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Anthropogenic impact on sediment composition and geochemistry in vertical overbank profiles of river alluvium from Belgium and Luxembourg

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Abstract

The geochemical study of alluvial sediments allows to reconstruct pollution through time. Geochemical and sedimentological variations recorded in 40 vertical overbank sediment profiles from Belgium and Luxembourg can be classified in three dominant pattern types: • type 1 profiles with dominantly non-anthropogenically influenced geochemical distribution patterns. These profiles are devoid of anthropogenic particles such as charcoal, plastic, brick and slag fragments, with the exception, in some cases, of their uppermost parts. Background concentrations thus are displayed throughout the profile (subtype 1A). However, in this group, profiles displaying anomalous values caused by the presence of heavy minerals (subtype 1B) or by base metal mineralisations in the catchment (subtype 1C) also occur; • type 2 profiles displaying clear evidence of anthropogenic influences. Most of these profiles display a gradual increase in heavy metal content in their upper part, with values doubling or tripling (subtype 2A). However, other profiles display a dramatic increase in pollution-related elements caused by past or present-day heavy industrial activities in the catchment (subtype 2B). Here also the sedimentological patterns reflect the influence of the industrial activities; • type 3 profiles contain features related to pedogenetic translocations of mobile elements. Apart from classical pedogenetic features such as illuviation/eluviation, the mobility of As and Cd is of particular importance. From a sedimentological point of view, these profiles do not necessarily differ from type 1 or 2 profiles. It should be noted that in some profiles, pattern types can be superimposed. Type 2B profiles are of particular environmental concern, because the potential release of heavy metals may have consequences for agricultural activities or groundwater contamination in the catchment. Furthermore, reworking of polluted sediments temporarily stored in the alluvial plain can also have negative effects on the ecosystem.

Keywords: Heavy metals; Pollution; Overbank sediments; Background concentrations; Mineralisation; Environmental assessment

1. Introduction

To assess the legacy of human activities on the environment, present concentrations of pollution-sensitive elements have to be compared with the pre-industrial, and preferably pre-anthropogenic, concentrations in a similar sampling medium at the same

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sampling locality. Overbank sediments are very suitable for this purpose (Ottesen et al., 1989; Swennen and Van der Sluys, 1998). Overbank sediments are deposited on the floodplain during or after flooding. In floodplains where sedimentation occurred, a vertical section through such overbank deposits represents a superposition of different succeeding flood events, providing that the profile has remained undisturbed. With depth, older flood layers can be sampled. The effect of man-related activities in the catchment is often reflected by variations in sedimentological profile characteristics, such as grain size variations, lack of bioturbations in highly polluted strata and the presence of anthropogenic particles, that is, charcoal, plastic, brick or slag particles, etc. ... (Swennen et al., 1997). A detailed sedimentological investigation thus helps to distinguish natural from man-influenced element patterns. Geochemical analysis of superimposed layers allows the reconstruction of the chemical evolution of these sediments through time (Macklin et al., 1992). The advantage of sampling overbank deposits lies in their ability to provide representative samples to characterize their catchment (Ottesen et al., 1989). During a period of high to extremely high rainfall, a large number of different sediment sources are activated and collected by the river system where they become intensely mixed, and may become deposited on the floodplain normally as fine-grained alluvium, making them suitable for geochemical analysis.

Because trace element variations occur between overbank sediment profile exposed over relatively short distances (Macklin et al., 1994; Ridgway et al., 1995; Taylor, 1996), detailed correlation between different overbank profiles and their geochemical signatures is often difficult, although the general evolution pattern in adjacent profiles is often comparable and pollution histories can, therefore, be deciphered (Swennen et al., 1994). This is in agreement with Langedal and Ottesen (1997), who noticed that lateral variations between bottom section of overbank sediment profiles were small and insignificant compared with differences between the bottom and upper sections.

The aim of this paper is to investigate the relationship between catchment land use histories and variations in sediment composition and geochemistry. Therefore, data on grain size and geochemical variation in overbank sediment profiles from Belgium and Luxembourg are presented. This area was chosen as test area to study the variation in overbank sediment geochemistry in time and space since on the one hand, the subsurface geology covers a wide spectrum in sedimentary rocks. Also some mineral deposits occur. On the other hand, the study area is highly industrialised, industrial agriculture is well developed and large forest area exists. Considering that a major part of the population of both countries, but in fact also in the rest of the world, lives in alluvial plain areas, it is important to pay attention to the geochemistry of these sediments, which in the case of being polluted may be harmful from both a human and ecotoxicological point of view. Based on the data presented below, a classification of the different geochemical patterns recognized in the profiles will be presented. This classification system allows to define areas with background patterns and those reflecting mineralisations and/or areas polluted with heavy metals. Since this classification is also applicable to other overbank geochemical studies recently carried out in Europe, it is hoped that it can be further developed and used as a decision-making tool.

2. Methodology

This research was carried out in parallel with a geochemical mapping project based on the recommendations of a former Western European Geological Surveys (WEGS) working group (Bölviken et al., 1990, 1996). For this mapping project, initially 66 overbank sites have been sampled in Belgium and Luxembourg (Van der Sluys et al., 1997; Swennen and Van der Sluys, 1998; Fig. 1). During the mapping project, overbank profiles representative of catchments between 60 and 600 km^2 were selected. Selection of the sampling site was based on a desk-study whereby geographical, hydrological and historical criteria of potential sampling locations were evaluated. This was followed by a field survey where at least three profiles were studied in detail aside from the natural profiles occurring along the river courses. In some areas also aerial photographs of different time periods were inspected allowing assessment of the stability of river courses through time. Preference was given to locations with stable, or slowly migrating river reaches occur, as recommended by Bogen et

