# Assessment of heavy-metal contamination of floodplain soils due to mining and mineral processing in the Harz Mountains, Germany

H.-E. Gäbler · J. Schneider

**Abstract** The floodplain soils of the Harz Mountains and the area around the northwest end of the Harz Mts. are contaminated with heavy metals from mines and mineral-processing plants. These soils have been investigated to characterise the heavy-metal contamination over large areas and to evaluate the hazard to the environment due to heavy-metal mobility. A 12.5 km$^2$ study area was assessed with respect to its heavy-metal load on the basis of the current guideline values. The heavy-metal loads of the soils in the study area have ranges of $<0.2$–200 mg kg$^{-1}$ for Cd, $<10$–30,000 mg kg$^{-1}$ for Pb, 7–10,000 mg kg$^{-1}$ for Cu and 50–55,000 mg kg$^{-1}$ for Zn. Mobility of the heavy metals was determined by extraction at different pH values. The acid neutralisation capacity (ANC$_x$) at these pH values was also determined to estimate the probability that the pH can drop to pH=$x$. The ANC values in the study area ranged from 6 to 3000 mmol H$^+$ kg$^{-1}$, from $-33$ to 800 mmol H$^+$ kg$^{-1}$ and from $-74$ to 160 mmol H$^+$ kg$^{-1}$ for ANC$_{3.5}$, ANC$_{5.0}$ and ANC$_{6.2}$, respectively. Together with pedological data, the extraction experiments permit differentiation between soil units that have been placed in the same environmental hazard class on the basis of total heavy-metal loads.

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## Introduction

Mining is always linked to an impact on the environment (Eggert 1994; Ripley and others 1996; Vartanyan 1989). Mining and mineral processing in the Harz Mountains of Germany has been carried out for centuries and has contaminated the floodplain soils of rivers draining the Harz Mts. with heavy metals (Köster and Merkel 1985). The heavy-metal contamination of these soils is a problem for the municipal government because the problem sites must be assessed with respect to their suitability for different land uses. The aim of this study was to (1) delimit problem sites in the large study area; (2) apply current guideline values for total heavy-metal concentrations; and (3) obtain information on heavy-metal mobility for assessing contaminated areas. The investigations were carried out as follows: contaminated areas were delineated prior to the field work on the basis of available information on known soil contamination and its origin. The study area was mapped and soil units determined. Representative profiles were selected for each soil unit. These profiles were sampled and analysed for their heavy-metal contents in the laboratory. The heavy-metal load was assessed using the current guideline values valid at that time. Additional information about the risk of heavy-metal mobilisation at contaminated locations was obtained by extraction of samples from the selected representative profiles. Because pH is one of the most important “master variables” governing soil solution composition (Wolt 1994) and heavy-metal mobility (Maskall and others 1995; Ross 1994), and because a change in land use may cause soil pH to drop, extraction experiments at different pH values were carried out. The heavy metals referred to in this paper are Pb, Zn, Cd and Cu.

## Geographical and geological settings

The 12.5-km$^2$ study area covers the agriculturally used floodplains of the Harz Mts. and the northwest foreland

