Indirect Dating of Historical Land Use Through Mining: Linking Heavy Metal Analyses of Fluvial Deposits to Archaeobotanical Data and Written Accounts

Carolin Schmidt-Wygasch,[1,*] Silke Schamuhn,[2] Jutta Meurers-Balke,[2] Frank Lehmkuhl,[1] and Renate Gerlach[3]

[1]*RWTH Aachen University, Department of Geography*
[2]*University of Cologne, Institute of Prehistoric Archaeology*
[3]*Landschaftsverband Rheinland, Rheinisches Amt für Bodendenkmalpflege*

Man-made heavy metal contamination of floodplains has existed for centuries—even dating back to the Middle Ages. Up to now, these contaminants have been analyzed with very time-consuming and costly techniques. Thus, to determine historical heavy metal contamination, the aim of this study is to link the following approaches to generate better comprehensive and interdisciplinary understanding of historical land use of the Inde River, Germany: (1) to analyze anthropogenic heavy metal contamination of fluvial deposits from before ca. 2800 B.C. onward; (2) to investigate the historical land use by applying archaeobotanical data; and (3) to weave information from written accounts, in order to indirectly date fluvial deposits. In this study, heavy metal concentrations were measured *in situ* using X-ray fluorescence spectroscopy. Subsequently, pollen and macroremains dating from the Early Modern Period were archaeobotanically analyzed. Finally, historical accounts were studied. We found that fluvial deposits of varying age show distinctly different concentrations of lead, zinc, and copper. Moreover, the archaeobotanical analyses indicated intensive land use through farming, husbandry, and forestry. Finally, the written accounts described mining activities since the Roman Period or even before. In conclusion, linking these three interdisciplinary approaches is ideal for gaining insight into the historical anthropogenic impact on the environment. © 2010 Wiley Periodicals, Inc.

INTRODUCTION

As floodplain deposits are important sinks for sediments (Thonon, 2006), they potentially represent rich archives showing how land has been used over the millennia. Among other things, these sediments contain associated heavy metals (Hudson-Edwards, Macklin, & Taylor, 1997; Lecce & Pavlowsky, 1997; Middelkoop, 2000; Knox, 2006). The most important source for heavy metal contamination of sediments is mining activities within the river catchment (Macklin et al., 1994). Thus,

*Corresponding author; E-mail: c.wygasch@geo.rwth-aachen.de.

Geoarchaeology: An International Journal, Vol. 25, No. 6, 837–856 (2010)

Published online in Wiley Online Library (wileyonlinelibrary.com). DOI:10.1002/gea.20334

mining and other human activities over time have left a distinct imprint in the resulting pollution from heavy metals such as lead, zinc, and copper. The historical changes in chemical concentrations as a result of anthropogenic activities can thus be used for indirect dating of floodplain deposits (Macklin & Klimek, 1992; Lecce & Pavlowsky, 2001). Since post-depositional redistribution of heavy metals is insignificant (Macklin et al., 1994), fluvial sediments can depict the historical changes in contaminants. Such contamination can be linked to mining history (Aston, Martin, & Jackson, 1998). Generally, it should be possible to differentiate between conditions before and after mining pollution. Thus, some authors have been able to date such contamination more precisely and link it to particular fluvial strata (Davies & Lewin, 1974; Wolfenden & Lewin, 1977; Macklin et al., 1994; Swennen, Van Keer, & De Vos, 1994; Brewer & Taylor, 1997; Hudson-Edwards, Schell, & Macklin, 1999; Middelkoop, 2000; Raab, Hürkamp, & Völkel, 2005).

Pollen and other botanical remains provide another means of reconstructing the environmental changes in a watershed. From the time of initial agricultural settlement (in Central Europe, around 5500 B.C.), human activities predominantly influenced changes in the vegetation composition (Macaire et al., 2006; Lechterbeck, Kalis, & Meurers-Balke, 2009). By using the characteristic composition from pollen data, different epochs can be identified. Moreover, these pollen data can help to reconstruct changes in paleovegetation and land use (Meurers-Balke et al., 1999; Meurers-Balke & Kalis, 2006; Zimmermann, Meurers-Balke, & Kalis, 2006).

Historical written accounts also provide a wealth of information about land use over the ages. For example, the polymath Georgius Agricola described contemporary mining technologies in his most famous treatise *De Re Metallica* (1556).

The Inde River in Germany (Figure 1) is an ideal location for studying the historical, anthropogenic impact on the environment. Because this catchment area offered ample water, rich soils, and dense forests, it drew human settlement to this area as early as 5500 B.C. Eventually (ca. 100 B.C.), the local population began to mine the raw materials occurring within the catchment area of the Inde River. For example, calamine (zinc carbonate, $ZnCO_3$) outcrops were used to produce weapons, household utensils, and jewelry. During the Roman Period (ca. 50 B.C.–A.D. 450) the mining industry in the Inde River valley, near the city of Stolberg, blossomed (Werner, 1881; Willers, 1907; Holtz, 1994; Rothenhöfer, 2005), with the people supposedly mining calamine and lead. However, mining of the heavy metals zinc and lead stalled during the subsequent centuries but rebounded during the High Middle Ages (ca. 12th century), with heydays during the 18th and 19th centuries (De Vos et al., 1996, Hindel et al., 1996).

Thus, the principal aim of this paper is to determine the historical heavy metal contamination as a result of these activities in the lower river reach of the Inde River. However, since studies to dates have typically employed a range of techniques without considering their interlinkages, another important objective of this investigation is to combine the following three approaches to promote a comprehensive and interdisciplinary understanding of historical land use, with a specific focus on mining:

1. To analyze anthropogenic heavy metal contamination of fluvial deposits from ca. 2800 B.C. onward in order to make a potential distinction between overbank deposits of varying ages,

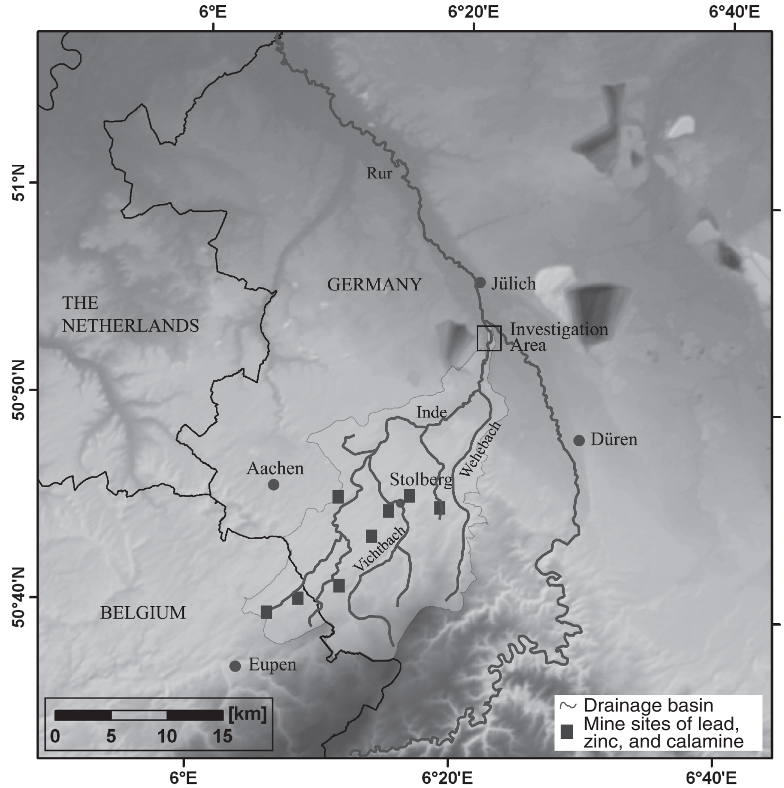

Figure 1. Catchment area of the Inde River. The squares represent the main zinc and lead mines. Generally, the mining and related processing developed along the Vichtbach River first, followed by the Inde River. Later, copper mills also used the water power of the lower part of the Wehebach River.