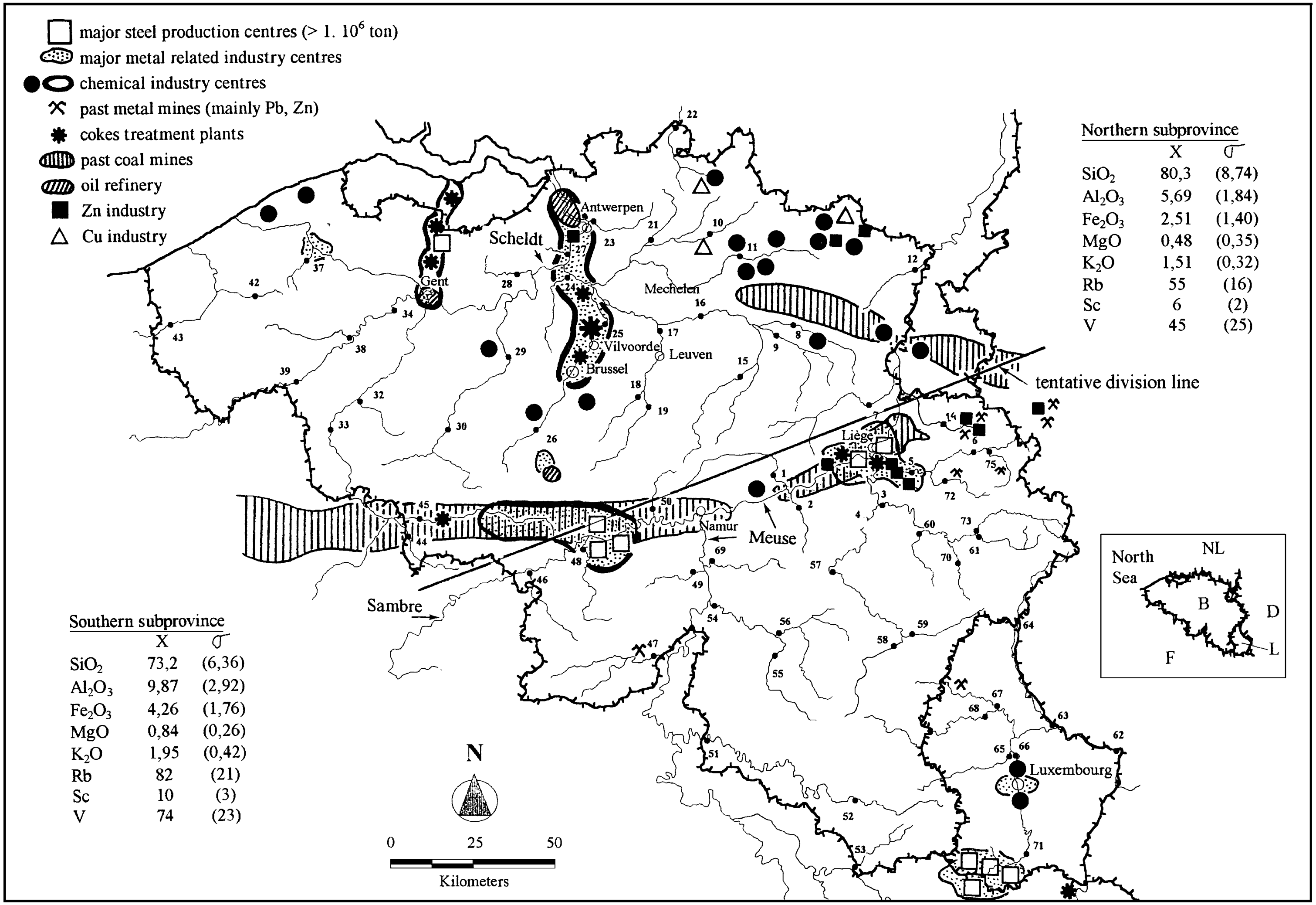

Fig. 1. Geographical location map of sampling sites with division in northern and southern sub-province and mean (X) and standard deviation (σ) data of some major (in wt.%) and trace elements (in ppm) of L (lower overbank)-samples illustrating the difference in pre-industrial values in both areas (see Swennen and Van der Sluys, 1998). Name of sampled river systems: 10: Kleine Nete; 15: Grote Gete; 16: Demer (Langdorp); 17: Dijle; 19: Dyle; 21: Molenbeek; 23: Groot Schijn (five profiles); 24: Vliet; 25: Zenne (four profiles); 28: Durme; 29: Dender; 30: Dendre; 32: Rhosnes; 33: Escaut; 34 and 39: Leie (four profiles); 37: Rivierbeek (four profiles); 38: Mandel; 42: Krekelbeek; 45: Haine; 47: Viroin; 53: Ton; 58: Ourthe occidentale; 60: Lienne; 61: Amblève; 62: Sûre; 65: Attert; 66 and 71: Alzette (five profiles); 67: Wiltz; 68: Sûre; 69: Bocq; 70: Salm; 72: Hoegne; 73: Warche.

al. (1992) and Langedal (1997) for this type of research. The profiles were dug in the immediate vicinity of the river channel, where highest metal concentrations often occur (Swennen et al., 1994; Langedal, 1997) (Fig. 2). Final selection was mostly based on sedimentological field criteria displaying evidences of representing the most complete record. After detailed field description, it was often possible to differentiate an upper profile part, where anthropogenic particles such as slags, plastic, brick fragments and charcoal occurred, and a middle and lower part where these particles are absent (Fig. 2). In a few profiles, no anthropologenic particles occurred within the profiles and the grain size distributions were uniform. In fact in general, grain size variations in most profiles are minor. Bioturbation often obliterates sedimentary structures such as laminations, but, in intensely polluted profile parts, bioturbations are often absent.