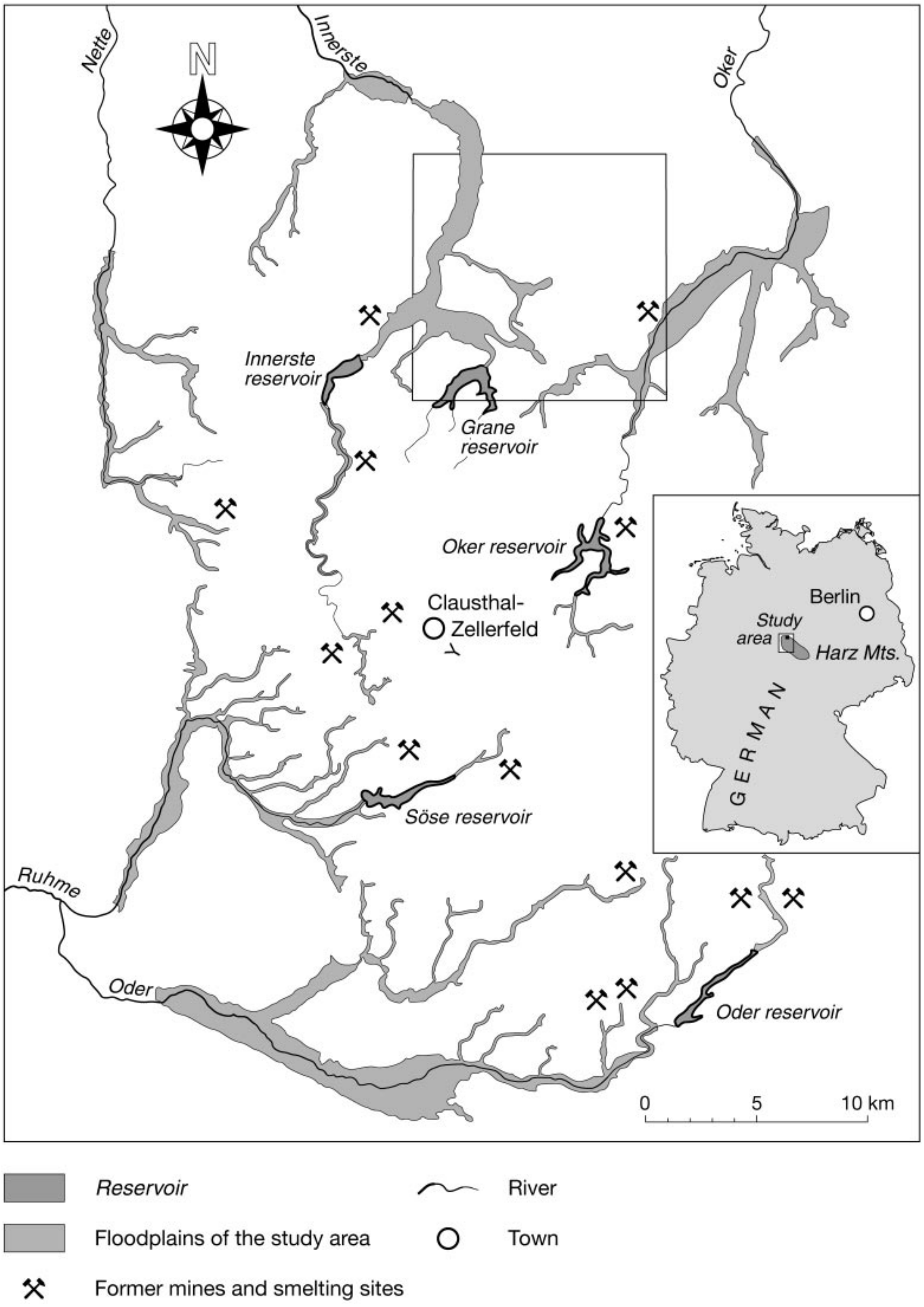

**Fig. 1**
Study area; the examples discussed in the text are within the marked sub-area, shown in Figs. 2 and 3

of the Harz Mts. (Fig. 1). The earliest records of mining in the Harz Mts. (vein-type and stratiform lead-zinc ore deposits) are from the year 968 (Liessmann 1992). But findings of slag and ore dating from the third and fourth centuries (Klappauf 1985) as well as geochemical investigations (Matschullat and others 1997) indicate even earlier mining activity took place in the Harz Mts. Today's heavy-metal contamination is a result of processing of these ores. In 1820, for example, 25% of the lead in the ore was lost during processing and released to the environment (Liessmann 1992). This lead was introduced with the tailings into the rivers and deposited on the floodplains during flooding. When the lead-zinc mine at Bad Grund was closed down in 1992, mining in the Harz Mts. came to an end.

Three periods of floodplain deposition can be distinguished in the study area (Dreschhoff 1974). The bottom layers of the oldest floodplain deposits (qh1) are Boreal in age; a younger layer (qh2) was deposited between 1000 and 1400 A.D.; the youngest floodplain sediments (qh3) have been laid down since the fifteenth century. Due to the presence of charcoal, slag and other anthropogenic materials, the qh3 horizon can be easily recognised during field work. These younger floodplain deposits are usually contaminated with heavy metals.

## Methods

### Sources of initial information

The available information was evaluated prior to the field work: historical information on mining and mineral processing in the Harz Mts., maps of ore deposits, maps of smelting sites and spoil dumps, the *Geochemical atlas of Western Germany* (Fauth and others 1985), and geological and soil maps of the Geological Survey of Lower Saxony.

