Environmental impact of the former Pb-Zn mining and smelting in East-Belgium.

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Abstract
In the mining district of Plombières-La Calamine (East-Belgium), extensive Pb-Zn mining activities resulted in an important contamination of overbank sediments along the Geul river. Moreover, a huge amount of heavy metals is stored in a dredged mine pond tailing, which is located along the river. In the dredged mine pond tailing sediments, Pb-Zn minerals control the solubility of Zn, Pb and Cd. Although Pb, Zn and Cd display a lower solubility in overbank sediments compared to the mine tailing pond sediments, elevated concentrations of Pb, Zn and Cd are still found in the porewater of the overbank sediments. The considerable 'actual' and 'potential' mobility of Zn, Pb and Cd indicates that the mine pond tailing sediments and the overbank sediments downstream from the mine pond tailing represent a considerable threat for the environment. Besides the chemical remobilisation of metals from the sediments, the erosion of overbank sediments and the reworking of riverbed sediments acts as a secondary source of pollution.

1. INTRODUCTION

From the Middle Ages until the beginning of the 20th century, extensive Zn-Pb mining and smelting was carried out in Plombières and La Calamine (eastern Belgium). Besides the important amount of waste that is stored in huge mine tailings, overbank sediments along the nearby Geul rive are severely contaminated with Zn, Pb and Cd (Swennen et al., 1994). The distribution pattern, the actual and potential mobilisation and (natural) attenuation of Pb, Zn and Cd in the mine pond tailing sediments of La Calamine and in overbank sediments downstream of La Calamine were investigated.

2. METHODOLOGY

Three vertical profiles were sampled in detail within overbank sediments along the Geul river in Plombières (East-Belgium), in Sippenaeken and Epen (South-Netherlands), respectively 7, 9 and 12 km downstream from the mine tailing pond of La Calamine. Total metal concentrations (determined after dissolution of the sample with concentrated HF, HNO_3 and HCl), pH and grain size were determined for all the samples. In the overbank sediments, CEC and organic carbon content were also measured. Furthermore, a mineralogical (petrography, XRD, SEM-EDX) investigation of a vertical profile in the dredged mine tailing pond sediments of La Calamine was carried out. The DIN 38414-S4 leaching test (extraction with water at a liquid/solid ratio of 10/1), which is used to evaluate leaching with landfill acceptance data (Anonymous, 2003), was carried out on the samples from the mine pond tailing. Single extractions with $CaCl_2$ (0.01 M) and ammonium-EDTA (0.05 M) (Quevauviller, 1998) were performed to estimate the 'actual' (i.e. porewater composition) and 'potential' mobilisation of Cd, Zn and Pb from the overbank sediments. The modified BCR sequential extraction scheme (Rauret et al., 1999) was applied on a selection of samples from the mine pond tailing and overbank sediments.

pH_{stat} leaching tests (Van Herreweghe et al., 2002) were performed on overbank sediment samples from Plombières, Sippenaeken and Epen.

3. RESULTS AND DISCUSSION

3.1 Mine pond tailing sediments

Elevated total concentrations of Pb, Zn, Cd and As were measured in the mine pond tailing (Table 1 and Fig.1). The main heavy metal bearing minerals in the La Calamine mine pond tailing, determined with XRD, were ZnS (wurtzite), $ZnCO_3$ (Smithsonite), anglesite ($PbSO_4$), pyrite (FeS_2) and marcasite (FeS_2). The oxidation of sulphide minerals within the mine tailing releases H^+, SO_4^{2-}, Fe^{2+}, and trace metals into the porewater. Subsequent pH-buffering in carbonate/sulphate-rich layers results in the precipitation of secondary minerals such as $ZnCO_3$, $FeCO_3$ and $CaSO_4.2H_2O$. These precipitation processes result in the formation of cemented layers (for example between 81 and 97 cm depth in Fig.1), which show an enrichment in Zn.