For this survey, all overbank profiles were sampled, after removal of the outer 10–20 cm of the exposure surface (Fig. 2), over 10- to 20-cm intervals for the follow-up study. One- to 2-kg samples were taken. Each of the samples thus consisted of a composite of several flood layers, as shown in profiles where flood laminations less than a few millimeters could be recognized. The detailed sampling was set up to test the assumption that pre-anthropogenic, or at least pre-industrial samples, could be taken from the lower part of most overbank

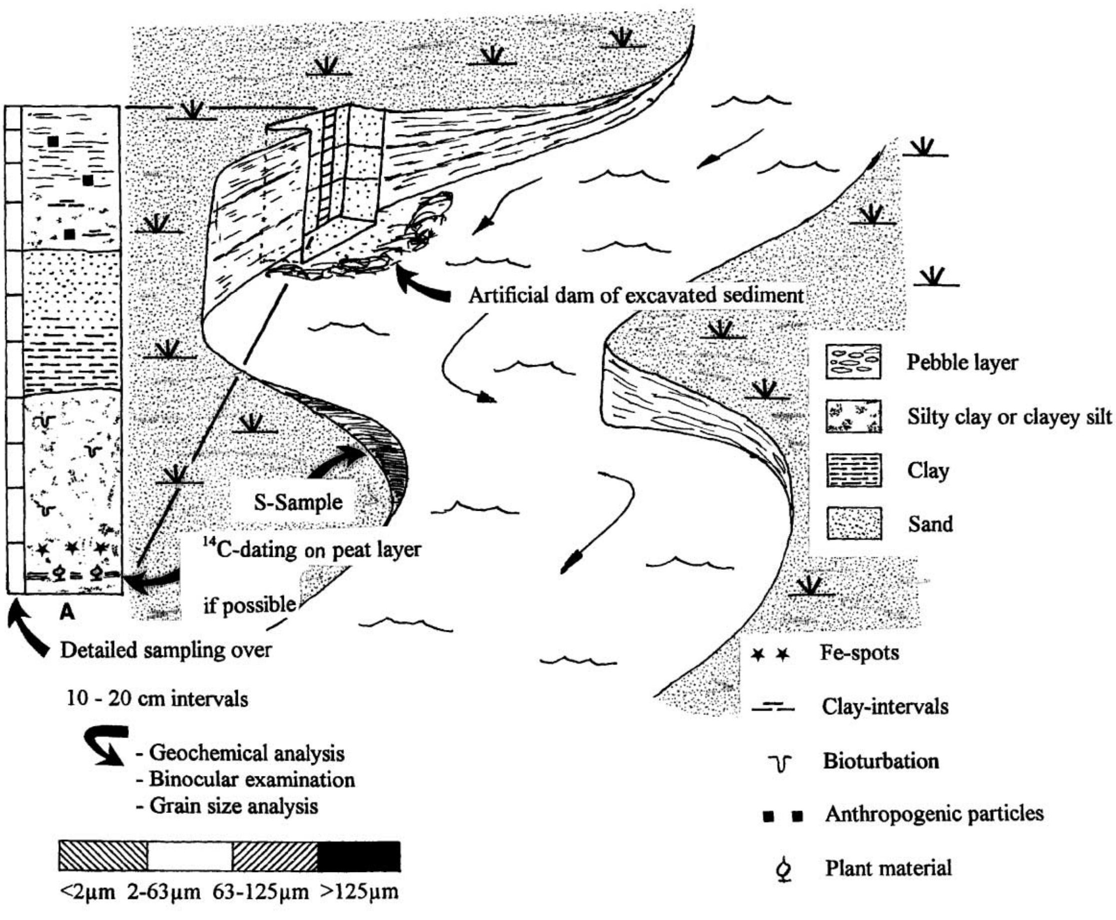

Fig. 2. Schematic presentation of the sampling strategy with illustration of some overbank profile characteristics. On the left, a schematic lithological log with indication of samples taken for detailed sedimentological and geochemical analysis is given.

profiles and that geochemical variations may occur between lower and upper section intervals in the profiles. Furthermore, it allowed an assessment of whether important vertical migration of elements occurred in the profiles. Finally, only 34 of the 66 sampled vertical profiles were analyzed in detail. Furthermore, in four river catchments, more than one overbank profile was sampled, bringing the total of analysed samples at about 800 in total. The selection of the latter profiles was based on the presence of anomalies or high trace element concentrations recognized in the mapping project or because of the need for reference profiles within certain areas. Preference was also given to profiles where ^{14}C-dating of the lower profile part was available (about 30% of the causes).

After drying at 40 °C, disaggregation and sample splitting, the <125-μm fraction was used for geochemical analyses by XRF (mainly major elements) and after three-acid digestion (HNO_{3conc}, HCl_{conc}, HF_{conc}) with ICP-AES and ICP-MS (mainly trace elements). Some elements have been determined by all analytical techniques (see Figs. 3–9). The following elements were determined (major elements expressed as oxides): SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3, Ba, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mn, Nb, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr. Flame-AAS was used for determination of Cd and As. Thus, by applying these analyses, total metal content was analysed. Reproducibility was tested by reanalyzing 5% of the samples. International soil standards and inhouse standards were added to the different batches. No significant statistical difference was found for the analysis carried out with each of the analytical methods used at a significance level of 5% for concentrations above two times the detection limit. Differences between XRF and ICP results may occur (see Figs. 3–9) and in several cases, simply relate to the fact that sediments analysed by both methods were not always taken from the same sampling interval. In fact, the XRF samples were taken from the mapping project, thus representing a bulk composite sample that should be as representative as possible to characterize the pre-industrial situation (see Swennen et al., 1997; Van der Sluys et al., 1997). The ICP analyses were done on sediments giving more detailed picture. Also the fact that some contaminants occur as particulate phases may play a role. Finally, it was observed that digestion according to the three-acid protocol was not always total, that is, some insoluble residues consisting of quartz (as determined by XRD) sometimes occurred. However, knowing the relatively high detection limit of XRD, other mineralogical phases also could have survived the digestion. However, SEM-EDX analysis of these residues did not show the existence of other phases than quartz. Finally, also the difference in sensitivity of the different methods should be taken into account. In this paper, only some of the geochemical patterns of lithology-sensitive major (e.g. SiO_2, Al_2O_2, K_2O, MgO) and pollution-sensitive trace elements (Zn, Pb, Cu, As) will be documented. Where relevant, other elements are presented. The entire data set of the profiles reported in this publication can be requested from the authors.