### Field work

Using the available information as a starting point, the floodplain areas were mapped and soil units delimited on the basis of data from a rapid photometric field test on soil samples from shallow boreholes and exploratory pits. Maps and pedological-profile descriptions were made using standard guidelines (AG Bodenkunde 1982; Benne and others 1992). Samples were taken to determine heavy-metal concentrations from each horizon down to the sandy-gravely subsoil by percussion drilling (80 mm), exploratory pits and natural outcrops (maximum depth: 2 m).

### Rapid photometric field test

The rapid photometric field test used for the on-site estimation of Pb-Zn concentration is based on the Bloom Test (Bloom 1955) – an analytical method for geochemical prospecting. Heavy metals are leached from the soil with an ammonium citrate buffer and determined photometrically on-site using dithizone as an indicator (Gäbler and Wisch 1997).

In the rapid photometric field test, a 0.75-ml sample is shaken vigorously with 10 ml buffer solution (50 g ammonium citrate, 8 g hydroxylammonium chloride in 600 ml deionized water) in a test tube for 30 s; 100 µl of the extract is transferred to a cuvette; 1.1 ml of the buffer solution and 5 ml of the dithizone solution (0.01 g dithizone in 1 l n – butyl acetate) are added and shaken vigorously for 15 s. After phase separation, the aqueous phase is discarded. The absorbance at 520 nm of the remaining organic phase (which indicates the Pb-Zn concentration of the soil sample) is measured with a portable photometer. The Pb-Zn concentration is estimated by comparing the absorbance with a calibration curve derived from floodplain deposit samples with different heavy-metal contents. Good agreement with results obtained in the laboratory is normally achieved.

### Total heavy-metal content

The samples were dried at 40 °C and sieved to obtain the < 2-mm fraction. The < 2-mm fraction of the sample was ground and analysed by ICP-AES after digestion with HF/HCl/$HClO_4$. For experimental details see Gäbler (1997).

### Heavy-metal mobility

The heavy-metal mobility in floodplain deposit samples is estimated by extraction at constant pH according to Obermann and Cremer (1992) and Gäbler (1997). In a $pH_{const}$ experiment, the heavy metals in a sample are extracted with water at constant pH in a flask with a pH electrode connected with a titrator via a control unit. For experimental details see Gäbler (1997).

The $pH_{const}$ experiments yield two parameter values: (a) the mobile fraction of the heavy metals ($w_{el}$) at a certain pH and (b) the buffering capacity of the sample material at this pH ($ANC_x$). The mobile heavy-metal fraction ($w_{el}$) is determined by analysing the heavy-metal concentration in the extract at the end of the $pH_{const}$ experiment (see Eq. 1); the buffering capacity ($ANC_x$) can be calculated from the amount of added acid or base necessary to maintain a constant pH during the extraction (see Eq. 2):

$$w_{el}(y) = \frac{c_{el}(y) \cdot (V + V_t)}{m} \qquad (1)$$

$$ANC_x = \frac{V_t \cdot c}{m} \qquad (2)$$

where $w_{el}(y)$ is the extracted mass fraction of the element $y$ relative to the dry weight of the sample (mg $kg^{-1}$); $c_{el}(y)$ is the concentration of the element $y$ in the extract at the end of the extraction (mg $l^{-1}$); $V$ is the volume of the extract at the beginning of the experiment (l); $V_t$ is the volume of the added acid or base (l); $m$ is the dry weight of the sample (kg); $ANC_x$ is the acid neutralisation capacity at pH=$x$ (mmol $H^+$ $kg^{-1}$); $c$ is the concentration of the added acid or base (mmol $H^+$ $l^{-1}$ or mmol $OH^-$ $l^{-1}$). The value of $c$ is positive for the addition of acid and negative for addition of a base.

## Results and discussion

### Mapping and sampling

Mapping of the soil of the floodplains in the study area using the described photometric field test yielded 76 soil units with 22 different soil types. This is documented on 21 maps (scale 1 :25,000; Kues and others 1995). The soil units on these maps were sampled for heavy-metal analysis. In larger soil units and soil units with elevated heavy-metal concentrations (according to the rapid photometric field test), several soil profiles were investigated. A total of 1616 samples from 415 soil profiles were analysed for their total heavy-metal concentrations. Of these samples, 73 were selected from 25 soil profiles, each representing one of the soil units to analyse for heavy-metal mobility.