Although these carbonate/sulphate-rich layers provide some natural attenuation of trace metals, elevated Zn-, Pb- and Cd- concentrations are found in the water extracts (DIN 38414-S4 leaching test) of the surface layers of the tailing (0-2.6 m depth) (Fig. 1), largely exceeding the criteria for landfill acceptance (Anonymous, 2003). Acid pH values (between 3 and 4.9) were encountered in the deeper part of the tailing (between 2.6 and 4 m depth). Nevertheless, a lower mobility of Zn, Pb and Cd was found compared to the upper part of the tailing, where pH was in the range 5-7. The higher metal solubility with increasing pH indicates that heavy metal mobility is not only determined by adsorption reactions, despite the clayey nature of the sediments and that a considerable amount of Zn, Pb and Cd is also contained in mineral phases. A multidisciplinary approach, combining pH_{stat} leaching tests, solid-phase characterization (XRD, SEM-EDX) and thermodynamical modelling (MINTEQA2) confirmed that the solubility of Zn, Pb and Cd in the mine pond tailing is mainly controlled by Pb-Zn minerals.

3.2 Overbank sediments

Overbank sediments along the Geul river are mainly contaminated with Zn, Pb and Cd and pH is between 5.4 and 8.0 (Table 1). The vertical distribution of Zn and Pb in the overbank profile (Fig. 2) can be related to the history of mining and smelting activities. The increase in Zn-content before a marked increase in Pb can be explained by the fact that the Zn-mining at the La Calamine open mine started before large-scale PbS-ZnS subsurface exploitations. (Swennen et al., 1994). Total Zn-, Pb- and Cd-concentrations in overbank sediments decrease with increasing distance from the mine pond tailing and display a low acid neutralizing capacity (ANC, Fig. 3) and CEC, resulting in a relatively low retention of heavy metals. The 'mobile' fraction of Cd and Zn (as determined with a $CaCl_2$ extraction) could be described as a funtion of EDTA-extractable Cd and Zn concentrations, pH and organic carbon content ($r=0.87$-0.95, $\alpha=0.05$), which indicates that EDTA-extractable Zn and Cd concentrations, organic carbon content and pH can be used to predict porewater concentrations of Cd and Zn. $CaCl_2$-extractable Zn and Cd concentrations also decrease with increasing distance from the mine tailings. Whereas Pb- and Zn-minerals control the solubility of Zn, Pb and Cd in the mine tailings, the retention of Zn, Cd and Pb in the overbank sediments mainly occurs by adsorption and coprecipitation.

The acid-extractable fraction of Zn, Pb and Cd in overbank sediments, as determined with the BCR sequential extraction, decreases downstream from the mine tailings (Fig. 3). However, we would expect an increase in the acid extractable fraction because the acid neutralizing capacity (ANC) decreases from Plombières to Epen (Fig. 3). This suggests a stronger binding of Zn, Pb and Cd in

overbank sediments downstream from the mine tailing. Despite the lower ANC in the downstream part of the alluvial plain, acidification yields a lower risk than in the overbank sediments located more upstream.

4. Conclusions

In the mine pond tailing of La Calamine, the solubility of Pb, Zn and Cd is highly dependent on mineralogical composition. Up to 27% and 49 % of the total Zn- and Cd-concentrations are released with the DIN38414-S4 test. Although Pb displays a much lower solubility than Zn and Cd, considerable concentrations (up to 17 mg/L) are released when the tailing material is brought in contact with water. In the overbank sediments, Zn, Pb and Cd have a lower solubility compared to the mine pond tailing and pH is an important factor in explaining the solubility of Zn and Cd. The porewater of the overbank sediments (as determined by a $CaCl_2$ 0.01M extraction) contains up to 42 mg/L of Zn, 247 µg/L of Pb and 456 µg/L of Cd. Consequently, the considerable 'actual mobility' of Zn, Pb and Cd, as determined with extractions with water and diluted salt solutions, indicates that the mine pond tailing sediments and the overbank sediments downstream from the mine pond tailing still represent a threat for the environment. Besides the chemical remobilisation of metals from the sediments, the erosion of overbank sediments and the reworking of riverbed sediments act as a secondary source of pollution.

For a sustainable development of the mining area of Plombières-La Calamine, run-off from the mine tailings must be limited. Further research will focus on the influence of changing environmental conditions on heavy metal mobility in overbank sediments along the Geul river. The feasibility of the addition of phosphates as a measure to reduce the release of Pb, Zn and Cd into the environment will also be investigated.