3. Results and discussion

Each of the vertical overbank profiles displays a location-specific sedimentological and geochemical pattern. Despite the sometimes complex distribution patterns, three dominant types can be differentiated.

Type 1 profiles are characterized over most of the section by uniform sedimentological and "natural" element distribution patterns. "Natural" is used to describe a situation where the geochemistry is dominantly controlled by natural factors such as by mineralogy, grain size, organic matter distribution, etc.... and where no apparent pollution exists. Lithological and related geochemical variations may occur, but in most profiles, variations are minor and concentrations equivalent to or below background levels are recorded. Three subtypes can be differentiated according to the dominant factors controlling the element distribution patterns.

In subtype 1A, profiles are characterized by low to relatively low heavy metal and As concentrations throughout the succession. Only in the upper profile parts, some slight concentration increase in these elements, with respect to the underlying strata, can be discerned, despite the fact that the lithology is normally uniform (Fig. 3). Nevertheless, the minor variations in element concentrations along the profiles relate mainly to differences in clay/sand or organic

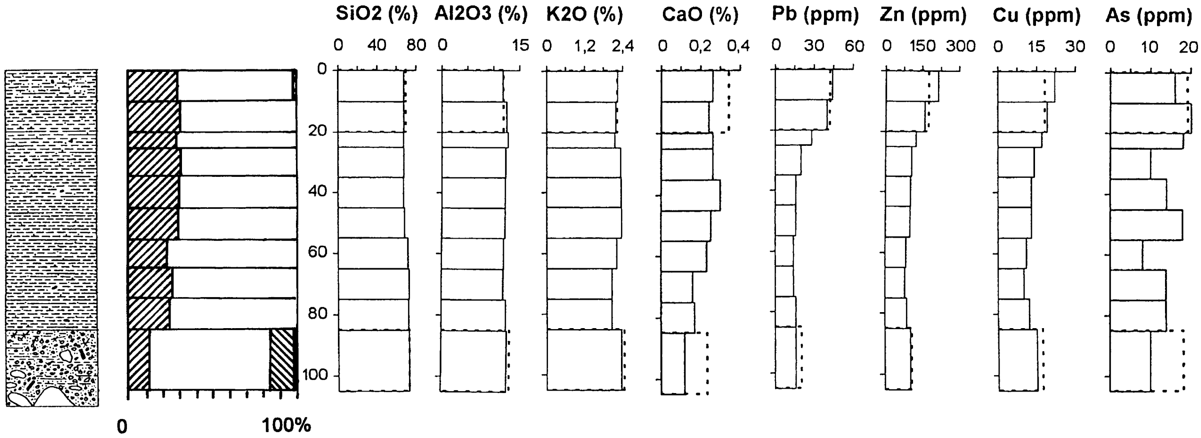

Fig. 3. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Lienne overbank profile (profile 60 in Fig. 1) where no apparent anthropogenic influences occur in the lower and middle profile parts (subtype 1A). The major element contents are relatively uniform with high Al_2O_3 and K_2O contents throughout the profile concurring with the clay- and silt-rich nature of this overbank profile. The increase in heavy metal content in the upper part of the profile can be explained by anthropogenic influences that would catalogue this profile also in subtype 2B; however, the increase in heavy metals (with the exception of Pb) is minor here.

matter concentration, which seems to exert a certain influence on the heavy metal contents. Based on a number of ^{14}C-datings, as well as on the absence of anthropogenic particles, the lowermost parts of these profiles clearly represent deposition during pre-anthropogenic or at least pre-industrial time (Swennen and Van der Sluys, 1998). The uniform distribution pattern in subtype 1A profiles consequently suggests that no major anthropogenic influences occurred near the sampling location sedimentation. This does not necessarily mean that the catchment area is pollution-free, since due to storage or slow transfer, pollutants still can be stored upstream. Historical research showed that these profiles systematically occurred in areas devoid of major former and present-day industrial activity.

Subtype 1B profiles are characterized by high to very high concentrations of elements such as Ti, Zr, Cr, Hf, Y, Nb, La and Ce (Fig. 4) that are linked to the presence of heavy minerals such as rutile, chromite, monazite, zircon, ilmenite, garnet, andalusite, and pyroxene (Hindel et al., 1996). They occur only in the northern part of Belgium where Tertiary and Quarternary fine sandy lithologies dominate. This is reflected in the virtual absence of clays and the dominance of the sand fraction in these profiles (Fig. 4). Here the concentration of heavy mineral-related elements is, in general, rather high throughout the profile. Locally, some sediment horizons yield extreme concentrations with values of up to 2.3% Zr, 5.1% TiO_2, 145 ppm Y, 110 ppm V, 80 ppm Th, 18 ppm Sc, 80 ppm Nb, 215 ppm La, 520 ppm Hf, 21 ppm U, 1134 ppm Cr and 360 ppm Ce being recorded at the base of the Kleine Nete profile (Fig. 4). The latter can be interpreted as placer deposit. It should be noted that there is no covariance between these elements and heavy metals or other major elements (except TiO_2 and P_2O_5).