**Table 1**
Guideline values from the conception of Eikmann and Kloke (Eikmann and Kloke 1993) for agriculturally used soils

| Guideline value | Pb [mg kg$^{-1}$] | Cd [mg kg$^{-1}$] | Zn [mg kg$^{-1}$] | Cu [mg kg$^{-1}$] |
|---|---|---|---|---|
| BW I | 100 | 1 | 150 | 50 |
| BW II | 500 | 2 | 300 | 50 |
| BW III | 1000 | 5 | 600 | 200 |

Only profiles representing soil units with high heavy-metal concentrations were chosen.

### Classification of total heavy-metal contents

The classification system of Eikmann and Kloke (1993) was used to classify the total heavy-metal contents, because this system classifies the heavy-metal content of soils according to land use and the need to protect man, vegetation and groundwater. At the time of the investigation this was the system normally used in Lower Saxony by state authorities. It uses the following classes:

A unrestricted land use possible, no hazard for man, vegetation or groundwater; heavy-metal content below BW I value (BW=Bodenwert, see Table 1);
B restricted land use, depending on the need to protect man, vegetation or groundwater and kind of land use; heavy-metal content between BW I and BW III;
C intervention is necessary, injury to man or impairment of vegetation or groundwater may occur and precautions are necessary; heavy-metal content above BW III.

Table 1 shows the guideline values BW I, BW II and BW III (Eikmann and Kloke 1993) selected in this study for classifying agriculturally used soils, the most common land use in the study area. Class B is divided into two subclasses by BW II. Between BW I and BW II an impact on human health is not assumed, between BW II and BW III the health risk is generally somewhat higher and changes of land use should be considered for the individual case (Eikmann and Kloke 1993).

Figure 2 shows the classification of the total heavy-metal contents of the upper humic horizons in the area of the 1:25,000 map sheet TK 4028, Goslar. Most of the floodplain soils in this area influenced by mining activity belong to class C, because the concentration of at least one heavy metal is above the BW III value. So additional information is needed to obtain a more differentiated picture of the environmental hazard in order to provide the municipal government with recommendations on land use. For this purpose heavy-metal mobility and pedological data are taken into consideration.

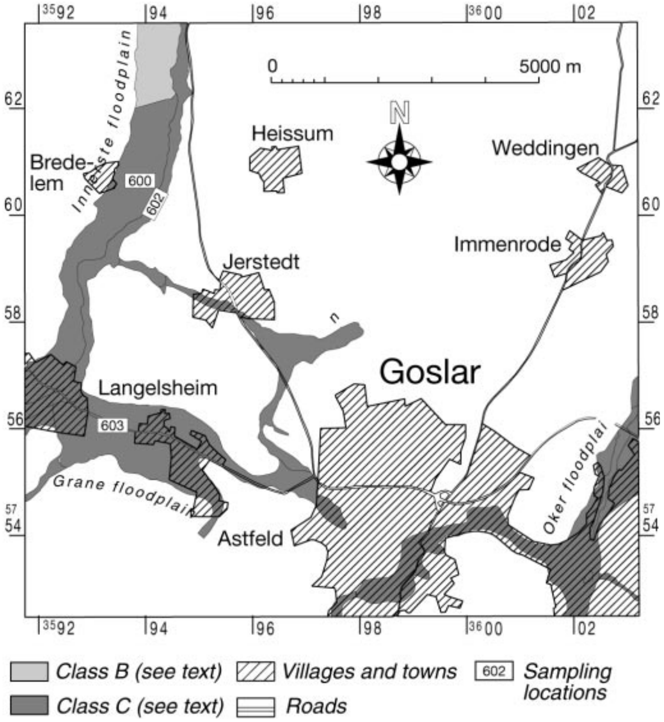

**Fig. 2**
Classification of soil units according to total heavy-metal content of the top soil of the sub-area in Fig. 1 using the classification scheme of Eikmann and Kloke (Eikmann and Kloke 1993)