2. To investigate historical land use of the catchment area of the Inde River employing archaeobotanical data, and
3. To incorporate information from written accounts in order to date fluvial deposits indirectly and to place the analytical results in the context of the regional mining history.

GEOGRAPHIC AREA AND METHODS

Regional Setting and Sampling Locations

The investigation was carried out in the Lower Inde Valley (Figures 1, 2) near the village of Altdorf. The catchment area of the Inde River is located in western Germany near the borders with Belgium and the Netherlands (Figure 1). Some 54 km from its source in Belgium, at about 400 m asl, the Inde flows into the Rur River at 80 m asl. The catchment area covers approximately 350 km^2.

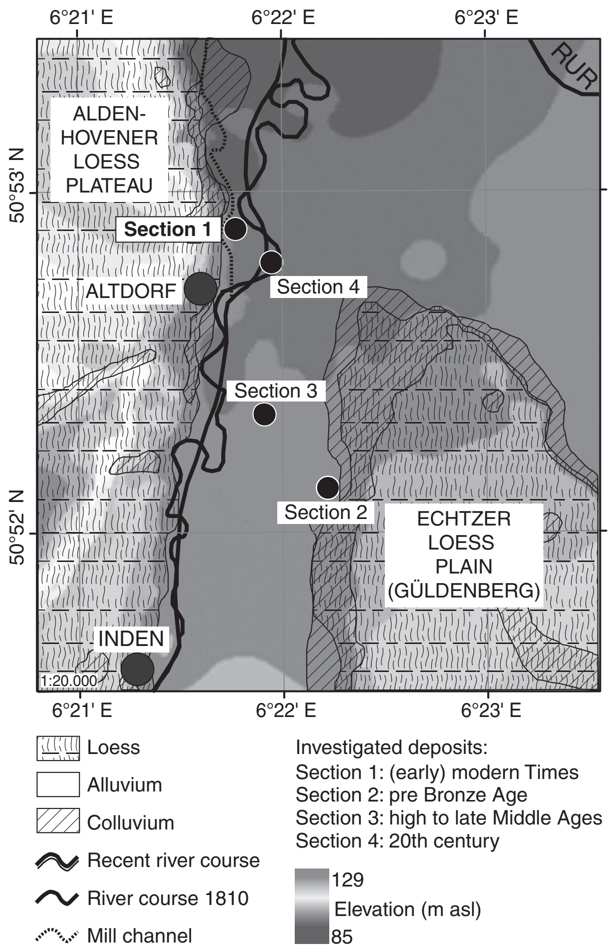

Figure 2. The Lower Inde valley and the location of the four sampling points. In the northeastern part, the floodplain of the Inde River meets the floodplain of the Rur River. In general, the Inde floodplain can be subdivided in older deposits in the eastern and younger deposits in the western part.

The climate in the catchment area is oceanic, with prevailing westerly winds, characterized by mild winters and mainly cool summers. The annual precipitation is between 600 and 800 mm, and the mean annual air temperature is 10°C (Glässer, 1978). The average discharge of the Inde River (at the Kirchberg gauging station) is $3.3\,m^3\,s^{-1}$. Under low water conditions, it is $0.46\,m^3\,s^{-1}$, and under flood conditions it is $45.8\,m^3\,s^{-1}$ (Bezirksregierung Köln, 2007; MUNLV, 2009).

The upper and middle reaches of the Inde River are part of the northern Eifel Mountains, with elevations of up to 580 m asl. This southwest–northeast trending mountain system is part of the NW Rhenohercynian Basin, and is composed of several geological units, which are mainly of Paleozoic origin. These units consist of

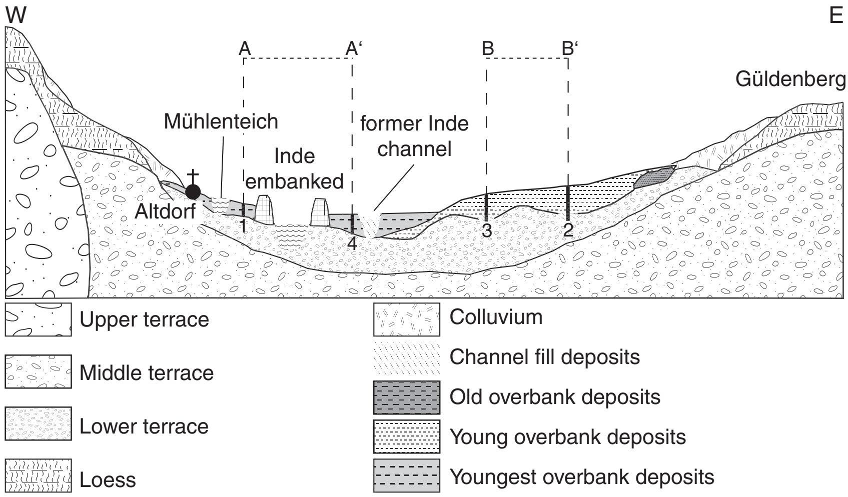

Figure 3. Schematic cross section of the Lower Inde valley. Numbers 1–4 are roughly the positions of the investigated sections. A precise depiction of the geometric relations of the sections (distances A–A' and B–B') is given in Figure 6.

Cambrian quartzite, shales, and slates in the southern region (De Vos et al., 1996; Hindel et al., 1996). In the northern part, sedimentary rocks are composed mainly of lime- and sandstones of the Devonian and Carboniferous (Sindern et al., 2008). Historically important lead and zinc mines (Figure 1) are commonly associated with the limestone of the middle and late Devonian eras. Zinc ore is mainly found at a depth of up to 18 m (Tylecote, 1987). At surface outcrops, zinc converts into calamine (Gussone, 1964; Mathar & Voigt, 1969; Friedrich, Scheps, & Keyssner, 1986; De Vos et al., 1996).

As Figures 2 and 3 illustrate, the Lower Inde Valley, as part of the Lower Rhine Basin, consists of a 1−km-wide asymmetric floodplain. The Holocene floodplain sediments are situated on top of the Pleistocene lower terrace, where they are flanked on both sides by the middle terrace, which is covered by loess sequences (Figure 3). Due to soil erosion, material is eroded from the loess and accumulated as colluvial deposits on the footslopes and bottom of the floodplain. According to Schalich (1968, 1981), three different overbank sediment sequences, all rich in silty loam, can be differentiated based on morphological, geological, pedological, and historic–cultural features of these sediments. Schalich concluded that the old overbank sediments were deposited between 8000 and 6500 B.C. Around 750 B.C., at the beginning of the Iron Age, the intermediate overbank sediments began to accumulate. The young overbank sediments started to develop at the beginning of the 19th century and are limited to small areas on both sides of the river. Generally, the older overbank sediments extend into the eastern part of the floodplain and the younger ones into the western part, respectively.