Subtype 1C profiles are characterized by relatively high heavy metal contents throughout. Anomalous heavy metal contents may occur in particular horizons (Fig. 5). They may even develop in the lower parts of the profile where sediments were deposited during pre-industrial or pre-anthropogenic time as attested by ^{14}C-dating. Sedimentologically, these profiles normally display uniform characteristics from top to bottom. Subtype 1C profiles have only been recognized in Southern Belgium where Paleozoic lithologies dominate and where Pb–Zn mineralisation has been recognized and sometimes mined in the past

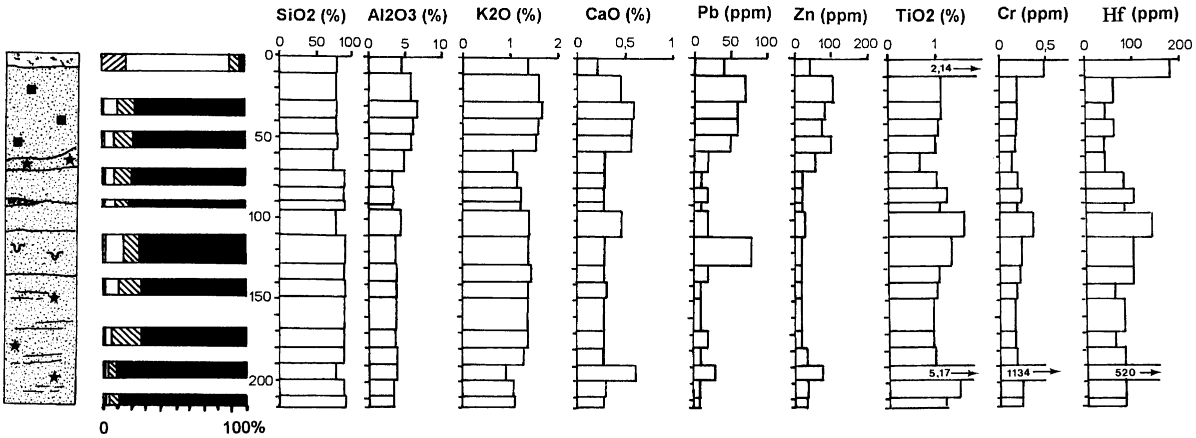

Fig. 4. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Kleine Nete overbank profile (profile 10 in Fig. 1) displaying high sand contents that relate to the Tertiary and Quaternary nature of the catchment. Mean grain size varies around 140 μm. Notice the high concentrations of different elements such as Ti, Cr, and Hf caused by the presence of heavy minerals (subtype 1B).

(e.g. Geul area: Swennen et al., 1994). The fact that higher metal concentrations in pre-industrial overbank sediments can be related to the occurrence of mineralisation supports the idea of using chemical analyses of these samples for mineral exploration in areas where pollution is severe (Ottesen et al., 1989; Bölviken et al., 1990, 1993; Demetriades and Ottesen, 1990; Shen and Yan, 1995; De Vos et al., 1996).

Type 2 profiles are characterized by anthropogenic influences, expressed by a clear increase in heavy

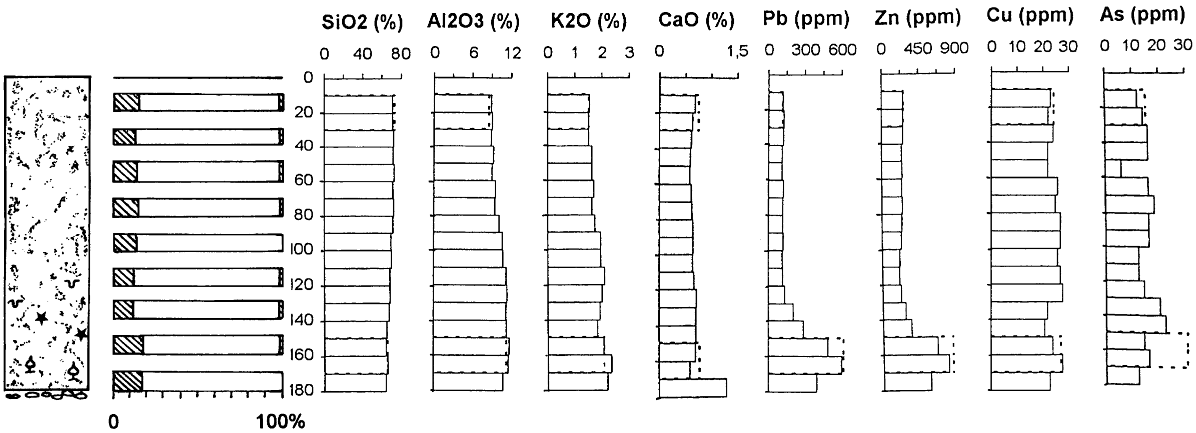

Fig. 5. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Viroin overbank profile (profile 47 in Fig. 1) displaying high heavy metal concentrations caused by the existence of base metal mineralisations in the catchment (subtype 1C). Notice that the highest concentrations in this lithologically uniform profile occur in the lower part which has been ^{14}C dated as being deposited about 8600 years ago.

metal or other pollution-related elements in the upper sections. Two major subtypes can be differentiated.