5. REFERENCES

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Table 1: pH and concentrations (in mg/kg) of Zn, Pb, Cd and As in the mine pond tailing sediments and in the overbank sediments along the Geul. n = number of samples

	mine tailings (n = 20)					overbank sediments (n = 100)				
	Zn	Pb	Cd	As	pH	Zn	Pb	Cd	As	pH
average	37513	19206	146	679	4.92	3858	1302	7	23	6.8
stdv	36371	13340	138	444	1.31	3413	1722	8	25	0.6
min	1439	2434	3	31	3.05	279	38	0.1	4	5.4
max	108108	39503	307	1491	6.97	13171	6530	37	121	8.0

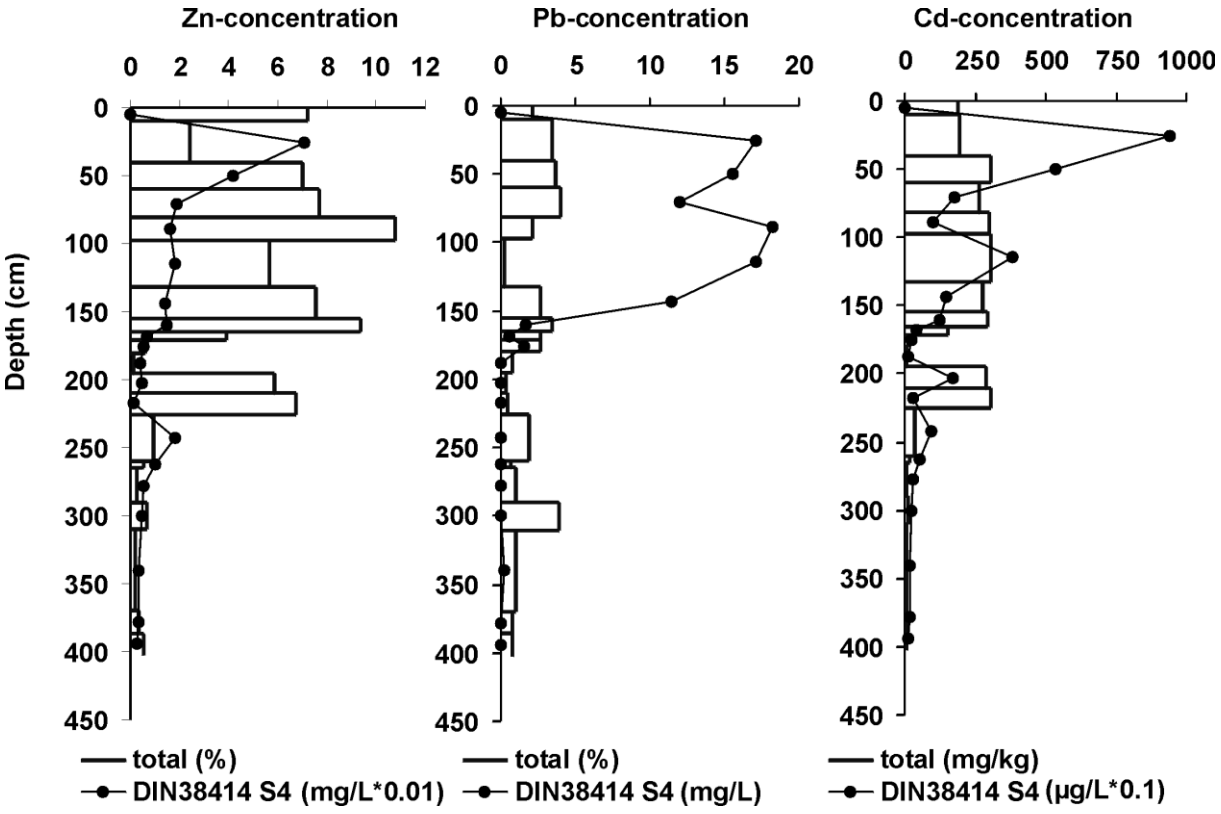


Fig. 1: Vertical distribution of Zn, Pb and Cd in the mine tailing pond of la Calamine and amount of Zn, Pb and Cd released with the DIN38414-S4 test