Figure 2 shows the four investigated sections of this floodplain. They are situated more or less on a west–east transect crossing the Holocene floodplain. The sediments from the pre-Bronze Age up to those of the Middle Ages (Sections 2 and 3) are located in the southeastern part of the research area. The dating of Section 2 is based on archaeological remains, for example, a sunken pit dated to the Bronze Age on top of the profile. Section 3 is dated by artifacts. Currently, this part of the catchment near Güldenberg is dominated by pasture and farmland. Some former oxbow lakes are still visible in the otherwise relatively flat surface. The sediments of the early Modern Period (Section 1) are situated north of the village of Altdorf. Situated between a mill channel and the recent river bed, this section is composed of a former channel covered with floodplain loam and is currently used for gardens and pasture. The sediments of the 20th century, represented in Section 4, dated by artifacts, are located directly next to the current channel of the Inde River.

The intermediate and young sediments have often been ignored in studies of archaeological contexts in the Rhineland. However, these deposits contain extensive information concerning landscape and environmental evolution. Thus, this study focuses on Section 1, representing the early Modern Period.

Materials and Methods

Between the recent river and the "Mühlenteich"—a mill leet—a trench of approximately 50 m in length was excavated. In the eastern part of this section, fluvial deposits of 3.45 m thickness (Section 1 in Figure 2), representing the early Modern Period, were sampled vertically every 5 cm. Altogether 69 samples were analyzed in Section 1. Sections 2 to 4 (Figure 2) were documented within archaeological excavations.

Heavy metal concentrations were measured *in situ*, using a portable X-ray fluorescence spectrometer (FPXRF, Niton XLt 700 series), applying an X-ray tube with a silver target, for quantitative detection of 22 chemical compounds. Measurement time was 90 s per sample. To verify the *in situ* measurements, every second sample was dried at 40°C, thoroughly ground, and pressed into a tablet. The tablets were measured with a stationary, energy-dispersive X-ray fluorescence spectrometer (Spectro, X-Lab 2000) and again with the FPXRF. The verification of the *in situ* measurements confirmed reliable results and a stable detection using the field portable X-ray analyzer for the investigated elements. To evaluate anthropogenic pollution, we studied selected heavy metals, namely lead, zinc, copper, rubidium, and strontium. All concentrations of the compared deposits were measured *in situ*, with the same devices and procedures previously described.

For grain-size analysis, the samples were air-dried and chemically treated with 0.3 ml of 30% H_2O_2 at 70°C for 24 hours to eliminate organic matter. Afterwards, to keep the particles dispersed, 0.25 ml of $Na_4P_2O_7$ was added to the samples for twelve hours. The grain-size measurement was conducted with a laser diffraction particle size analyzer (Beckmann Coulter LS 13 320). This device calculates the average diameters of the particles over a size range of 0.04–2000 μm.

The pH value was recorded using 10 g of each sample, which was placed in an aluminium crucible, and 25 ml of $CaCl_2$ was added and stirred. A pH meter (Knick Labor-pH-Meter, Model 766) was used to measure the pH of the fluid.

Organic carbon content (C_{org}) was calculated with the following formula:

$$C_{org} = C - C_{anorg}$$

where the total carbon (C) content was determined on air-dried samples using a CHNS Analyser (HECAtech EuroEA3000). Inorganic carbon (C_{anorg}) was measured as calcium carbonate ($CaCO_3$) concentration, which was 12%.

The phosphorus content of the samples was measured by the P_{citro}-method, which determines the total phosphorus (TP) content. For this method, 5 g of sediment were mixed with 50 ml citric acid, placed in an Erlenmeyer flask, and vibrated on a plate for 48 hours. A 5 ml aliquot of filtrate was mixed with distilled H_2O, to which 0.5 ml sodium sulphate solution and 0.5 ml sulphuric acid were added. After heating the samples at 50°C for six hours in a drying oven, the intensity of the fluid color was measured using a spectrophotometer (Shimadzu). The soil horizons are described according to the German soil classification system (AG Boden, 2005).

Archaeobotanical Analysis and Written Accounts

In the lower part of Section 1, represented by samples 1 to 40, archaeobotanical investigations were carried out. Chemical preparation of the pollen samples was based on Faegri and Iversen (1989). For analyzing the macroremains, 14 samples were sieved (at 2 mm, 1 mm, and 0.25 mm) using "semi-flotation," as described by Hosch and Zibulski (2003).

Finally, for the literature investigation, historical accounts were analyzed from Werner (1881), Willers (1907), Schwickerath (1954), Schleicher (1956), Friedensburg and Krengel (1962), Kohlhaas (1965), Schunder (1968), Mathar and Voigt (1969), Eyll (1971), Holtz (1994), Schreiber and Schreiber (1998), and Rothenhöfer (2005).

RESULTS

Comparison of Methods and Definition of Background Levels

Figure 4 shows the results of the different methods of evaluating the heavy metal concentrations. It depicts, for example, the comparison of the measurement methods using the results for lead in Section 1. Thresholds within the several measurements can be explained by differences in water content *inter alia* (Hürkamp, Raab, & Völkel, 2009).

The catchment background levels were defined empirically (Matschullat, Ottenstein, & Reimann 1999). The mean values of the concentrations from overbank deposits in Section 2 (Table I), accumulated before the Bronze Age, were used to assess the geological background element concentrations. By further comparison with Sections 1, 3, and 4, the degree of metal contamination was evaluated (see below).

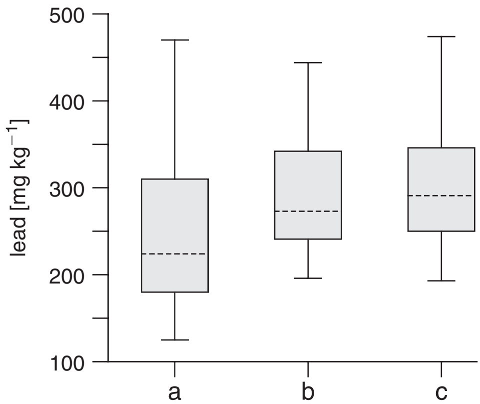

Figure 4. Box plot of lead concentrations in Section 1, detected with three different measurement methods. Each time, every second sample was measured. (a) *In situ* measurements; (b) results of stationary X-ray analyzer; and (c) tablets, measured with field portable X-ray analyzer. *Dotted line* indicates median concentration for each unit; *box* defined by the lower and upper quartiles of lead; the *caps* at the end of each box are the extreme minimum and maximum values.

Sedimentology and Heavy Metal Concentrations

The sediment record of Section 1 (Figure 5) consisted of channel fill covered by overbank deposits. Here a precise boundary between these layers was not perceptible, neither optically nor by grain-size analyses. Due to the changing silt and sand contents, there was a continuous transition from the channel fill to the floodplain loam. Apart from samples 45 and 49 (loam and sandy loam, respectively), every sample consisted of silty loam. Moreover, the channel fill was generally finer with higher silt content. The channel fill composition reflected slow sedimentation, which is typical for flooded abandoned river channels.

The pH values (Figure 5) were relatively consistent in their vertical distribution. With a mean value of 6.2, the pH ranges showed low to average acidity. With the exception of the uppermost samples (base of the A horizon), the pH values were within the range of 4.6 to 6.8), in which lead and copper are immobile; zinc is only slightly mobile here (Herms & Brümmer, 1980).

