: 2251-2269

Wendland A, Rank G, Barth A (1999) Verteilung des Arsens in den Rotliegendsedimenten Sachsens (Distribution of arsenic in sediments from the Rotliegend formation in Saxony, Germany). In: Rosenberg F and Röhling HG (eds) Arsen in der Geosphäre. Schriftenreihe der Deutschen Geologischen Gesellschaft 6: 93-100 [in German]

Wenzel WW, Kirchbaumer N, Prohaska T, Stingeder G, Lombi E, Adriano DC (2001) Arsenic fractionation in soils using an improved sequential extraction procedure. Analytica Chimica Acta 436: 309-323

Zeien H, Brümmer GW (1989) Chemische Extraktionen zur Bestimmung von Schwermetallbindungsformen in Böden (Chemical extractions for the determination of heavy metal bonding forms in soils). Mitteilungen der Deutschen Bodenkundlichen Gesellschaft 59: 505-510 [in German]

List of Figures

Figure 1 Geographical and geological position of the investigation area (1a: in Northrhine-Westphalia; 1b: within the Münsterland Cretaceous Basin; 1c: geology, hydrology and distribution of elevated soil As in the investigation area)

Figure 2 PBIO types and their differences in mineralogy and Fe content

Figure 3 Examples of thin sections under the microscope (3a: rock sample from the Dülmen-layers; 3b: PBIO type 3; Q – Quartz, G – Glauconite, G(ox) – Glauconite, altered through oxidation, F – Foraminifera, Goe – Goethite)

Figure 4 SEP results for samples taken from the range of the Dülmen-layers

Figure 5 SEP results for samples taken from the range of the Haltern-layers

Figure 6 Temporal changes of groundwater redox potential (black curve) in one well within the Haltern-layers for six years (2000 to 2006). The darker greyish line marks the Eh borderline of species transition from As(V) to As(III) at a nearly constant pH value of 6.4. The lighter greyish line illustrates the beginning process of reductive dissolution of Fe-hydroxides

Figure 7 Model of the spatial and temporal development of As sources and sinks in the investigation area

Table 1 Catalogue of conditions for the identification of geogenic As sources

Condition No.	Description	Requirements – The As source should…	Possible examination methods
1	Link between As source and sink	… be hydro(geo)logically linked with the sink (surface run-off and/or groundwater flow direction should be vectored towards the sink)	Consultation of maps, (Hydro-)Geological mapping, Tracer tests etc.
2	Mineralogy	… contain potential As sinks (Fe-(hydr)oxides, pyrite etc.)	X-ray diffractometry (XRD), (Polarization) microscopy
3	Total As concentration	… contain As concentrations significantly exceeding the geogenic background values	Digestion of solid samples; As analysis using ICP-OES or AAS
4	As fractionation / Mobilization potential	… contain significant amounts of As potentially soluble under natural conditions	Sequential extraction procedure (SEP)
5	Actual mobilizability / Redox conditions	… be located within a hydrochemical environment suitable for As mobilization, e.g. reducing in the case of Fe-hydroxide being the As host	Measurement of Eh and pH in surface water and groundwater, ideally observation of these parameters for a longer time span
6	As output	… cause elevated As concentrations not only in the sink but also on transport pathways towards the sink	Determining As concentrations in surface water, groundwater and stream sediments

Table 2 Sequential extraction procedure

Fraction no.	As fraction	Extractant	Procedure	Reference
1	Exchangeable	$(NH_4)_2SO_4$ (0.05 M)	4 h shaking, 20 °C	Wenzel et al. 2001
2	Surface-bound	$NH_4H_2PO_4$ (0.05 M)	16 h shaking, 20 °C	Wenzel et al. 2001
3a	Bound to carbonates	NaOAc/HOAc (1 M, pH 5)	6 h shaking, 20 °C	Han and Banin 1995
3b	Bound to Mn-(hydr)oxides	NH_2OH-HCl (0.1 M) + NH_4OAc (1 M, pH 6)	30 min shaking; wash step: 25 ml NH_4OAc (1 M, pH 6), 10 min shaking	Zeien and Brümmer 1989
4	Bound to amorphous Fe-(hydr)oxides	NH_4-oxalate (0.2 M, pH 3.25)	4 h shaking in the dark; wash step: 25 ml NH_4-oxalate (0.2 M, pH 3.25), 10 min shaking in the dark	Wenzel et al. 2001
5	Bound to crystalline Fe-(hydr)oxides	NH_4-oxalate (0.2 M) + ascorbic acid (0.1 M), pH 3.25	30 min in a water basin (96 °C); wash step: 25 ml NH_4-oxalate (0.2 M, pH 3.25), 10 min shaking in the dark	Wenzel et al. 2001
6	Residual	As (total) – As (sum steps 1-5)		

Table 3 Analytical data for the examined solid samples (HCl/HNO_3 digestion)

Range	Sample type	Sample #	As (ppm)	Fe (ppm)	Mn (ppm)	Calcite (wt. %)
Dülmen-layers	hard rock	1	6.1	6339	826	32.4
		2	3.2	8180	797	45.8
		3	6.3	10959	1306	41.1
		4	4.4	5528	499	47.0
		5	1.5	7164	842	58.6
		6	1.6	4650	412	52.8
		7	4.7	6428	736	48.7
		8	8.4	9038	952	44.8
Haltern-layers	pure sand	12, sand	<1.0	855	104	n/a
	PBIO type 0	10	159.0	108527	35069	n/a
		11	204.4	150003	209079	4.8
	PBIO type 1	12	1.5	45275	2749	n/a
		13	23.0	45675	2603	n/a
		16	58.5	29858	147	n/a
	PBIO type 2	9a	<1.0	161629	469	n/a
		9b	8.8	234663	1353	n/a
		9c	5.2	70310	996	n/a
		14a1	37.0	129236	20873	n/a
		14a2	25.0	83795	515	n/a
		14b2	3.4	227557	6526	n/a
		14b3	18.0	161660	5043	n/a
	PBIO type 3	15	9.8	294683	2310	n/a
		17	22.5	279565	1318	n/a
		18	139.9	249817	98	n/a
		19	39.0	144524	1018	n/a
	PBIO type 4	14b1	1.8	141465	2670	n/a
		14c	1.4	116071	2044	n/a
Dülmen-layers	stream sediment	20B	<1.0	2611	497	n/a
		21B	1.1	2111	749	n/a
		22B	1.3	2994	1023	n/a
		23B	2.1	2456	231	n/a
		24B	2.6	2384	703	n/a
		25B	3.1	1875	725	n/a
		26	2.2	3194	104	n/a
		27	4.0	3416	504	n/a
Haltern-layers	stream sediment	28B	1.0	2143	2038	n/a
		29B	6.8	7017	457	n/a
		30B	1.0	1475	352	n/a
		31B	2.4	2819	303	n/a
		32B	8.5	7849	611	n/a