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Heavy metal contamination in overbank sediments of the Geul river (East Belgium): Its relation to former Pb–Zn mining activities

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Abstract Overbank sediments of the Geul River (East Belgium) are highly contaminated by the heavy metals Pb, Zn, and Cd due to former Pb–Zn mining activities in the drainage basin. Geochemical variations in vertical overbank sediment profiles sampled 1 km north of the mine tailings of Plombières allow metal fluxes back to the 17th century to be reconstructed. The vertical profiles are subdivided into three major units corresponding to different industrial periods based on sedimentological criteria as well as on the distribution of contaminants. Alluvial sediments with the highest heavy metal concentrations correspond to the major period of mining activity of the 19th century. The fact that Zn mining at the La Calamine open mine started before large-scale mining of the PbS–ZnS subsurface exploitations is reflected in the vertical profiles by an increase in Zn content before a marked increase in Pb and Cu. The regional extent of contamination in the alluvial deposits was evaluated on the basis of the geochemical analysis of sediments at depths of the 0–20 cm and 80–100 cm. Most of the upper samples are extremely contaminated. Significant local variations in heavy metal concentration in the lower samples are interpreted in terms of which overbank sediment horizon has been sampled at a depth of 80–100 cm. This indicates that “blind” sampling of overbank sediments to characterize the degree of contamination in shallow boreholes can give very erratic results.

Key words Heavy metal contamination · Overbank sediments · Pb–Zn mining

Introduction

Stream and overbank (levee or river plain) sediments deposited along rivers that drain mining areas are often highly contaminated (Mann and Lintern 1983; Bradley and Cox 1986; Jones 1986; Brook and Moore 1988; Macklin and others 1992, Macklin 1992). Overbank deposits are produced when the water discharge exceeds the capacity of a river channel, causing deposition of a part of the suspended load on the river plains (floodplains) or on the riverbank levees. As reported by Webb and Walling (1982) for rivers of the Exe basin (UK) 50 percent of the suspension load was transported during such flood events, i.e., during 3 percent of the year. This is also the case for the Geul river (Leenaers 1989a). During the declining stages of such flood events, the suspended sediment is deposited on the floodplain, giving rise to horizontally laminated strata. Overbank sediments therefore are a very representative medium for characterizing the geochemical signature of the catchment area and its evolution through time (Ottesen and others 1989; De Vos and others 1994). Furthermore they may form important sinks of contaminated sediment. Erosion and transportation of these deposits may cause a temporary increase in high heavy metal contents in the stream sediment.

The aim of this paper is to investigate in detail the geochemical signature and distribution pattern of overbank sediments in an area downstream of the Pb–Zn mining district of Plombières-La Calamine (East-Belgium). Information on the sedimentological and geochemical floodplain evolution was evaluated through the analyses of overbank profiles. The local geochemical distribution of contaminants was investigated using floodplain sediments taken at a depth interval of 0–20 cm and 80–100 cm. Variations in heavy metal content in the lower part of floodplain profiles show that sampling of overbank sediments at depth may give quite different results over small distances.

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Geographical and geological setting

The Geul is a meandering river flowing in East Belgium. From its source to its confluence with the Meuse river, its length is 56 km. The catchment covers an area of 350 km² (Fig. 1). On the Belgian part it is incised in alternating successions of Famennian sandstones, Tournaisian to Lower Viséan dolomites, Viséan limestones and Namurian shales (Swennen and Viaene 1990), while in the Netherlands the river mainly flows on Cretaceous chalk and Tertiary sands. It is within the Palaeozoic part of the catchment area that the largest mined Pb–Zn mineralizations of Belgium were situated. Total production in this area reached about 1.1 million tons of metallic zinc and 0.13 million tons of metallic lead metal (Dejonghe and Jans 1983). The most important centers of mining and ore treatment were La Calamine, Plombières and Schmalgraf (Fig. 1). The ore deposits were actively mined during the last century and the beginning of this century. Historical documents indicate that small-scale mining took place as early as Medieval times (Dejonghe and others 1993). Industrial mining at the La Calamine orebody started in 1806 and ceased in 1882, while the industrial operations date from 1844–1845 until 1882 at Plombières and from 1868–1869 to 1932 at Schmalgraf (Dejonghe and others 1993). The first orebody consists nearly entirely of Zn oxides while in all other orebodies Pb–Zn sulfides dominate. Mine activity in the whole area ceased around 1936. The only rem-

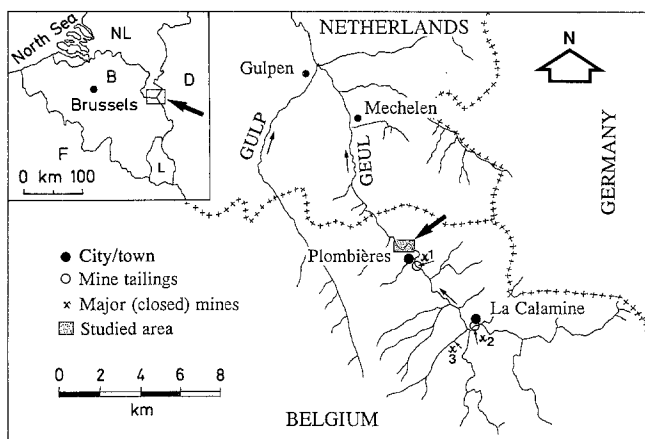


Fig. 1 Geographical overview of the Geul river, the study area, and the position of the three largest mined mineralizations (1. Plombières; 2. La Calamine; 3. Schmalgraf)

nants of this important industry are huge mine tailings that disfigure the landscape.