The total phosphorus (TP) content in Section 1 showed a clear differentiation between the channel fill and the overbank sediments (Figure 5). The values of the lower part fluctuated from 630 to 3680 mg kg^{-1}, whereas the upper part of the profile was characterized by more stable contents on a lower level with a mean value of around 230 mg kg^{-1}. The channel fill was an anaerobic system with predominant slack water deposits. High amounts of blue iron ore (Vivianite, $Fe_3^{2+}[PO_4]_2 \cdot 8\ H_2O$) led to a strong enrichment of TP. Most probably, the lower concentration of TP in the floodplain was attributed to grain-size effects. In this part the silt value decreased, whereas the proportion of sand increased. A connection with organic carbon may

Table I. Heavy metal concentrations in fluvial deposits of different ages of the Inde River. The sediments show an increase of lead, zinc, and copper as sediments get younger, as shown by the fluctuating concentrations.

		Strontium		Rubidium		Lead		Zinc		Copper	
		mg kg^{-1}	n	mg kg^{-1}	n	mg kg^{-1}	n	mg kg^{-1}	n	mg kg^{-1}	n
Pre-Bronze Age (39)	Sect. 2	111.77	*39*	61.99	*39*	38.23	*28*	298.04	*39*	<40*	*0*
High to late Middle Ages (20)	Sect. 3	89.23	*20*	50.21	*20*	191.67	*20*	516.49	*20*	90.43	*5*
(Early) Modern Period (69)	Sect. 1	104.30	*69*	55.34	*69*	246.34	*69*	1248.22	*69*	127.34	*37*
20th century (54)	Sect. 4	86.58	*54*	39.17	*54*	628.24	*54*	2690.83	*54*	437.77	*51*

Numbers in parens = number of sediment samples; n = number of samples in which the element could be detected.
* Lower limit of detection (for copper).

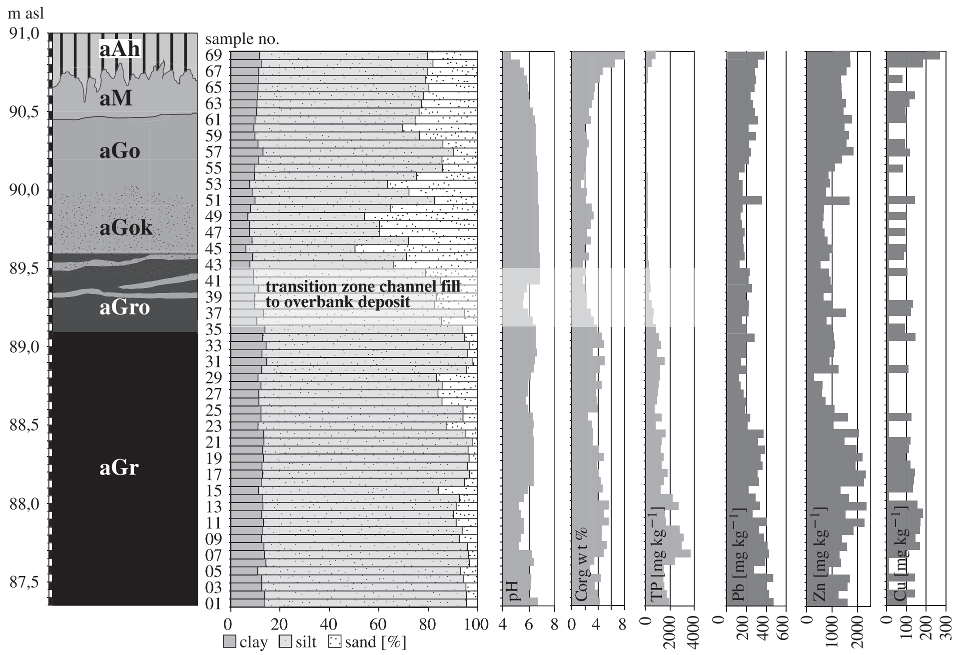

Figure 5. Grain sizes, soil parameters, and selected heavy metal concentrations of Section 1. Altogether, 69 samples were analyzed. In the lower part, in the region of the samples 1–40, archaeobotanical samples were removed. Key: *aAh* = A horizon; *aM* = laminated alluvium; *aGo* = gleyic, oxidized; *aGok* = gleyic, oxidized with concretions; *aGro* = gleyic, reduced, predominently oxidized; *aGr* = gleyic, reduced; C_{org} = organic carbon in weight per cent; *TP* = total phosphorous; *Pb* = lead, *Zn* = zinc; *Cu* = copper, the last four elements are given in mg kg^{-1}.

be insignificant, in as much as the increase in organic carbon (for example, in samples 48 to 50) did not lead to higher TP values. However, after assessing the TP levels and the specific conditions of the deposits, no conclusion could be drawn regarding former land-use intensities.

The concentration of organic carbon (C_{org}; Figure 5) followed a pattern similar to the TP. Here, the channel fill was rich in humus, with values ranged from 2.7 to 5.6% by weight. The elevated values of samples 44 to 52 were notable. The increase in C_{org} levels in the upper part of Section 1 originated from soil material added through erosion and recent bioturbation. In general, both the TP and C_{org} parameters showed a more or less similar trend, as might be expected. The values of the channel fill were higher than those of the overbank sediments, with a mean value of TP of ca. 1530 mg kg^{-1}% compared to 210 mg kg^{-1} and mean values of 4% by weight to 2.8% by weight for C_{org}.

Figure 5 shows the vertical distribution of lead, zinc, and copper in Section 1. The fluctuations principally mirrored the sedimentation conditions of the internal profile. There were no clear stratigraphic features in this section. The chronological resolution was generated by comparing with the other sections.

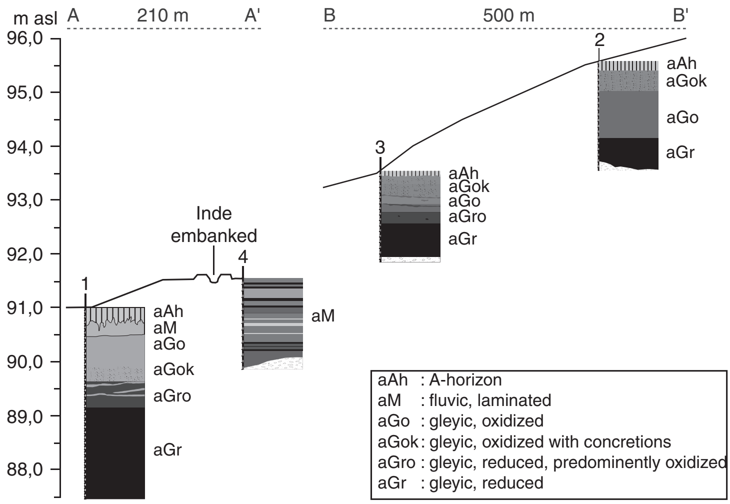

Figure 6. Geometric relations and stratigraphies of the four investigated Sections. A–A' is situated in the northwestern part of the lower Inde valley, B–B' in the southeastern part. Between these two sections is a north–south distance of approximately 800 meters.

The geometric relations and profile structures of the other sections are summarized in Figure 6. Sections 2 and 3 had the same stratigraphy as Section 1, in contrast to Section 4, which was composed of laminated fluvial sediments. The channel fill in the Sections 1–3 was covered with overbank sediments. Figure 7 depicts the variations in grain size, although silty loams dominate. The lower parts of the profiles had a typically finer grain size than the upper part of the deposits. Table II gives an overview of the results of pH, TP, and C_{org}.

The relative distribution of strontium, rubidium, lead, zinc, and copper within Sections 2–4 was similar to the distribution in Section 1, even though with different absolute total values. The exception was copper, which could not be detected in pre-Bronze Age sediments in Section 2 (Table I).