### Determination of the mobile fraction of heavy metals

The risk to the environment arising from heavy-metal contamination cannot be assessed only on the basis of total heavy-metal content. Heavy-metal mobility must also be taken into consideration. Experiments at pH$_{const}$ (Gäbler 1997; Obermann and Cremer 1992) were carried out to determine values for this parameter. This kind of experiment was developed to predict the long-term response of a given material to pH changes by the simulation of a worst-case scenario (Obermann and Cremer 1992). The pH$_{const}$ experiment yields values for the parameters $w_{el}$ and ANC$_x$. The parameter $w_{el}$ reflects the amount of heavy metal that is able to be mobilised at a certain pH under laboratory conditions. Transfer of the results of a pH$_{const}$ experiment to environmental conditions is only qualitatively possible because they are obtained under conditions that do not exist in nature, e.g. a water/soil ratio of about ten and destruction of the natural layering of the material. The ANC$_x$ parameter reflects the buffering capacity of a material and can, therefore, be used to estimate the probability that the pH can drop to a certain level. A high ANC$_x$ value indicates a low probability that the pH value of the pH$_{const}$ experiment will become reality in the given natural system and vice versa. The pH values used for the pH$_{const}$ experiments were chosen to reflect the buffering intervals defined by Ulrich (1981) for soils: pH=6.2 (lower limit of the carbonic acid/carbonate buffer), pH=5.0 (lower limit of the carbonic acid/silicate buffer and upper limit of the buffering range of the exchange sites of the soil materials) and pH=3.5 (aluminium and iron buffer region; this is a realistic pH for forest soils in the Harz Mts.). Fig. 4 shows the frequency distributions of ANC$_{3.5}$, ANC$_{5.0}$ and ANC$_{6.2}$ in the study area. The ANC$_x$values are assigned to the classes “relatively low”, “moderate” and “relatively high”. Note that these classes are valid only for this study area. A comparison of data from $pH_{const}$ experiments with data from other elution procedures is given by Sommerfeld and Schwedt (1996).

### Classification of soil units with respect to heavy-metal mobility

Besides the heavy-metal concentrations and the results of the $pH_{const}$ experiments, additional factors are taken into consideration to assess the hazard to the environment emanating from a contaminated site: soil type, sequence of horizons, permeability of the saturated soil to water, organic matter content and soil pH. The sampling sites could be classified relative to each other in the following classes:

1. Class I: locations without hazard to the environment. The heavy-metal concentrations are below the respective BW III which means an unrestricted (class A) or restricted (class B) land use is possible. Mobile fractions of heavy metals cannot be detected by the $pH_{const}$ experiment.
2. Class II: locations with a relatively low risk to the environment in the long-term.
   At least the heavy-metal concentration in one sample is above BW III, the $ANC_x$ values are high, the distance between the contaminated horizons and the groundwater horizon is high and the mobile heavy-metal content is low.
3. Class III: locations with low risk to the environment at present, but a hazard to the environment may arise under changing pH conditions.
   At least the heavy-metal concentration in one sample is above BW III, the $ANC_x$ values are moderate or high, the mobile heavy-metal contents are moderate, and above the groundwater table there is at least one soil horizon with a high $ANC_x$ value.
4. Class IV: locations that are a considerable hazard to the environment.
   At least the heavy-metal concentration in one sample is above BW III, the $ANC_x$ values are moderate or low, the mobile heavy-metal contents are high, and the distance between the contaminated horizons and the groundwater table is low.

### Examples of the assessment of hazards to the environment

Twenty-five locations in the study area each representing one soil unit were investigated using $pH_{const}$ experiments (Kues and others 1995). These locations were then assigned to classes I–IV. In this paper, locations 600, 602 and 603 are discussed as examples (Figs. 2 and 3, Table 2–4). The total heavy-metal concentrations at all three locations are higher than BW III, which means these locations are in class C of the classification scheme of Eikmann and Kloke (1993), the intervention class. Tables 2–4 show the sequence of the horizons, the soil types, the total heavy-metal concentrations and the results of the $pH_{const}$ experiments for the three example locations.