These dumps presently are major point sources for the pollution of heavy metals, especially since the Geul river crosses the mine tailings of La Calamine and Plombières (Fig. 1). Consequently, dump and slag material is immediately available for downstream transportation. Part of this material was deposited within the Geul valley. However, subsequent reworking of these contaminated overbanks also accounts for a nonnegligible part of heavy metals in the active river sediment. This is a characteristic common for many mining areas (e.g., Macklin and Dowsett 1989). The overbank sediments thus act as a line source. Leenaers (1989b) calculated the annual input of the Geul in terms of the transport of sediment, water, and contaminants (Table 1). When compared with values of the Meuse river near the Belgian–Dutch border, the contribution in terms of water of the Geul is small, but the total discharge of sediment, Pb, Zn, and Cd is in the order of 4–10 percent.

Sample collection and analytical methods

Three vertical profiles (Fig. 2) were sampled within the overbank sediments adjacent to the Geul river, approximately 1 km north of the mine tailings of Plombières. More than 1 kg of bulk samples were taken over ± 10 cm depth intervals within discrete sedimentary units. Furthermore about 40 shallow boreholes (100 cm deep) were placed within an area 1.8×1.0 km within the Geul alluvial plain (Fig. 6 below). Due to the cohesive nature of the overbank sediments, it was not possible to take undisturbed samples. This and the fact that no significant macroscopic grain size and textural variations were recognizable hampered a detailed description of the lower parts of the boreholes. In this paper only the results from the intervals 0–20 cm and 80–100 cm will be discussed.

Overbank and soil sediments were also sampled in the Geul valley upstream of La Calamine at a location situated outside the mineralized area to evaluate background metal levels. This area (henceforth termed the reference area) has a similar geology to the area north of Plombières.

Particle-size analysis was performed by standard sieving and, for fractions smaller than 36 μm , by sedigraph 5000D analysis (Stein 1985).

Samples were dried at 40°C, disaggregated, and homogenized. Fractions smaller than 1 mm and smaller than 125

Table 1 Estimated annual contribution of the Geul compared with the Meuse^a

	Water (10 ⁸ m ³)	Sediment (10 ⁴ tonnes)	Zn (tonnes)	Pb (tonnes)	Cd (tonnes)
Geul ^b	1.3	3	70.5	13.9	0.4
Maas ^c	103	50	906	144	9.3
Geul/Maas · 100	1.2	6	7.7	9.7	4.3

^a All data from near the Belgian–Dutch border

^b From Leenaers (1989b); data from 1983

^c From RIWA (1988); data from 1986

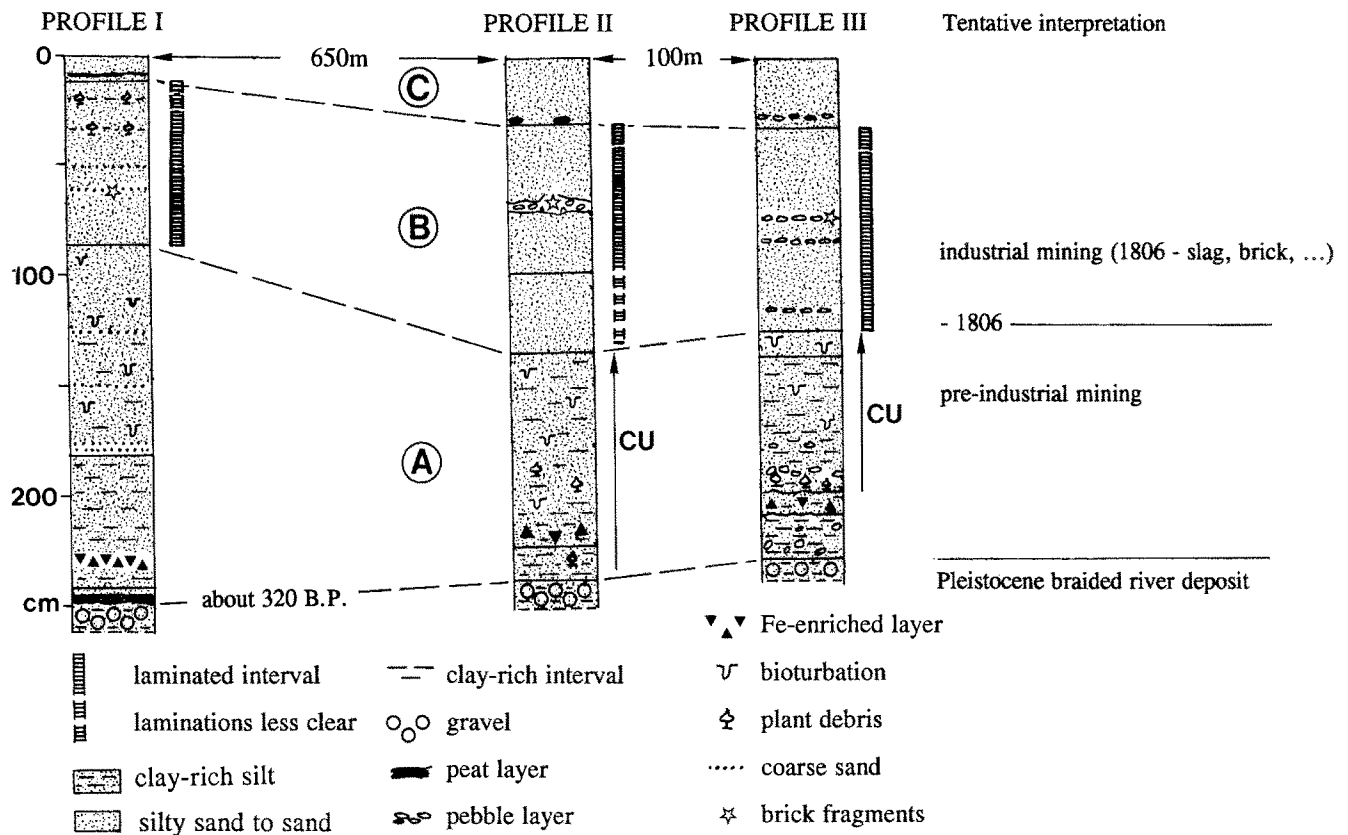


Fig. 2 Stratigraphy of the three profiles sampled adjacent to the Geul (C.U. = coarsening upward cycle)

however, precision was poorer where concentrations were closer to the detection limit (< 1 ppm).