Compared with the geologic background, given in Section 2, lead showed a five-fold enrichment in medieval, compared to 6.5 times higher in (early) modern sediments and more than 16 times higher in deposits of the 20th century. Zinc showed a similar but less marked behavior, with enrichment values of 1.7, 4.2, and 9 times in the three periods, respectively. Copper could not be detected in the natural background. For the investigated sediment deposits, input started in the Middle Ages and was 4.8 times higher by the 20th century. The geologic elements strontium and rubidium (Herms & Brümmer, 1980) behaved more or less similarly during the different time periods. They were not enriched by human activity. The small variations might possibly be explained by the slight grain-size differences in the different sections. The constant values of strontium and rubidium made the contamination with lead, zinc, and copper with increasing human pollution obvious.

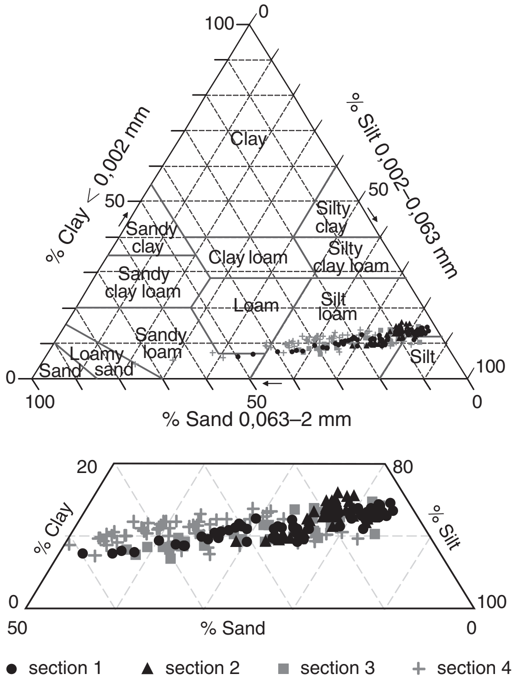

Figure 7. Triangular plot of the grain-size distributions of the four sections. At the bottom, the enlargement of the silty loam and silt areas is shown.

Table II. Laboratory results of the four sections. The mean pH values show more or less a similar markedness, while the organic carbon and total phosphorus contain clear differences within the deposits of different ages.

		pH		C_{org} (wt %)		TP (mg kg^{-1})	
		Min–Max	Ø	Min–Max	Ø	Min–Max	Ø
Pre-Bronze Age (39)	Sect. 2	5.3–7.3	6.6	0.2–2.1	0.7	100–2051	559
High to late Middle Ages (20)	Sect. 3	3.8–7.2	5.9	0.5–3.5	1.5	37–1321	215
(Early) Modern Period (69)	Sect. 1	4.6–6.8	6.2	0.8–4.7	2.1	82–3681	937
20th century (54)	Sect. 4	2.9–7.3	6.7	2.1–8.3	4.3	217–1558*	721*

Numbers in parens = number of sediment samples; Min = minimum value; Max = maximum value, Ø = average.
* Every second sample.

Archaeobotany

The pollen diagram in Figure 8 shows the presence of 24 pollen types in Section 1. Particularly noticeable is the high amount of non-arboreal pollen (NAP) and cereal pollen. High values of Poaceae (grasses), *Plantago lanceolata* (ribwort plantain), and *Trifolium pratense* (red clover) suggests the importance of animal husbandry

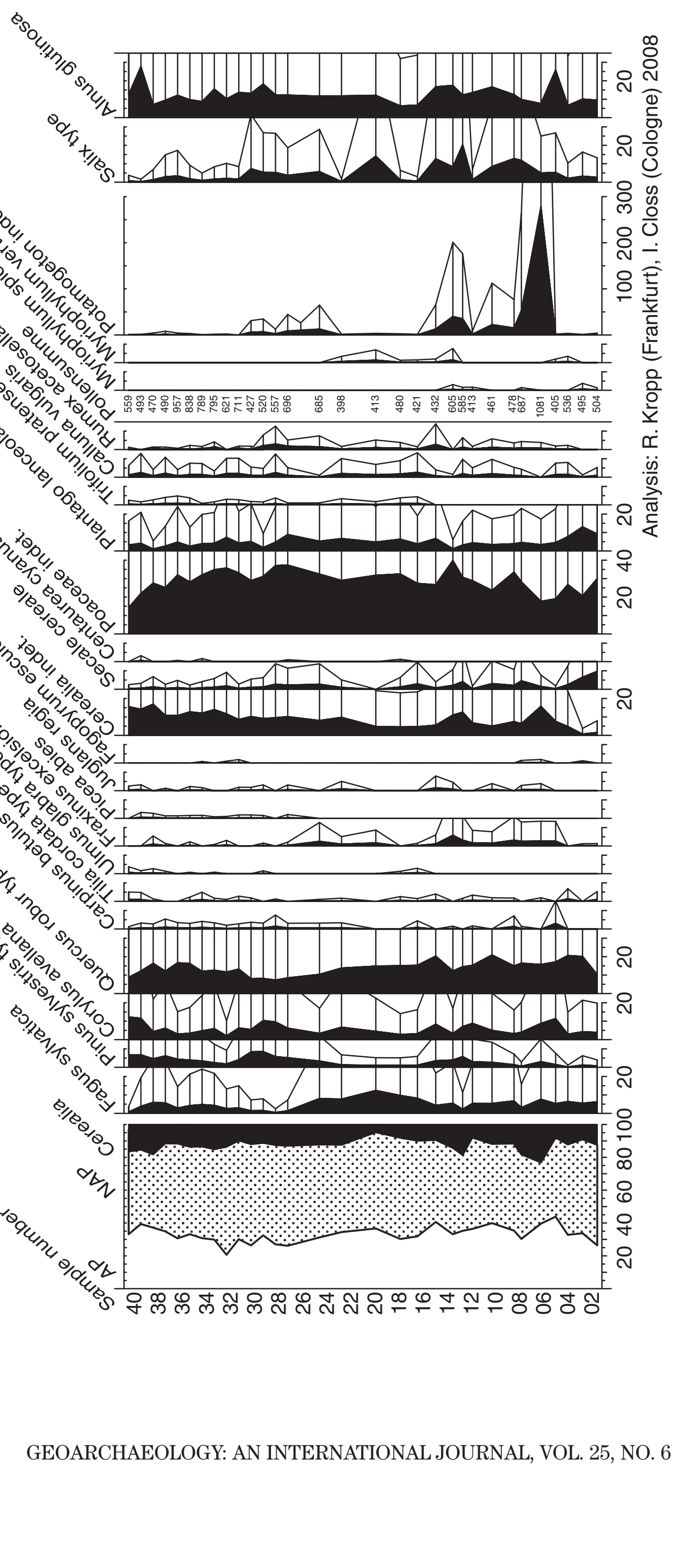

Figure 8. Selection of pollen types in Section 1. The sampling numbers on the left show the position of the sediment samples. Key: *AP* = arboreal pollen; *NAP* = non-arboreal pollen.

just nearby. Cereal pollen is most likely to have originated from arable land on the elevated loess area. The arboreal pollen spectra were dominated by *Quercus* (oak), followed by *Fagus* (beech), *Corylus* (hazel), and *Pinus* (pine). The local vegetation was represented by *Potamogeton* (pondweed) and *Salix* (willow), and numerous leaves and fruits of both were also detected.