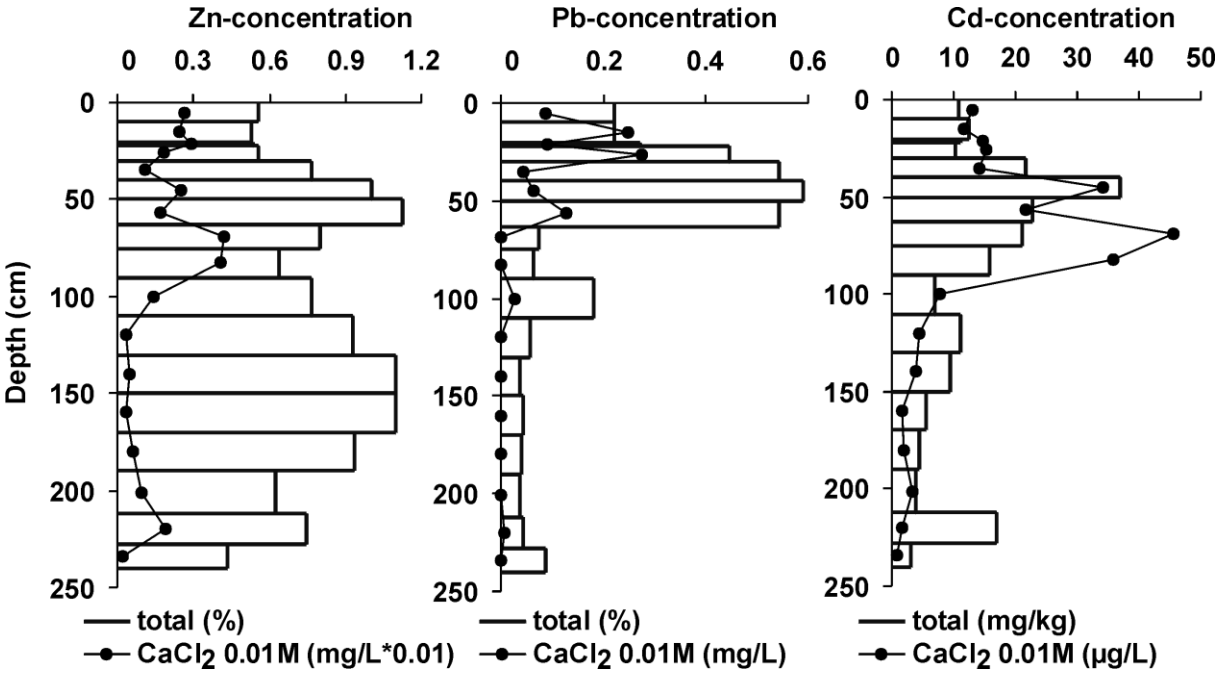
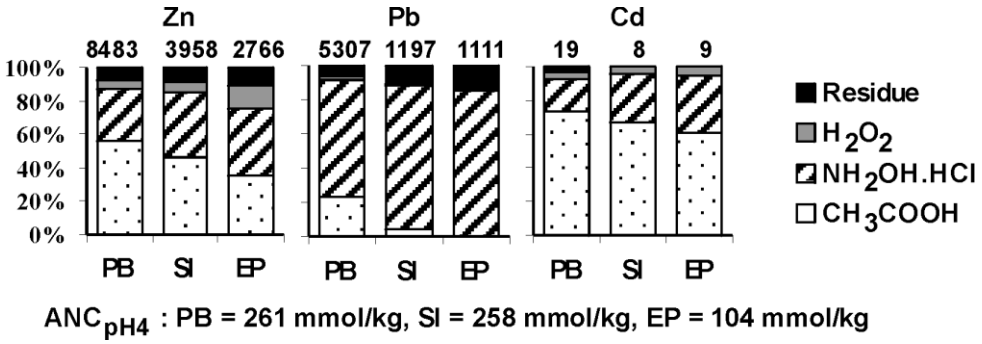


Fig. 2: Vertical distribution of Zn, Pb and Cd in the overbank sediment profile in Plombières and Zn-, Pb- and Cd- concentrations in the $CaCl_2$ extract



ANC_{pH4} : PB = 261 mmol/kg, SI = 258 mmol/kg, EP = 104 mmol/kg

Fig. 3: Fractionation of Zn, Pb and Cd according to the modified BCR sequential extraction scheme in overbank sediments in Plombières (PB), Sippenaeken (SI) and Epen (EP) (resp. 7, 9 and 12 km downstream from the mine pond tailing). Total metal concentrations (in mg/kg) are given on top of each graph and ANC_{pH4} is also mentioned.