μm were analyzed. Since the difference in total concentration of the analyzed elements is virtually nonexistent between both fractions, we will only report on the $< 125\text{-}\mu\text{m}$ fraction. Furthermore, Leenaers (1989b) concluded that no difference can be observed in terms of total concentration and in terms of partitioned concentrations of heavy metals in the grain size fraction $> 63\ \mu\text{m}$ and $< 63\ \mu\text{m}$. We preferred to analyze the $< 125\text{-}\mu\text{m}$ fraction since particle-size analysis shows that most of the samples are composed of a large amount of particles of the very fine sand and silt fraction. Furthermore, available studies indicate that mine and smelter tailings may provide metal-rich particulate contamination, so a coarser sediment fraction than the usually $< 63\text{-}\mu\text{m}$ fraction (IGCP 259 and IGCP 360 recommendation) also should be analyzed (Bradley and Cox 1986; Jones 1986; Moore and others 1987; Brook and Moore 1988). One gram of the sample was decomposed in a mixture of hydrochloric acid (37 percent; 4 ml), nitric acid (65 percent, 2 ml), and hydrofluoric acid (48 percent, 2 ml). After the reaction was completed, the dissolved sample was evaporated and the procedure was repeated. After evaporation, the residue was subsequently dissolved in 20 ml hydrochloric acid (2.5 N). After filtration, the fluid was diluted to 50 ml. Zn, Pb, Cd, Cu, Fe, and Mn were analyzed by atomic absorption spectrometry. Ten analyses for As and Sb were carried out using the hydride extraction method. Analytical precision was generally better than 10 percent at the 95 percent confidence level. For Cu and Cd,

Vertical profiles

Lithology and mineralogy

The base of the three vertical profiles was taken at a thick gravel unit, characterized by a grey-green-colored clay matrix. Flint pebbles dominate, but shale and sandstone pebbles also occur. Sorting is poor with gravel size grading from very fine pebbles to large cobbles. Gravel with ventifacts at their surface, "driekanter"-shaped cobbles and splintered fragments regularly occur. This gravel unit occurs in the three profiles at a depth of more than 200 cm.

Different units, each characterized by slightly different lithological and sedimentary features and vertical variations, occur above this gravel unit. Detailed correlation of individual units is, however, difficult. In general, three sedimentary units, each composed of several subunits, can be differentiated (Fig. 2). They are:

Unit A is mainly composed of bioturbated clay-rich silt subunits that are separated by sharp erosive boundaries. A general coarsening upward trend is evident from the particle-size analysis of profiles II and III. In profile I this trend is less pronounced. Different discrete coarse sand and pebble layers, 2–5 cm in thickness also occur. At the base of unit A in profile I an 8-cm-thick peat layer occurs.



Fig. 3 Horizontally laminated upper interval of the overbank profile of the Geul river

Dispersed wood fragments, with three twigs and branches (up to 30 cm long) occur in the lower part of this unit in profile II and III. Also present at the base of this unit is an Fe-rich layer. This layer marks the transition between brown–beige- and grey–green-colored lithologies. The thickness of this unit varies between 100 and 155 cm.

Unit B consists of parallel laminated sediments (Fig. 2) composed of alternations of about 1-mm-thick laminae of brown–beige-colored silt with beige–yellow–brown-colored medium to fine grained sand (Fig. 3). In general this unit is less bioturbated than the underlying sediments. Small brick and slag fragments are common in the upper part of this unit where laminations are less well developed. Several discrete pebble or coarse sand layers, 2–4 cm in thickness, also occur. In the central part of profile II, a lenticular pebble layer up to 20 cm in thickness can be followed laterally over several meters. The thickness of this unit is variable, ranging between 85 and 100 cm in the profiles investigated. Within meander cutoffs it can be seen that such thickness variations may occur over lateral distances of some 20 m.

Unit C mainly consists of medium to fine grained sand. This unit is heavily rooted and generally homogeneous. A

vague laminated aspect locally is discernible. In profile I, this unit is less than 10 cm thick, in profiles II and III it is up to 30 cm thick. At the base of this unit in the latter profiles a pebble layer has been recognized.

XRD analysis of the < 2 μm fraction of samples taken within the three units showed the presence of kaolinite and illite as the dominant clay minerals. Locally minor amounts of smectite and chlorite have been recorded. No systematic variation is recognizable.

Based on the wide range of particle sizes and the characteristics of the pebbles, the lower gravel bed has been interpreted as a Pleistocene braided river deposit (Van de Westeringh 1980). The overlying unit A is much younger in age. Carbon-14 dating indicated that the peat layer at the base of unit A in profile I has an age of about 320 yr BP. The occurrence of different numbers of erosive contacts between the different subunits and the fact that it is impossible to correlate in detail the different subunits over short distances suggest that these units are the results of deposition and subsequent erosion in response to channel readjustment. The general coarsening upward trend can be explained by increased soil erosion (mainly loess) due to growing agricultural activity and clearance of the natural vegetation through time (Van de Westeringh 1980). Sedimentation rates were low enough to allow intensive bioturbation. The pebble and coarse sand interlayers reflect deposition during peak discharge periods. The contact between oxidizing and reducing conditions is marked by the Fe-rich illuviation layer. It occurs at the mean ground-water level.