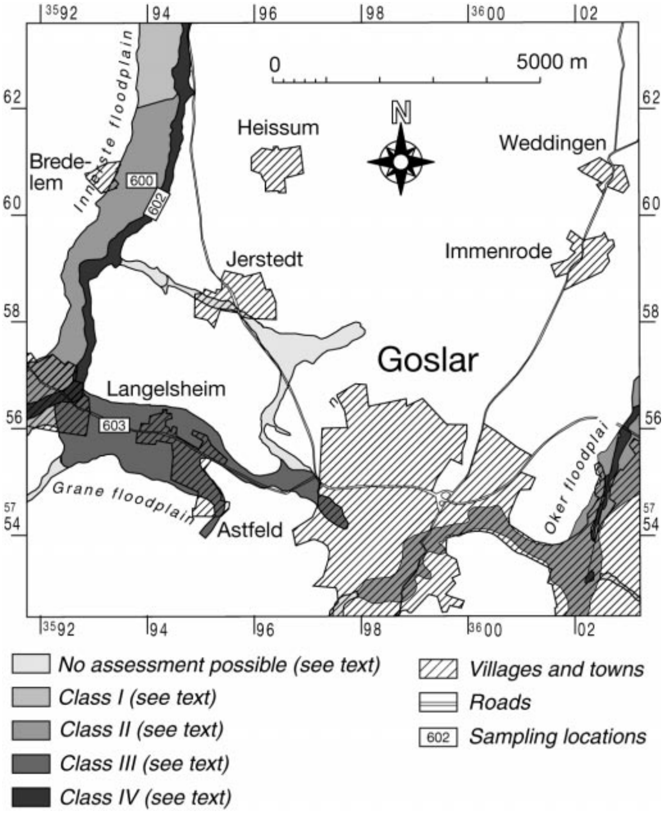

**Fig. 3**
Assessment of soil units of the sub-area in Fig. 1 with respect to the hazard to the environment arising from heavy-metal contamination

#### Location 600

Location 600 is used for agriculture today and is no longer periodically flooded. The groundwater table fluctuates at a depth of 70–80 cm. The soil horizons have slightly alkaline pH values between 7.9 and 8.1 (Table 2). The $ANC_{6.2}$ value of 122 mmol $H^+$ $kg^{-1}$ of the top layer is relatively high (Table 2, Fig. 4). At this pH (pH=6.2), just 1 mg Zn $kg^{-1}$ is mobilised in the $pH_{const}$ experiment, other mobile heavy-metal loads were not detected. No heavy metals are mobilised at pH=6.2 below the top layer (600/2–600/4, Table 2). Detectable Cd and Pb loads are just mobilised from the top layer (600/1, Table 2) if the pH drops from 7.9 to below 5. This drop in pH and the corresponding heavy-metal mobilisation are unlikely because the top layer has a high buffering capacity and liming adds additional buffer substances. If the land use at location 600 remains agricultural (with the attendant application of fertilisers and lime), migration of heavy metals into the groundwater is not expected. The risk to the environment at location 600 is relatively low in the long term, so this location is assigned to class II.

**Table 2**
Data for location 600

| Site/sample<br>a: depth [cm]<br>b: horizon[a]<br>c: texture[a]<br>d: pH ($H_2O$) | Procedure[b] | Total content and $w_{el}$ [c] respectively | | | | $ANC_x$ [mmol $H^+$ $kg^{-1}$] |
|---|---|---|---|---|---|---|
| | | Cd [mg $kg^{-1}$] | Zn | Pb | Cu | |
| 600/1 | Total content | 2.49 | 963 | 5969 | 185 | |
| a: 0–30 | $pH_{const}$ 3.5 | 0.99 | 101 | 170 | 5 | 337 |
| b: Ap | $pH_{const}$ 5.0 | 0.15 | 16 | 5 | <0.5 | 216 |
| c: Ut4/g1 | $pH_{const}$ 6.2 | <0.09 | 1 | <1.5 | <0.5 | 122 |
| d: 7.88 | $pH_{const}$ 6.9 | <0.09 | <0.3 | <1.5 | <0.5 | 87 |
| 600/2 | Total content | 1.33 | 378 | 1046 | 51 | |
| a: 32–50 | $pH_{const}$ 3.5 | 0.43 | 34 | 16 | 1 | 123 |
| b: M | $pH_{const}$ 5.0 | <0.09 | 3 | <1.5 | <0.5 | 37 |
| c: Ut3/g1 | $pH_{const}$ 6.2 | <0.09 | <0.3 | <1.5 | <0.5 | 39 |
| d: 7.96 | $pH_{const}$ 7.0 | <0.09 | <0.3 | <1.5 | <0.5 | 30 |
| 600/3 | Total content | 0.59 | 214 | 282 | 29 | |
| a: 50–70 | $pH_{const}$ 3.5 | 0.15 | 11 | 2 | <0.5 | 121 |
| b: M | $pH_{const}$ 5.0 | <0.09 | 1 | <1.5 | <0.5 | 58 |
| c: Ut3/g2 | $pH_{const}$ 6.2 | <0.09 | <0.3 | <1.5 | <0.5 | 35 |
| d: 8.03 | $pH_{const}$ 7.0 | <0.09 | <0.3 | <1.5 | <0.5 | 24 |
| 600/4 | Total content | 0.36 | 194 | 179 | 30 | |
| a: 75–95 | $pH_{const}$ 3.5 | 0.12 | 8 | 2 | 1 | 101 |
| b: Go | $pH_{const}$ 5.0 | <0.09 | 1 | <1.5 | <0.5 | 46 |
| c: Slu/g3 | $pH_{const}$ 6.2 | <0.09 | <0.3 | <1.5 | <0.5 | 26 |
| d: 8.10 | $pH_{const}$ 7.1 | <0.09 | <0.3 | <1.5 | <0.5 | 22 |