Mining History

After small-scale mining during the Roman Period and probably during the early Middle Ages, the exploitation of calamine in the catchment area resulted in increased mining activity. By studying the historical evidence of mining in the catchment area, it is known that at the end of the 16th century, brass makers from Aachen moved to Stolberg. Different reasons were decisive for the new intensive settlement along the rivers Inde and Vicht. Besides economic reasons, the predominantly Protestant tradesmen could practice their religion freely (Schleicher, 1956; Eyll, 1971; Holtz, 1994), which marked the beginning of the blossoming brass industry in the Inde catchment area. Up to A.D. 1650, the brass industry of Stolberg monopolized other industries (Mathar & Voigt, 1969). In addition, the majority of copper mills were built during the 17th century (Schleicher, 1956).

At the beginning of the 19th century, it was possible to smelt sphalerite (zinc sulfide, ZnS) directly for the first time (e.g., Hindel et al., 1996). The first working zinc smelter started in Stolberg in 1819 (Friedensburg & Krengel, 1962; Holtz, 1994), heralding a giant leap forward for the brass industry in the Stolberg region.

DISCUSSION

Element Concentrations in Sediment Deposits of Different Ages

The anthropogenic elements lead, zinc, and copper could be directly related to the local historical mining of lead and zinc, as well as the brass industry. The lack of copper in the background samples and also its increase in the young sediments could be explained by the import of copper for the brass industry. The concentrations of lead, zinc, and copper in Section 1 were high compared to those in Section 2 (geologic concentrations, not anthropogenically influenced) as well as in Section 3 (medieval sediments). Due to mining during the high and late Middle Ages (ca. A.D. 1200 onward), an anthropogenic enrichment was apparent in the corresponding deposits. Based on the higher concentrations in Section 1, it is suggested that these sediments must be younger than the medieval sediments. It is likely that these sediments were deposited around the beginning of the blossoming brass industry in the Inde catchment, as reflected by the degree of contamination. Nevertheless, the concentrations in Section 1 did not reach the values of the highly contaminated sediments of the 20th century in Section 4 (Table I). Thus, the main sedimentation in Section 1 probably stopped before the middle of the 19th century. Due to the technical innovation in zinc mining and processing, a concomitant detectable increase in environmental pollution by zinc would be expected from this time. However, a rapid rise of the zinc values was not visible in Section 1.

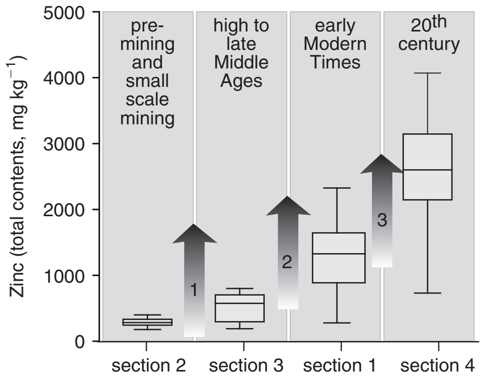

Figure 9. Box plot of zinc concentrations in the four sections. Within these time spans, three main changes in mining history led to increasing zinc values with diminishing age: (1) Medieval extension of mining; (2) heydays of mining and brass industry due to strengthened settlement of moved copper millers from Aachen; and (3) technological change and industrialization. Symbols are as in Figure 4.

The comparison of the heavy metal content in the overbank deposits of different ages gaves an estimation of the degree of contamination during the individual mining phases in the Lower Inde Valley. The historical written accounts helped to fit the deposits into a chronology. Changes in lead, zinc, and copper contents reflected the pollution caused by mining in the catchment area. The Roman Period was not recognizable within the floodplain sediments investigated. However, the medieval and following mining periods were active enough to leave individual stamps in the overbank deposits. Figure 9 summarizes, as an example, three main phases of calamine and zinc mining.

Land-Use Interpretation

To understand more about the land-use consequences of the mining history, the pollen record was used to reconstruct the former vegetation cover and land use for the early Modern Period. The pollen record (Figure 8) in Section 1 was dominated by NAP, species characteristic of meadows and water plants. The high amount of *Potamogeton*, in particular in the lower half of the analyzed samples, pointed to the fact that the water was stagnant or slowly moving, as also seen in the sedimentology. It is quite likely that Section 1 represents a former channel (oxbow lake) silting up.

Species such as *Nymphaea alba* and *Myriophyllum verticillatum* indicate the eutrophication of the stretch of water. The increased nutritient content could be explained by the practice of husbandry in the surroundings, as reflected also by the high amount of dung spores in the section. Both grass and cereal pollen were indicative of a landscape similar to that which is documented on the Tranchot and Müffling map of 1801–1807: pasture land was dominant within the floodplain zone, and arable land was situated on the elevated loess areas (Figure 10). The loess-covered areas in the lower catchment of the Inde River were almost free of forest. The recorded

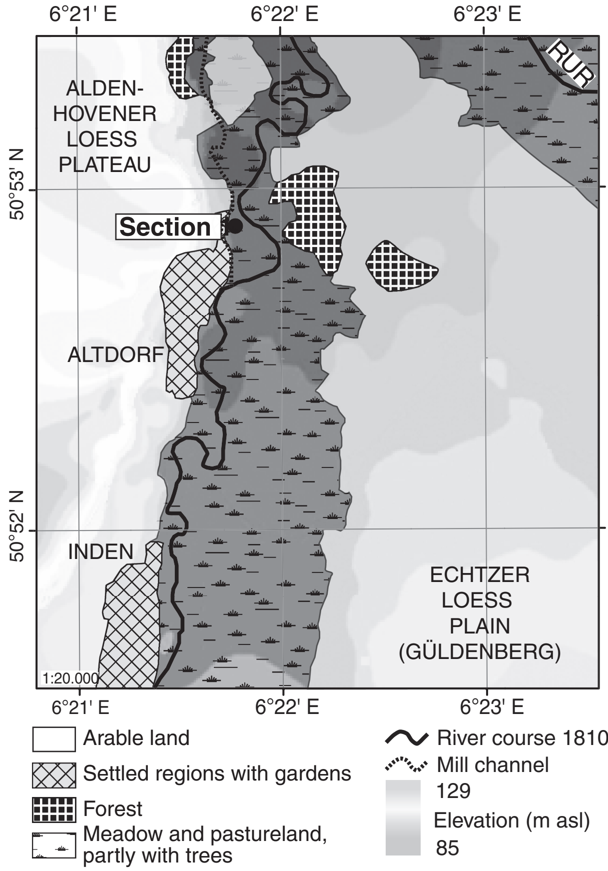

Figure 10. Reconstruction of land use at the lower Inde valley. The drawing partly follows the map of Tranchot and Müffling (1810). The elevated loess sites as well as drier parts of the floodplain were used for farming. Within the floodplain, animal husbandry dominated.

arboreal pollen was mainly transported by the Inde tributaries or by wind from the Eifel Mountains and their foothills.