An important change in the Geul river regime is reflected at the transition from unit A to B. From then onwards coarser sediments were deposited in alternating layers of coarse silt and medium- to fine-grained sand. The most dramatic change in the Geul catchment area that could have caused this changes in lithofacies would be the start of large-scale industrial mining activity. At La Calamine this dates back to 1806. However, this change might also correspond with the installation of the hydraulic pumping system at Plombières, which started in 1844–1845 (Dejonghe and others 1993). It is also around this period that a major population increase was recorded (256 people in 1816 and 2572 people in 1858 for the city of La Calamine; Malvoz personal communication). The presence of brick and slag fragments testifies that this layer is influenced by major anthropogenic activity. This period was characterized by intensified deforestation and channelization of the Geul in the mining area with an increased water discharge due to groundwater pumping from subsurface mines. The fact that this unit is little bioturbated may point to increased sedimentation rates and/or it could be that the very high heavy metal contents of this unit limited the biological activity. According to unpublished mine records and unpublished local papers, water discharge during winter was higher than during summer. It is therefore tempting to relate the alternating laminae to be an effect of seasonality. Also in this unit, major flood events are likely to have produced the thin pebble and coarse sand interlayers. The sheetlike gravel unit in profile

III is interpreted as gravel-splay. Similar observations have been reported by various authors (e.g., Lewin and others 1977, 1983; Graf 1979; Bradley and Cox 1986), who showed that mining activity was accompanied by changes in sediment supply directly related to "mining sediment" and indirectly through an increase in runoff after deforestation in the drainage area.

Particle-size distribution of unit C is comparable to the medium- to fine-grained layers of unit B. This unit, however, is heavily bioturbated and originally laminations are severely disturbed. Otherwise the change from parallel laminated to unstructured alluvium could reflect the change in regime of the Geul at the cessation of underground mine water pumping that occurred for most mines at the end of the 19th century. Carbon-14-dating of the uppermost organic-rich layer in profile I gave a recent to subrecent age.

In light of the geochemical analysis (see below), the base of unit B most likely corresponds with the onset of industrial mining activity at La Calamine in 1806. If the base of unit C corresponds to the cessation of mining activity in the area, then vertical accretion rates for the preindustrial mining (unit A), the industrial mining (unit B), and the recent period (unit C) can be calculated (Table 2). Vertical accretion rates are highest within the industrial mining period, with mean values of 0.94 cm/yr, and lowest in the upper unit, with values varying around 0.26 cm/yr. Based on the distribution patterns of ^{137}Cs activity in profiles of the Geul river in the Netherlands, Leenaers (1989b) calculated deposition rates of 0.4–1.4 cm/yr over the time interval 1963–1986.

A similar approach using sedimentological and trace metal analysis of fine-grained flood sediments, together with analysis of historical records has been used by Macklin and others (1992) to construct the flood record and calculate the vertical accretion rates of the river Tyne in northern England over the last 100 years. Here also, higher vertical accretion rates, varying between 3 and 7 cm/yr, characterize the period when active mining occurred in the drainage area, lowering to 0.3–1.2 cm/yr in the years postdating active mining.

Geochemical patterns

In Fig. 4 the vertical geochemical patterns of profiles I and II are given. The latter is representative for profile III. There exists a clear contrast between the three lithological units, with highest values occurring in unit B and lowest

values in unit A and in the underlying muddy gravels. In general, a covariant behavior between Pb, Cu, and, to a lesser extent, Cd is present. The Zn pattern is rather irregular. None of these heavy metals displays a clear covariant behavior with Mn or Fe. The latter two display a similar pattern.

Unit A

The geochemical pattern is rather uniform, with values varying around 6000 ppm for Zn, 600 ppm for Pb, 15 ppm for Cu, and < 10 ppm for Cd. An increase in Cd concentration in the upper part of unit A also was observed in profiles I and III. A slight increase in Pb values towards younger strata occurs. Fe and Mn values are rather constant in the upper part of the unit where values vary around 1.7 percent and 0.5 percent, respectively. Below the oxide enriched layer, Fe and Mn values are clearly lower. The high heavy metal contents in the sediments of unit A are too high to reflect background values. They are much higher than the values in the reference area (Table 3). They most likely relate to incorporation of contaminated sediments, which can be explained by small-scale mining activities in the drainage area in the 17th and 18th centuries. Different historical documents indicate that artisanal mining dates back to the 14th century (Dejonghe and others 1993). The gradual Cd increase most likely relates to downward percolation of mobilized Cd from the anomalous unit B. The pattern of Fe and Mn reflects the classical pattern near the groundwater interface. It is, however, important to note that coprecipitation processes are not likely to play an important role in the profiles considered, since no obvious correlation exists between the heavy metals and Fe or/and Mn. The lowering in Fe and Mn content below the water table is due to mobilization of their oxides/hydroxides under suboxic to reducing conditions.

Unit B

The highest Pb and Cu contents occur in the middle part of unit B where values of 3000 ppm and 45 ppm, respectively, are reached. Cd contents also are higher here. At or near the base of this unit, highest Zn values have been recorded in all profiles studied. Cd also is high at this level, while Pb and Cu remain at a concentration level that is similar to that of the underlying sediments. However, Zn contents clearly drop up-profile, while Pb and Cu and

Table 2 Vertical accretion rates for different units in Geul overbank profiles^a

	A thickness	Sed. rate	B thickness	Sed. rate	C thickness	Sed. rate
Profile I	155	0.88	75	0.80	10	0.11
Profile II	100	0.57	90	0.96	30	0.33
Profile III	100	0.57	100	1.06	30	0.33
Time interval (yr)		176		94		92
Mean sed. rates		0.67		0.94		0.26