[a] According to AG Bodenkunde (1982)

[b] $pH_{const}$ $x$ is a $pH_{const}$ experiment at pH=$x$

[c] $w_{el}$ is the mobile heavy-metal fraction determined by a $pH_{const}$ experiment

### Location 602

Location 602 is unused land and is periodically flooded; the groundwater table fluctuates between 10 and 20 cm below ground level. Locations 600 and 602 are adjacent to each other, but belong to different soil units. The top layer has a neutral pH (pH=7.3), while the deeper layer shows a slightly alkaline pH (pH=7.7; Table 3). The $ANC_{6.2}$ value of the top layer at location 602 (602/1, Table 3) is 28 mmol $H^+$ $kg^{-1}$; this is a moderate value compared with the $ANC_{6.2}$ values at other locations (Fig. 4). At pH=6.2, distinct amounts of Cd (1.4 mg $kg^{-1}$) and Zn (158 mg $kg^{-1}$) are mobilised from this material (Table 3). The deeper layer (602/2, Table 3) has a high buffering capacity at pH 6.2 ($ANC_{6.2}$) and large amounts of heavy metals are released at this pH. Due to the high buffering capacity of 158 mmol $H^+$ $kg^{-1}$ at pH 6.2, a drop from pH=7.7 to pH=6.2 is not very probable. But a pH range from pH=7.7 to 6.7 is more poorly buffered ($ANC_{6.7}$= 48 mmol $H^+$ $kg^{-1}$, Table 3), resulting in the release of large amounts of heavy metals. Mobilisation of heavy metals from both horizons occurs even with a small drop in pH. The deeper layer is affected by groundwater fluctuation, making input of heavy metals into the groundwater possible. Location 602 is unused land without any input of additional buffering substances, hence, a drop of pH in the future is possible leading to increasing heavy-metal migration. For these reasons, the hazard to the environment resulting from mobilisation of heavy metals is relatively high at location 602, and hence this location is assigned to class IV.

### Location 603

Location 603 is also used for agriculture; the groundwater table fluctuates around a depth of 30 cm. The pH is slightly alkaline (7.7–8.4, Table 4). Both the top soil (603/1, Table 4) and the deeper horizon (603/2, Table 4) are contaminated with heavy metals. The buffering capacity at pH=6.2 ($ANC_{6.2}$) is relatively high, the mobile fraction of heavy metals at this pH is relatively low, but measurable (Table 4). The difference between $ANC_{5.0}$ and $ANC_{6.2}$ of the layer within which the groundwater table fluctuates (603/2, Table 4) is low, but the mobile Zn fraction (146 mg $kg^{-1}$) at pH=5.0 is relatively high. Due to the high buffering capacity, the thickness of 30 cm of the top soil and the input of buffering substances, a drop of pH below pH=6.2 seems to be relatively improbable, provided that the agricultural land use of this location is not changed. Thus, mobilisation of heavy metals from the contaminated soil into the groundwater is relatively improbable. If pH conditions are changed, for example, due to disturbance of the natural layering by excavation for buildings, heavy metals could be mobilised. For these reasons location 603 is assigned to class III.