Although the composition of the pollen record is influenced by diverse factors such as transport, sedimentation, and overrepresentation of the local vegetation (Lechterbeck, Kalis, & Meurers-Balke, 2009), the low proportion of arboreal pollen reflects the open land in the catchment area. Low values of AP also provide a chronostratigraphical classification of the deposits. The openness of the landscape could be linked to the historically described overutilization of the forests in the Eifel Mountains. Even by the 16th century, the requirement for charcoal caused an intense use of the forest. Due to the neglect of the forest, Duke Wilhelm V investigated the state of the forests through a commission in 1556 (Schreiber & Schreiber, 1998). Before the first half of the 18th century, there was forest in the neighborhood of the mine sites, and its wood was sufficient as fuel for the smelters, especially for the smelting and processing of the ores. After this time, the population of trees, especially beech trees, was exhausted. Moreover, the intense use and rapid deforestation caused a bitter conflict between several mine owners, and there was a possibility that smelting would stop because of the lack of charcoal (Kohlhaas, 1965; Mathar & Voigt, 1969; Schreiber & Schreiber, 1998). The historical tradition could be correlated to the decreasing amounts of beech trees in the pollen record, which decrease to as little as 1% in some parts of the profile.

The pollen record also supports the theory that the sedimentation in Section 1 ceased before the middle of the 19th century. At this time, the Prussian forestation of the Eifel Mountains began (Schwickerath, 1954). However, no phase of forestation was discernible within the pollen data in this section. Both pollen data and heavy metal concentrations reflected different parts of the former land use and its influence on the environment. To some extent, individual land uses were connected. For example, mining activities affected the natural resources, such the decreasing spread of forests.

CONCLUSION

Since the high and late Middle Ages (ca. A.D. 1200 onward), there was a profound increase in the contamination of fluvial sediments with zinc, lead, and copper. Moreover, the intense deforestation in the early Modern Period, as supported by the aforementioned archaeobotanical data, was attributed to ore processing, for which considerable amounts of wood were needed to fire the smelters. Furthermore, the archaeobotanical results of our study indicate that husbandry and farming were the most important historical human activities in the Lower Inde Valley.

As taken from written accounts, the increasing zinc pollution of the fluvial sediments can be categorized into three main mining phases:

1. A recovering mining period during the Middle Ages,
2. A migratory period during which brass makers from Aachen moved to Stolberg, and
3. A technical phase when zinc smelting was possible.

Consequently, our study indicates that all the three interdisciplinary approaches used—that is, empirical chemical analysis of sediments, archaeobotanical analysis, and literary analysis—can be interlinked to generate a comprehensive understanding of historical land use.

In addition, we were able to show that the use of portable field X-ray fluorescence spectrometer is not only useful for assessing the contamination degrees of contaminated sediment deposits for remediation measures (Piorek, 1994; Kalnicky & Singhvi, 2001; Vanhoof, Corthouts, & Tirez, 2004), but also is a useful application to answer and address geoarchaeological and montanarchaeological questions and issues.

We would like to thank Dr. R. Kropp (Frankfurt) for allowing us to use unpublished pollen data and Dr. A.J. Kalis (Frankfurt) for useful remarks. We are also indebted to I. Closs (Cologne) and M. Dohms (Aachen) for their technical assistance. Furthermore, we would like to say a special thank to the reviewers, who were very helpful with their constructive and useful comments as well as their editorial support. This research was funded by the foundation Stiftung Archäologie im rheinischen Braunkohlenrevier.

REFERENCES

AG Boden. (2005). Bodenkundliche Kartieranleitung, 5th ed. Hannover.
Agricola, G. (1556). De re metallica libri XII. Basel.
Aston, M., Martin, M., & Jackson, A. (1998). The use of heavy metal soil analysis for archaeological surveying. Chemosphere, 37, 465–477.
Bezirksregierung Köln. (Ed.). (2007). Hochwasseraktionsplan Inde/Vicht. Köln: Author.
Brewer, P.A., & Taylor, M.P. (1997). The spatial distribution of heavy metal contaminated sediment across terraced floodplains. Catena, 30, 229–249.
Davies, B., & Lewin, J. (1974). Chronosequences in alluvial soils with special reference to historic lead pollution in Cardiganshire, Wales. Environmental Pollution, 6, 49–57.
De Vos, W., Ebbing, J., Schalich, J., Swennen, R., & Van Keer, I. (1996). Geochemical mapping based on overbank sediments in the heavily industrialised border area of Belgium, Germany and the Netherlands. Journal of Geochemical Exploration, 56, 91–104.
Eyll, K. van (1971). Die Kupfermeister im Stolberger Tal: Zur wirtschaftlichen Aktivität einer religiösen Minderheit. Köln: Forschungsinstitut für Sozial- und Wirtschaftsgeschichte an der Universität zu Köln.
Faegri, K., & Iversen, J. (1989). Textbook of pollen analysis, 4th ed. Chichester: John Wiley and Sons.
Friedensburg, F., & Krengel, R. (1962). Die wirtschaftliche Bedeutung des Metallerzbergbaus und Metallhüttenwesens in der Bundesrepublik Deutschland. Berlin: Duncker and Humblot.
Friedrich, G., Scheps, V., & Keyssner, G. (1986). Planung und technische Durchführung eines lagerstättenkundlichen Bohrprogramms im Paläozoikum der nördlichen Eifel. Fortschritt Geologie Rheinland und Westfalen, 34, 93–102.
Glässer, E. (1978). Die naturräumlichen Einheiten auf Blatt 122/123 Köln-Aachen. Bonn-Bad-Godesberg: Geographische Landesaufnahme 1:200 000. Naturräumliche Gliederung Deutschlands.
Gussone, R. (1964). Untersuchungen und Betrachtungen zur Paragenesis und Genesis der Blei-Zink-Erzlagerstätten im Raum Aachen-Stolberg. Doctoral dissertation, RWTH Aachen University, Aachen.
Herms, U., & Brümmer, G. (1980). Einfluß der Bodenreaktion auf Löslichkeit und tolerierbare Gesamtgehalte an Nickel, Kupfer, Zink, Cadmium und Blei in Böden und kompostierten Siedlungsabfällen. Landwirtschaftliche Forschung, 33, 408–423.
Hindel, R., Schalich, J., De Vos, W., Ebbing, J., Swennen, R., & Van Keer, I. (1996). Vertical distribution of elements in overbank sediment profiles from Belgium, Germany and the Netherlands. Journal of Geochemical Exploration, 56, 105–122.
Holtz, F. (1994). Vom Messing bis zur Großchemie. Stolberg: Heimat- und Handwerksmuseum.
Hosch, S., & Zibulski, P. (2003). The influence of inconsistent wet-sieving procedures on the macroremain concentration in waterlogged sediments. Journal of Archaeological Science, 30, 849–857.
Hudson-Edwards, K., Macklin, M., & Taylor, M. (1997). Historic metal mining inputs to Tees River sediment. Science of the Total Environment, 194, 437–445.
Hudson-Edwards, K.A., Schell, C., & Macklin, M.G. (1999). Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. Applied Geochemistry, 14, 1015–1030.
Hürkamp, K., Raab, T., & Völkel, J. (2009). Two- and three-dimensional quantification of lead contamination in alluvial soils of a historic mining area using field portable X-ray fluorescence (FPXRF) analysis. Geomorphology, 110, 28–36.
Kalnicky, D.J., & Singhvi, R. (2001). Field portable XRF analysis of environmental samples. Journal of Hazardous Materials, 83, 93–122.
Knox, J.C. (2006). Floodplain sedimentation in the Upper Mississippi Valley: Natural versus human accelerated. Geomorphology, 79, 286–310.
Kohlhaas, A. (1965). Geschichte des Steinkohlenbergbaues im heutigen Stadtgebiet von Stolberg (Rhld.). Stolberg: Stolberger Handelsdruckerei J. Leufgens.
Lecce, S.A., & Pavlowsky, R.T. (1997). Storage of mining-related zinc in floodplain sediments, Blue River, Wisconsin. Physical Geography, 18, 424–439.
Lecce, S.A., & Pavlowsky, R.T. (2001). Use of mining-contaminated sediment tracers to investigate the timing and rates of historical flood plain sedimentation. Geomorphology, 38, 85–108.