^a Sed. rate = sedimentation rate in cm/yr; thickness in cm

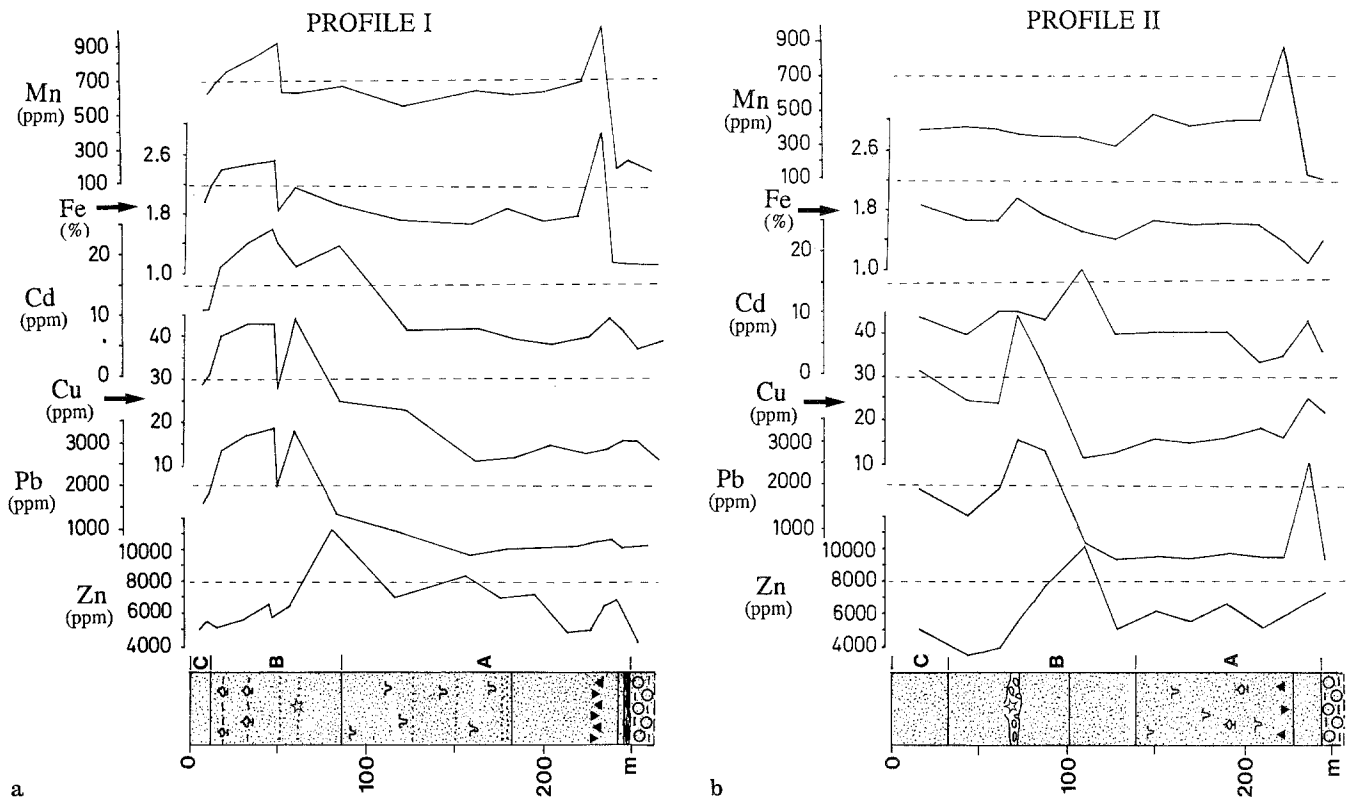


Fig. 4 Vertical geochemical patterns of profiles I and II (see Fig. 2 legend)

to a lesser extent Cd contents increase. Zn values subsequently reach values below those recorded in unit A, while Cu and Pb remain very high over an interval of about 30 cm. In the upper part of unit B, a drop in Cu and Pb content is apparent in profile II (and also in profile III, which is not shown); in profile I this drop is less clear. The distribution

pattern of Fe and Mn, which behave covariantly, is different from the heavy metal patterns.

These patterns can be explained as follows: artisanal mining existed in the drainage area at the beginning of sediment deposition of unit B, but a new Zn contamination source became available, as is indicated by the very high Zn contents. Concomitant change in the drainage regime of the Geul, which is reflected by the coarser nature and laminated aspect of the sediment, most likely corresponds with the start of large-scale mining operations at La Calamine in 1806. This ore body, which is the largest in the Geul catchment, consists nearly entirely of Zn-ore. In the first decades of mining only large ore blocks were mined, while the fines were washed and dumped. Some of these dumps were located along the banks of the Geul river. The absence of any significant increase in Pb content in the lower part of unit B relates to the fact that Pb minerals only occur in very minor amounts in this deposit. The start and further improvement of a new Zn ore treatment plant in 1848–1850 in La Calamine and the cessation of mining activity at this locality in 1882 may explain the gradual decrease in Zn content. The sudden increase in Pb and Cu most likely relates to the onset of subsurface mining in Plombières in 1844–1845 and at other places where galena and sferite were excavated. From this period onwards, huge quantities of sulfide ore were also imported from abroad and treated at the industrial plants at Plombières and La Calamine. The drop, especially in Pb and Cu in the upper part of profiles II and III, most likely relates to closure of most mines at the end of the 19th century. The high contamination level in the upper part of unit B in profile I can be explained by input of contaminants from point sources such as the huge dumps and from ore treat-

Table 3 Trace element concentrations of different Belgian soils

	Ref area ^a (n = 4) ^b	Soil geochem ^c (n = 4)	Belgian top soil ^d (n = n.s.)
Zn			
Range	396–793	86–107	30–500
Mean	652	97	—
Pb			
Range	114–269	136–210	10–40
Mean	183	172	—
Cu			
Range	11–16	5–7	8–30
Mean	14	6	—
Cd			
Range	2–3	—	0.05–0.20
Mean	3	—	—

^a Ref area = Walhorn reference area

^b n = number of samples; n.s. = not specified

^c Soil geochem = Van der Biest (1986) topsoil in Walhorn syncline (analytical procedure identical to the methodology used in this paper)

^d De Temmerman and others (1984); total acid extract of stony loam—heavy clay soils above Paleozoic and Mesozoic parent material

ment plants, which were still operational until 1950 (however, at a lower production rate) and from the redistribution of contaminated sediments. Note that the sediments with higher heavy metal contents do not necessarily possess higher Fe or Mn contents, indicating that the heavy metals do not necessarily relate to Fe–Mn oxides/hydroxides.