In subtype 2A, the increase in pollution-sensitive elements in the upper part of the profile is gradual but significant and results in a two-to-three-fold rise in the concentration of heavy metals in comparison with the lower section (Fig. 6). Sedimentary texture and structure, however, generally do not change. This elemental pattern is in fact present in most studied profiles (i.e. about 60%) and also occurs in profiles from catchments where no industrial activities have been or are developed. However, the latter systematically occurs downwind of nearby industrial sites. It is therefore considered very likely that the increase in contaminant content relates to atmospheric deposition. It is possible that originally wind blown metal-bearing particles were deposited randomly in the catchment, subsequently becoming fluvially transported and deposited as overbank sediment. However, these higher metal contents may also relate to direct deposition of metal-bearing particles during normal rainfall periods on floodplain sediments. In both cases, it is not unlikely that the minute particles subsequently percolated downward under the influence of infiltrating rainwater. Considering Ni deposition rates for an area north of the Cu–Ni smelter at Nickel (Kola, Russia), Langedal and Ottesen (1997) had to assume fluvially reworked particle-bound airborne Ni, in addition to direct deposition of airborne Ni. Similar processes have also been reported from the river Severn in England (Walling and Bradley, 1988).

The second subtype, 2B, consists of profiles with a dramatic increase in heavy metal concentration, mainly in the upper part. This increase is nearly always concomitant with a change in lithological characteristics such as grain size and other sedimentary features in the section. The change in lithological characteristics, that is, to coarser or finer grained sediments or a marked sediment lamination lacking bioturbation, probably relates to man-induced changes in the drainage system. The absence of bioturbation could indicate an environment hostile to biota due to the presence of pollutants. Within such intervals, concentrations with the values for Zn and/or Pb $\geq$1000 ppm often occur (Fig. 7). An anthropogenic influence is inferable from the presence of slag or/and magnetic particles (e.g. magnetite, ilmenite,...). Profiles that display anomalous heavy metal values throughout the entire sampled depth interval are also present (Fig. 8). Here grain size variations are minor. These profiles make up about 5% of the selected profiles. Anthropogenic particles have been identified at the base of some of these profiles, providing

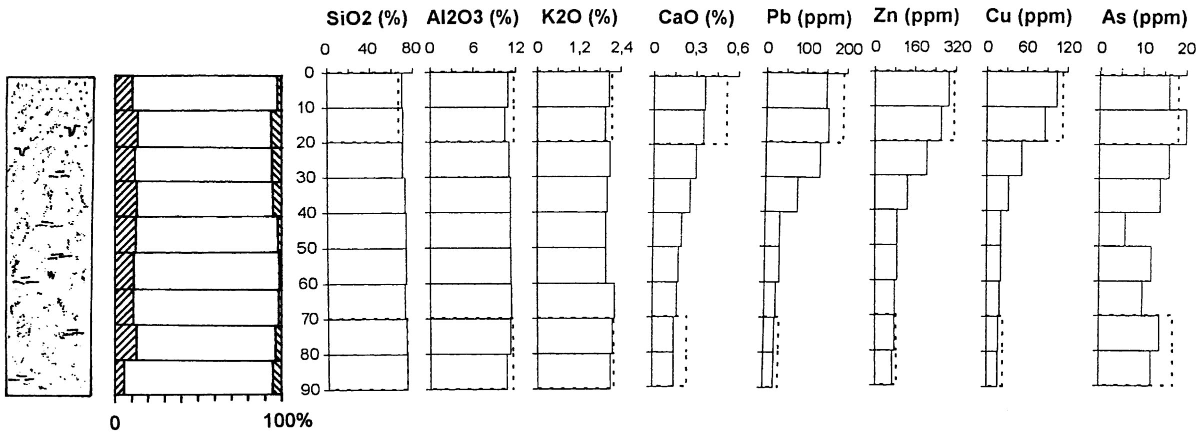

Fig. 6. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Warche overbank profile (profile 73 in Fig. 1) where an apparent increase in heavy metals in the upper section part relates to anthropogenic influences (subtype 2A). The latter do not concur with a change in lithology.

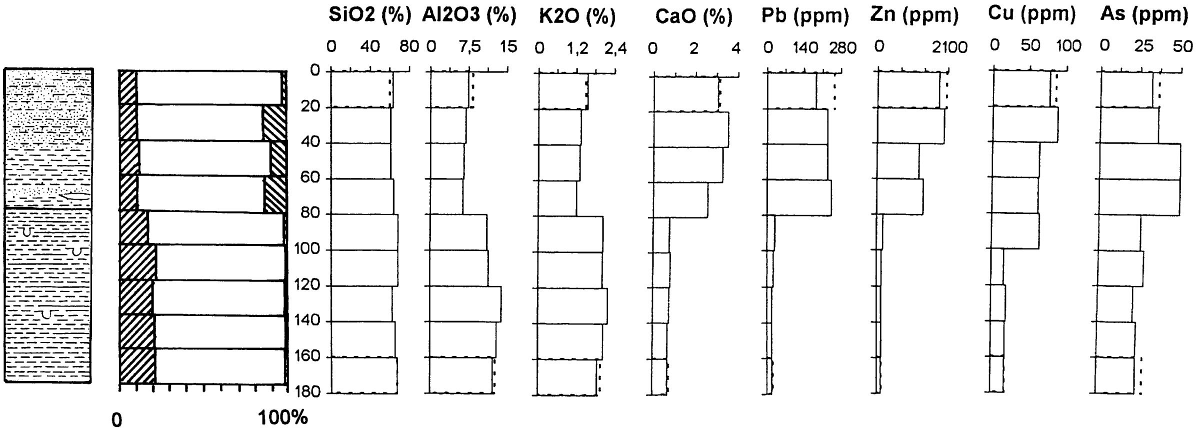

Fig. 7. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Alzette overbank profile (profile 71 in Fig. 1). The profile is characterized by a dramatic increase in heavy metals in the upper more sandy unit. The latter mainly relates to pollutants originating from mining and steel industry in the catchment (subtype 2B; Swennen and Van der Sluys, 1998). Notice the decrease in Al_2O_3 and K_2O content (and possibly also SiO_2) which relates to a shift in grain size and the increase in CaO (and in fact also P_2O_5) contents which can be explained by the mining of phosphate-rich Fe-ores which started around 1870.

evidence that sediments displaying natural (i.e. background) concentrations, which normally occur at depth either never have been deposited, or have been eroded or still occur at larger depths.