Lechterbeck, J., Kalis, A.J., & Meurers-Balke, J. (2009). Evaluation of prehistoric land use intensity in the Rhenish Loessboerde by canonical correspondence analysis: A contribution to LUCIFS. Geomorphology, 108, 138–144.

Macaire, J.-J., Bernard, J., Di-Giovanni, C., Hinschberger, F., Limondin-Lozouet, N., & Visset, L. (2006). Quantification and regulation of organic and mineral sedimentation in a late-Holocene floodplain as a result of climatic and human impacts (Taligny marsh, Parisian Basin, France). The Holocene, 16, 647–660.

Macklin, M.G., & Klimek, K. (1992). Dispersal, storage and transformation of metal-contaminated alluvium in the Upper Vistula Basin, southwest Poland. Applied Geography, 12, 7–30.

Macklin, M., Ridgway, J., Passmore, D.G., & Rumsby, B. (1994). The use of overbank sediment for geochemical mapping and contamination assessment: Results from selected English and Welsh floodplain. Applied Geochemistry, 9, 689–700.

Mathar, I., & Voigt, A. (1969). Über die Entstehung der Metallindustrie im Bereich der Erzvorkommen zwischen Dinant und Stolberg, 2nd ed. Aachen: M. Brimberg Druck- und Verlagsgesellschaft.

Matschullat, J., Ottenstein, R., & Reimann, C. (1999). Geochemischer Hintergrund: Berechenbar? In T. Wippermann (Ed.), Bergbau und Umwelt, Langfristige geochemische Einflüsse (pp. 1–23). Geowissenschaften und Umwelt. Berlin: Gesellschaft für UmweltGeowissenschaften.

Meurers-Balke, J., Kalis, A.J., Gerlach, R., & Jürgens, A. (1999). Landschafts- und Siedlungsgeschichte des Rheinlandes. In H. Koschik (Ed.), PflanzenSpuren (pp. 11–66). Köln: Landschaftsverband Rheinland Rheinisches Amt für Bodendenkmalpflege.

Meurers-Balke, J., & Kalis, A.J. (2006). Eisenzeit: Landwirtschaft und Landnutzung in der Bronze- und Eisenzeit. In J. Kunow & H.-H. Wegner (Eds.), Urgeschichte im Rheinland (pp. 267–276). Jahrbuch 2005 des Rheinischen Vereins für Denkmalpflege und Landschaftsschutz. Köln.

Middelkoop, H. (2000). Heavy-metal pollution of the River Rhine and Meuse floodplains in the Netherlands. Journal of Geosciences, 79, 411–428.

Ministerium für Umwelt und Naturschutz, Landwirtschaft und Verbraucherschutz des Landes Nordrhein-Westfalen (MUNLV). (Ed.). (2009). Ergebnisbericht Rur und südliche sonstige Maaszuflüsse. Bearbeitungsgebiet Maas-Deutschland (Süd). Wasserrahmenrichtlinie in NRW: Bestandsaufnahme. Düsseldorf: Häfner and Jöst GmbH.

Piorek, S. (1994). Principles and applications of man-portable X-ray fluorescence spectrometry. Trends in Analytical Chemistry, 13, 281–286.

Raab, T., Hürkamp, K., & Völkel, J. (2005). Detection and quantification of heavy metal contamination in alluvial soils of historic mining areas by field portable X-ray fluorescence (FPXRF) analysis. Proceedings of International Conference on Problematic Soils, 25–27 May 2005, Eastern Mediterranean University, Famagusta, N-Cyprus, Vol. 1 (pp. 299–306).

Rothenhöfer, P. (2005). Die Wirtschaftsstrukturen im südlichen Niedergermanien. Untersuchungen zur Entwicklung eines Wirtschaftsraumes an der Peripherie des Imperium Romanum. Doctoral dissertation, Universität zu Köln.

Schalich, J. (1968). Bodenkarte von Nordrhein-Westfalen 1:25 000. Erläuterungen zu Blatt 5104 Düren. Krefeld: Geologisches Landesamt Nordrhein-Westfalen.

Schalich, J. (1981). Boden- und Landschaftsgeschichte in der westlichen Niederrheinischen Bucht. Fortschrift Geologie Rheinland und Westfalen, 29, 505–518.

Schleicher, K. (1956). Geschichte der Stolberger Messingindustrie. Stolberg: Stolberger Handelsdruckerei J. Leufgens.

Schreiber, K., & Schreiber, H. (1998). Als im Vichttal das Eisen noch glühte . . . Hammer- und Reitwerke im Süden Stolbergs. In Stolberger Heimat- und Geschichtsverein e.V. (Eds.), Mühlen, Hammerwerke und Kupferhöfe im Tal der Vicht und ihre Besitzer (pp. 9–81). Beiträge zur Stolberger Geschichte Series 23. Stolberg.

Schunder, F. (1968). Geschichte des Aachener Steinkohlenbergbaus. Essen: Verlag Glückauf GmBH.

Schwickerath, M. (1954). Die Landschaft und ihre Wandlung auf geobotanischer und geographischer Grundlage entwickelt und erläutert im Bereich des Meßtischblattes Stolberg. Aachen: Verlag Dr. Rudolf Georgi.

Sindern, S., Warnsloh, J.M., Trautwein-Bruns, U., Chatziliadou, M., Becker, S., Yüceer, S., Hilgers, C., & Kramm, U. (2008). Geochemical composition of sedimentary rocks and imprint of hydrothermal fluid flow at the Variscan front: An example from the RWTH-1 well (Germany). Zeitschrift der Deutschen Gesellschaft für Geowissenschaften, 159, 623–640.

Swennen, R., Van Keer, I., & De Vos, W. (1994). Heavy metal contamination in overbank sediments of the Geul River (East Belgium): Its relation to former Pb-Zn mining activities. Environmental Geology, 24, 12–21.

Thonon, I. (2006). Deposition of sediment and associated heavy metals on floodplains. Doctoral dissertation, University of Utrecht.

Tylecote, R.F. (1987). The early history of metallurgy in Europe. London: Longman.

Vanhoof, C., Corthouts, V., & Tirez, K. (2004). Energy-dispersive X-ray fluorescence systems as analytical tool for assessment of contaminated soils. Journal of Environmental Monitoring, 6, 344–350.

Werner, F.v. (1881). Beiträge zur ältesten Geschichte von Gressenich. Zeitschrift der Aachener Geschichtsvereins, 3, 146.

Willers, H. (1907). Neue Untersuchungen über die römische Bronzeindustrie von Capua und von Niedergermanien. Hannover: Hahnsche Buchhandlung.

Wolfenden, P., & Lewin, J. (1977). Distribution of metal pollutants in floodplain sediments. Catena, 4, 309–317.

Zimmermann, A., Meurers-Balke, J., & Kalis, A.J. (2006). Das Neolithikum. In J. Kunow & H.-H. Wegner (Eds.), Urgeschichte im Rheinland (pp. 159–202). Jahrbuch 2005 des Rheinischen Vereins für Denkmalpflege und Landschaftsschutz. Köln.

Received 30 September 2009
Accepted for publication 6 May 2010
Scientific editing by the guest editors