Unit C

Recorded metal values in this unit are in the same order of magnitude as or slightly lower than the values measured in the upper part of unit B. Mine dumps and redistribution of contaminated overbank sediment are the most likely sources to explain the high metal contents.

In Fig. 5 a synthesis of the vertical geochemical pattern in overbank sediments of the Geul north of the Plombières deposit is given. This synthesis is deduced from patterns of profiles I to III. It shows that elevated concentrations are present throughout the profile. Differences in heavy metal and Fe contents enable further differentiation to be made in the vertical profile. Unit A is split up into four subunits based on the Fe and Cd content and differentiation of three subunits in unit B relates mainly to the Zn, Pb, and Cu patterns. The upper B₃ subunit possesses many characteristics in common with unit C.

Regional geochemical distribution patterns

In Fig. 6A and B the regional variations of the Zn, Pb, Cu, and Cd contents in the 0- to 20-cm (henceforth called

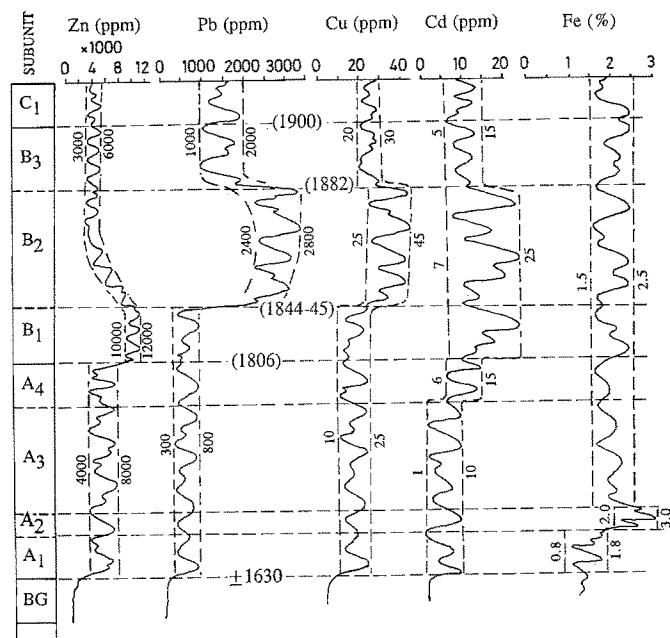


Fig. 5 Generalized vertical geochemical pattern in vertical overbank profiles of the Geul in the study area with ¹⁴C dating below and interpreted datings (in parentheses)

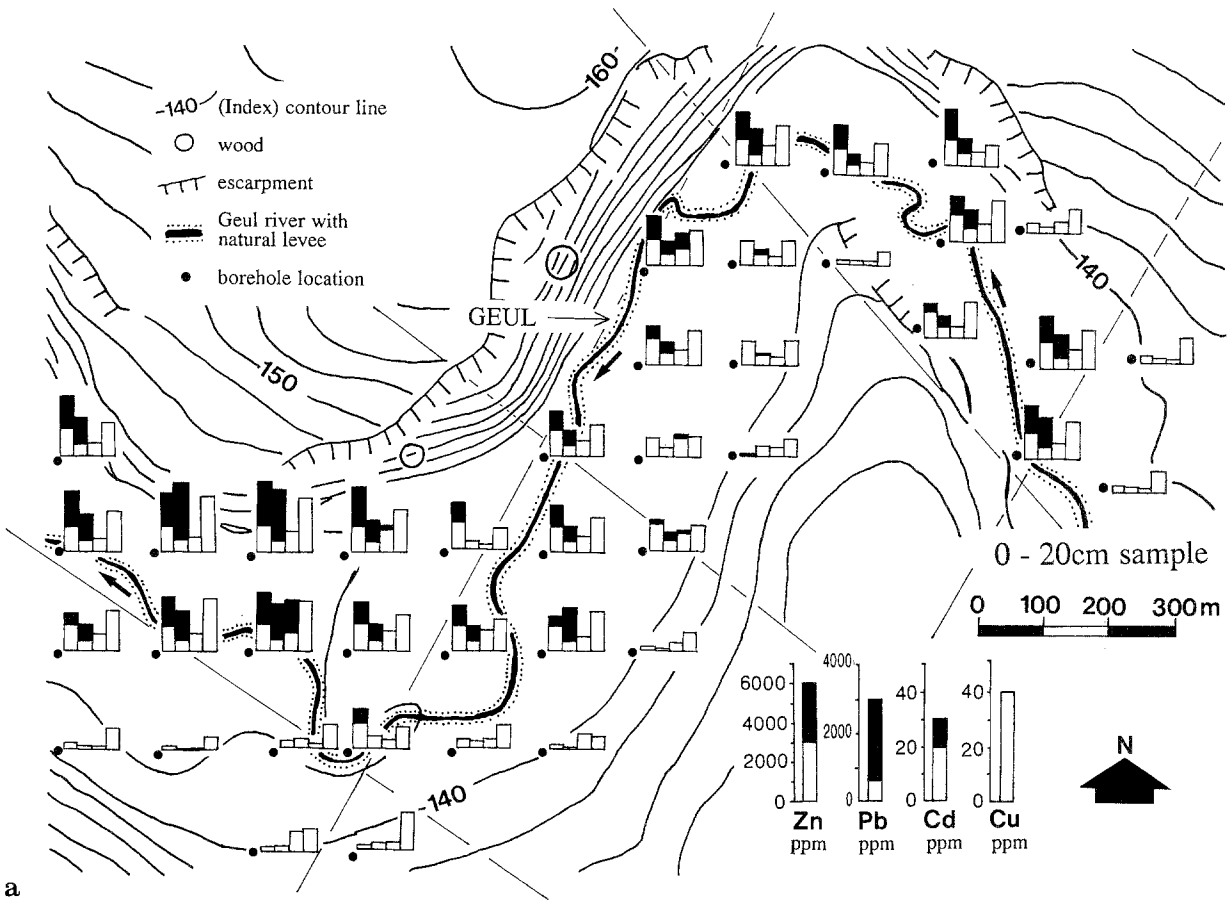
“upper”) and 80- to 100-cm (henceforth called “lower”) samples are shown. To facilitate the discussion, the study reach is subdivided into different sectors (numbered I–III and a–d). Detailed data can be obtained on request from the first author.