Subtype 2B profiles occur in areas with heavy industries, especially mining and steel industries, in the catchment. Zn- and Pb-bearing particles (such as Zn-bearing spinels, iron oxy/hydroxides,...) have

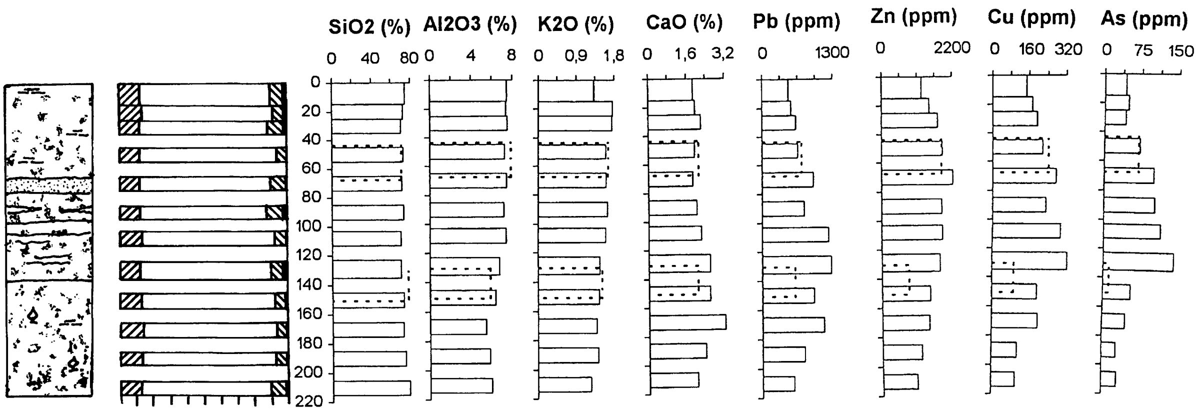

Fig. 8. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Zenne overbank profile (profile 25 in Fig. 1) (notice that below 30 cm only every second sample was analysed). Elevated heavy metal concentrations occur throughout the profile even to a depth of > 2.0 m. The existence of anthropogenic particles in the lower profile parts indicates that even at this depth, it was not possible to take pre-industrial samples. The high heavy metal content relates to the heavy industry in the catchment (subtype 2B).

been identified with Gandolfi-X-ray diffractometry. Sulfide particles have only exceptionally been identified despite the fact that they have been commonly recognized in some of the mining dumps upstream from subtype 2B-profile sites (Kucha et al., 1996).

In these catchments, huge amounts of polluted sediments are stored in the alluvial plain (Swennen et al., 1994). Plant growth rates, be it natural or in relation to agricultural activities, may be affected (e.g. Lepp, 1981; Wallnöfer and Engelhardt, 1984). In the Geul area, this is clearly visible since dwarfed growth of higher plants occurs and during dry periods, the retreat of grass cover is common. There is also a potential hazard for drinking water wells on highly polluted alluvial plains, as demonstrated by analysis of pore waters in these catchment areas (research in progress). Furthermore, the polluted sediment may be eroded and retransported and thus form an important secondary source of pollution, even long after the original source disappeared (Lenaers and Schouten, 1989; Hudson-Edwards et al., 1998). The relative contribution of this secondary input to the total degree of pollution can be important, especially since in many countries like Belgium and Luxembourg, waste discharges have been reduced over the last years. A typical example is found in the Alzette catchment in Luxembourg (Fig. 7). Several historical watermills and dams along the river were recently removed with the major aim to allow the river to regain its natural course. However, upstream of each watermill, a terrace had formed over the last decades, temporarily storing vast amounts of, in this case, heavily polluted sediment caused by the iron mining and steel industries upstream. Due to the destruction of the sediment retaining structures, huge amounts of polluted sediment are now transported downstream by this small river to the river Moselle (Swennen and Van der Sluys, 1998). Furthermore, since groundwater abstraction occurs in many alluvial plain sediments like the Alzette, attention should be paid to those areas where mobilization of pollutants might affect water quality.

Type 3 profiles reflect pedogenic movement of soil constituents; these processes are always superimposed on type 1 or 2 distribution patterns. Phenomena such as illuviation/eluviation and gleying have been recognized in some of the studied overbank sediment profiles. They mainly affect the distribution of Fe and Mn, as well as clay and organic constituents. In general, it seems that coprecipitation of heavy metals with Fe/Mn oxy/hydroxides has only a minor importance in element fixation or immobilization. In none of the data sets acquired in this study a significant correlation between Fe or Mn with the heavy metals has been recorded, neither has microprobe analysis provided evidences of increased heavy metal concentrations in Fe/Mn oxy/hydroxides. The absorption of heavy metals to clays and organic matter is more clearly developed in the southern than in the northern part of the sampling area, as shown by stronger correlations between these variables (Brusselmans et al., 1998). This relates to the fact that Paleozoic shales are the most vulnerable weathered lithology in the southern part of Belgium while in the northern part, unlithified Tertiary sands are more easily eroded. Clear downward migration processes have been recognized only for As and Cd in subtype 2B profiles (Fig. 9). According to many authors (e.g. Alloway, 1996), these are the most mobile elements in the near-surface environment. This mobility is manifested by gradual downward tailing of the As and Cd distribution patterns, reaching below the interval with high Zn and Pb concentrations. In this mobilised interval, no covariance between As, Cd and the other heavy metals such as Zn, Pb, Cu, Ni, and Co has been recognized. For the latter heavy elements, there is a sharp decrease in concentration from ‘‘polluted’’ (based on the geochemical profile characteristics) downwards into lithologically differentiable ‘‘non polluted’’ strata (e.g. Fig. 9). Whether the Cd and/or As occur in discrete mineral phases is unknown, but if so they do not relate to transported pollutants, since they occur below the polluted interval. If present, they are authigenic in origin, relating to the precipitation due to downward migration of Cd and/or As. This suggests that, with the exception of Cd and As, vertical migration of other elements is insignificant, at least within the time scale (several 100× years) considered here. However, this will be highly dependent on the buffer capacity of the system and possibly the effect of acid rain (Edén and Björklund, 1994). This problem is clearly less severe in the southern part of Belgium and Luxembourg where carbonate rocks or marls (reflected in higher CaO and MgO contents) occur in nearly all catchments. In the northern part of