Values display a wide range in the upper and lower samples, with the highest values occurring in the upper samples. In general, the lowest values are present within samples taken close to the alluvial valley flanks. Highest concentrations predominantly have been recognized along the Geul in sectors Ib and IId. However, metal contents in lower samples taken along a more or less north–south-oriented Geul transect vary considerably. This shows that rather important variations may occur over very short distances.

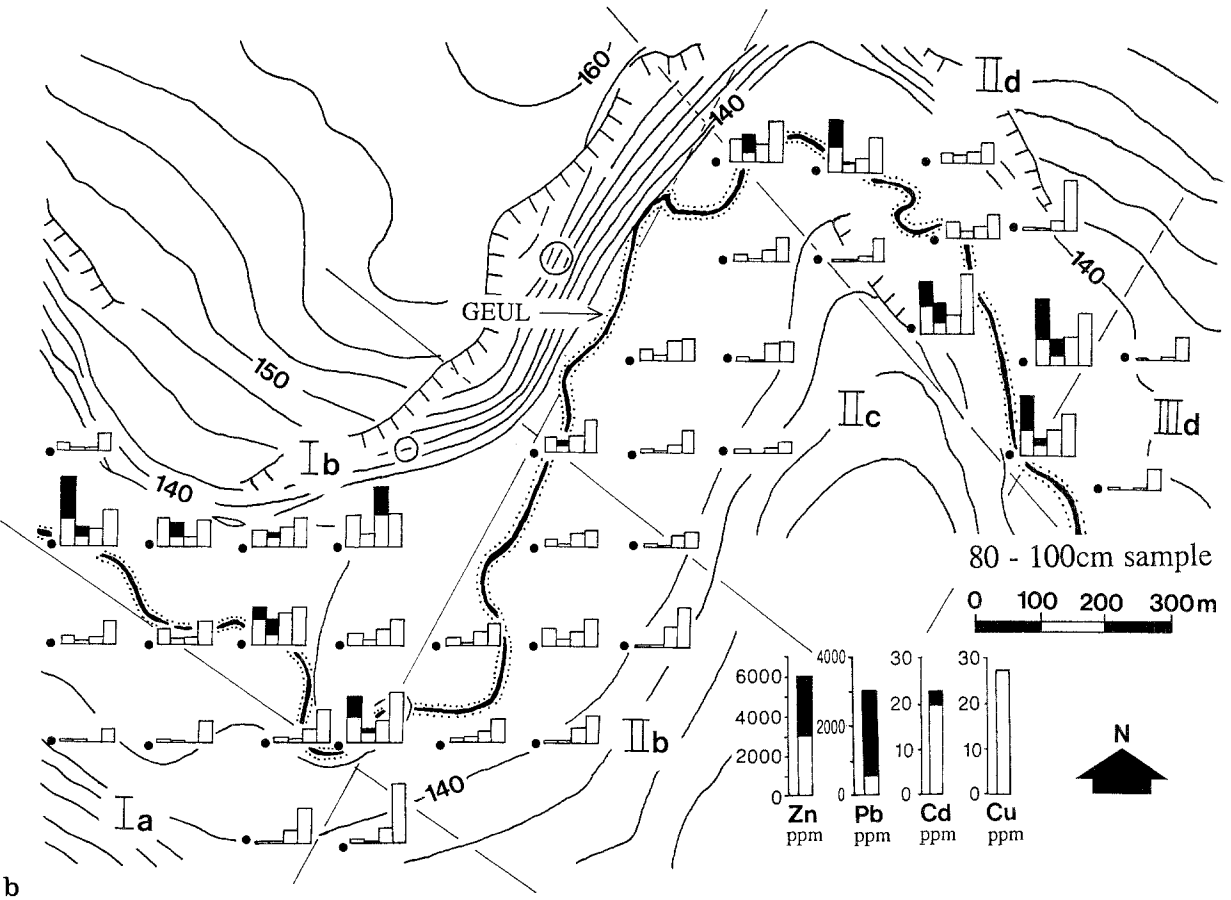
Zn values of the upper and lower samples vary between 134–6665 ppm and 70–6730 ppm, respectively. Where the lower sample shows a higher Zn content than the upper interval (five cases), it is very likely that the B₁ subunit of the generalized vertical profile (Fig. 5) was sampled. Most of these samples occur within 10 m of the Geul river. Many of the values in the sectors Ia, I Ib, and I Ic are lower than the lowest values recorded in the vertical profiles. The lowest values (<150 ppm) could correspond to the background soil population and most likely should not be treated as overbank sediment. Van der Biest (unpublished data) reported similar background values from soils in the Geul catchment area (Table 3). These values are also in the range of the concentrations reported by De Temmerman and others (1984) for Belgian top soils (Table 3). Most of the other values plot between 220 and 800 ppm. They are interpreted as local preindustrial background population. Preindustrial overbank samples of the Geul river in the Netherlands (Hindel and others 1994) and the alluvial samples from our reference area display similar concentrations (Table 3). They most likely reflect artisanal medieval mining activity.

Pb values of the upper and lower samples vary between 101–3750 ppm and 37–1701 ppm, respectively. Only in one case was the content of the lower sample higher than in the upper sample. This could indicate that the B₂ subunit (Fig. 5) was sampled. In six cases where Pb concentrations are >1000 ppm, the B₃ or C₁ subunit of Fig. 5 possibly was sampled. They occur in sectors Ib and IId, close to the present Geul river. Unit A was sampled where values of the lower samples vary around 500 ppm, while values below 200 ppm may correspond to soil and/or preindustrial overbank sediments not present in the studied vertical profiles. The latter predominate in sectors Ia, I Ib, I Ic, and I Id. Similar concentrations have been recorded in the sediments of the reference area (Table 3) and in the soil data reported by Van der Biest (unpublished data). These

Fig. 6 Regional variations of Zn, Pb, Cu, and Cd in the study area of the 0–20 cm (A) and 80–100 cm samples (B) (white and black bars indicate, respectively, below and above C norm value of the respective element as used by the Dutch VROM (VROM 1990)



a



b

values, however, are clearly an order of magnitude too high when compared with data reported by De Temmerman and others (1984) for Belgian soils (Table 3).

Cd values of the upper and lower samples vary between 3–52 ppm and <1–30 ppm, respectively. In six cases the Cd value of the lower sample exceeds the value of the upper sample, suggesting that the samples of the lower interval were taken within the B₂ to B₁ subunits of Fig. 5. Some of these localities occur adjacent to the Geul river, others are rather far away from it. Furthermore, five lower sample locations (in sectors Ia, IIb, and IIIId) yield Cd values in excess of 10 ppm. Most likely, the A₄ subunit or a horizon nearby was sampled. Most other lower samples display values below 5 ppm and are comparable to values detected in the reference area (Table 3). These values are, however, high when compared with the Cd contents of Belgian soils (De Temmerman and others 1984).

Cu values of the upper and lower samples vary between 14–57 ppm and 6–36 ppm, respectively. Locations with values >20 ppm or where the content of the lower sample exceeds the upper value are interpreted to correspond to the B₂ level (Fig. 5). Only two samples fulfill this criterion. In general values are low and comparable with reported values by Van der Biest (unpublished data) and De Temmerman and others (1984).

Only eight samples of the lower interval had Fe values higher than in the upper samples and concentrations >2.0 percent. They all occur close to the alluvial valley flank (Fig. 6). Some of these samples also possess higher Mn values. Here most likely the lower sample was taken close to or within the A₂ subunit.

As and Sb contents of 10 randomly chosen samples vary between <1–77 ppm and <1–12 ppm, respectively.

The nonsystematic variation in element concentrations in the lower overbank sediments can be explained in terms of which subunit was sampled at depth. Whether a certain sediment layer will be deposited at a certain locality or not will be controlled by the extent of flooding and the displacement of the riverbed. Irregular bank elevations ensure that the bankfill discharge varies along the channel and certain parts of the floodplain receive overbank sediments more frequently than others. As also illustrated by Bradley and Cox (1986), this may result in metalliferous sediments accumulating in discrete sedimentary zones on the floodplain. This clearly illustrates how misleading and difficult interpretation can be whenever geochemical data of overbank sediment samples taken within different sediment horizons have to be evaluated. However, research conducted in fine-grained alluvial plains often will have to deal with samples that have not been taken in an undisturbed way or that come from profiles without any clear lithological variation with depth. Another interesting result of the present research is that the evolution in floodplain development influenced by mining can be traced in some detail from the study of the geochemical profiles as far as reliable datings are available (research in progress). This is of special importance since the investigation of floodplain development is hampered by the fact that laboratory experiments provide unrealistic results and field observa-

tions are not so reliable due to the lack of long-term data or good datings within vertical profiles.

Conclusions

As the result of historic mining activity in the Geul catchment, floodplain soils and overbank sediments downstream of the mines are especially contaminated with Pb, Zn, and Cd. The heavy metal distribution patterns have been studied within three vertical overbank sediment profiles and in a 1.8-km² alluvial plain in an area occurring north of the main (Pb–Zn) mineralization area in East Belgium. Mining activities mainly relate to the last century. The following conclusions can be made:

1. The vertical patterns of heavy metals in the overbank sediment profiles can be interpreted in terms of the development of mining operations in the largest deposits, e.g., the Zn oxide-bearing La Calamine ore body and the Pb–Zn sulfide-bearing Plombières ore body and the evolution in the ore treatment plants. The marked change in sedimentary characteristics (grain size, texture, etc.) within the vertical overbank profiles is related to the onset of industrial mining activities in the drainage basin.

2. Elevated values in heavy metals, however, occur in sediments deposited in preindustrial mining times. Sediments deposited in the 17th and 18th centuries possess Zn values between 4000 and 8000 ppm, Pb values between 300 and 800 ppm, and Cd values up to 10 ppm.

3. Detailed geochemical research on overbank profiles allowed a detailed monitoring through time. However, not all sedimentary units deposited in the alluvial plain are represented in these profiles. Furthermore, a thorough knowledge of the industrial history and age dating of the sediments is necessarily for unraveling the geochemical distribution patterns.

4. The data gathered from the regional investigation illustrate the vast amount of contaminated sediments presently stored. Today, contaminated sediments in the Geul river can either originate directly from the mine tailings or come from reworking of contaminated overbank sediments. The former act as a point source while the latter is a major line source. Data on the regional geochemical distribution in vertical profiles could provide useful information about floodplain development.

5. Sampling of alluvial sediments at different locations at different or even the same depth interval may give very different results, even over small distances. Therefore, routine sampling of overbank sediments from boreholes, without careful examination of the sediments, can give misleading results.

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