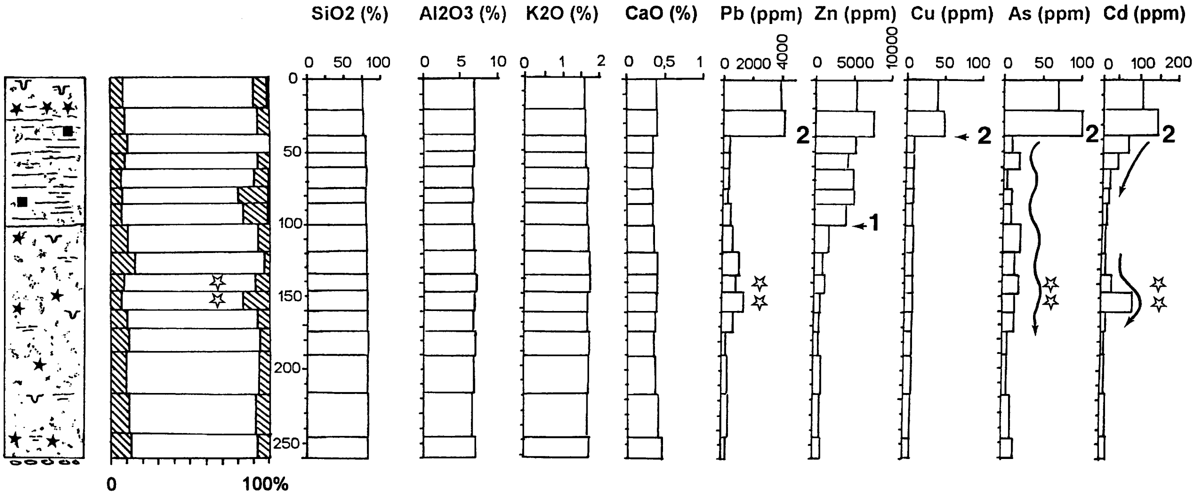

Fig. 9. Grain size and geochemical variations of overbank profiles from Belgium and Luxembourg. In most profiles, the results of the XRF (mainly major elements) and ICP-AES and/or ICP-MS (mainly trace elements) analysis are shown. Results of the XRF analysis (often from bulk samples taken for the mapping project; Van der Sluys et al., 1997) are indicated by a dashed line and allow comparison between the analytical techniques. For legend, see Fig. 1. Geul overbank profile (profile 14 in Fig. 1) with clear evidence of very high heavy metal concentrations in the upper part of the profile which relates to mining and smelting activity in the catchment. Zn-oxide and -silicate mining started around 1806 (1) while Pb- and Zn-sulfide subsurface mining started around 1844–1845 (2). Notice the downward translocation of As and Cd where elevated contents of these elements occur in some coarser grained strata in the lower part of the profile (indicated with *). For more details, see Swennen et al. (1994).

Belgium, carbonate-bearing sands exist, but especially in the northeast of Belgium, the lack of carbonate-bearing substrates and overbank sediments, and the soil pH with values as low as 4 will influence the mobility of Cd and As. The results are in line with data reported by Macklin et al. (1994), where no significant vertical migration for Pb and Zn was reported from English and Welsh overbank sediment systems and where the soil buffer capacity was normal to high.

4. Conclusion

The geochemistry of vertical overbank sediment profiles allows the examination of element variations through time. Changes might relate to natural variations, that is, changes in grain size, organic matter content, provenance, as in type 1 profiles. The difference of the geological substrate in the study area is clearly reflected in these profiles. Noteworthy is that in relation to these substrates, natural anomalies may occur, that is, in relation with placer-like heavy mineral accumulations and mineralisations. However, in most profiles in Belgium and Luxembourg, the gradual increase in heavy metals in the upper tens of centimeters is interpreted to reflect pollution (type 2A profiles), whereby the only plausible explanation for the existence of pollution in areas where no past or present-day industrial or mining activity occurs relates to atmospheric deposition. Alluvial plains where the uppermost strata display drastic increases in heavy metal concentrations (and other pollutants) at 100–1000 ppm levels are clearly of environmental concern (type 2B profiles). These elevated concentrations relate to historical (and locally even present-day) industry, with mining, smelting and metal manufacturing being the dominant polluting activities. The pollutants have been laid down as overbank sediments and even after polluting industries have lowered or ceased their pollutant discharges, erosion and retransportation of temporarily stored polluted sediments from alluvial plains remains a potential hazard for the environment. Protection measurements are needed to control this situation. Overbank sediments in these areas should be used in environmental assessments before developments in catchment basins. Finally, since pedogenic translocation is rather limited and only seen to affect As and Cd, the time-related geochemical signals seem to be well preserved in the overbank sediments.

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