## Example assessment of hazards to the environment for part of the study area

The map in Fig. 3 shows the assessment of the hazard to the environment for a sub-area of the study area. The assessment is done on the basis of the results from different locations each representing a different soil unit (locations 600, 602, 603 and others). The $pH_{const}$ experiments

**Table 3**
Data for location 602

| Site/sample<br>a: depth [cm]<br>b: horizon[a]<br>c: texture[a]<br>d: pH (H$_2$O) | Procedure[b] | Total content and w$_{el}$ [c] respectively |  |  |  | ANC$_x$ [mmol H$^+$ kg$^{-1}$] |
|---|---|---|---|---|---|---|
|  |  | Cd [mg kg$^{-1}$] | Zn | Pb | Cu |  |
| 602/1 | Total content | 35.04 | 9150 | 11800 | 649 |  |
| a: 0–12 | pH$_{const}$ 3.5 | 27.04 | 7044 | 2033 | 91 | 484 |
| b: Ah | pH$_{const}$ 5.0 | 9.66 | 1815 | 58 | 2 | 160 |
| c: Su2 | pH$_{const}$ 6.2 | 1.42 | 158 | 2 | <0.5 | 28 |
| d: 7.32 |  |  |  |  |  |  |
| 602/2 | Total content | 39.71 | 9400 | 26850 | 1220 |  |
| a: 12–32 | pH$_{const}$ 3.5 | 36.99 | 9006 | 1557 | 390 | 1681 |
| b: M-Go | pH$_{const}$ 5.0 | 25.65 | 4043 | 379 | 71 | 792 |
| c: Su3 | pH$_{const}$ 6.2 | 13.65 | 995 | 29 | 2 | 158 |
| d: 7.70 | pH$_{const}$ 6.7 | 5.44 | 281 | 4 | 1 | 48 |

[a] According to AG Bodenkunde (1982)
[b] pH$_{const}$ $x$ is a pH$_{const}$ experiment at pH=$x$
[c] w$_{el}$ is the mobile heavy-metal fraction determined by a pH$_{const}$ experiment

**Table 4**
Data for location 603

| Site/sample<br>a: depth [cm]<br>b: horizon[a]<br>c: texture[a]<br>d: pH (H$_2$O) | Procedure[b] | Total content and w$_{el}$ [c] respectively |  |  |  | ANC$_x$ [mmol H$^+$ kg$^{-1}$] |
|---|---|---|---|---|---|---|
|  |  | Cd [mg kg$^{-1}$] | Zn | Pb | Cu |  |
| 603/1 | Total content | 5.28 | 2945 | 1915 | 248 |  |
| a: 0–29 | pH$_{const}$ 3.5 | 2.90 | 680 | 36 | 10 | 779 |
| b: Ap | pH$_{const}$ 5.0 | 0.89 | 142 | 5 | 2 | 569 |
| c: Ul3/g2, x2 | pH$_{const}$ 6.2 | 0.09 | 10 | <1.5 | <0.5 | 157 |
| d: 7.68 | pH$_{const}$ 6.7 | <0.09 | 2 | <1.5 | <0.5 | 93 |
| 603/2 | Total content | 2.89 | 4310 | 2906 | 412 |  |
| a: 30–50 | pH$_{const}$ 3.5 | 1.19 | 1011 | 97 | 43 | 180 |
| b: M-Go | pH$_{const}$ 5.0 | 0.28 | 146 | 2 | 1 | 67 |
| c: Slu/g3 | pH$_{const}$ 6.2 | <0.09 | 16 | <1.5 | <0.5 | 64 |
| d: 8.4 | pH$_{const}$ 7.4 | <0.09 | 1 | <1.5 | <0.5 | 32 |

[a] According to AG Bodenkunde (1982)
[b] pH$_{const}$ $x$ is a pH$_{const}$ experiment at pH=$x$
[c] w$_{el}$ is the mobile heavy-metal fraction determined by a pH$_{const}$ experiment

make it possible to differentiate between soil units which have been placed in the same environmental hazard class (Fig. 2) of Eikmann and Kloke's classification scheme (Eikmann and Kloke 1993). According to the assessment based on the pH$_{const}$ experiments, the highly contaminated areas nearest the Innerste River (location 602) have the highest potential (class IV) for mobilisation of heavy metals with the present land use. Soil units further from the river (location 600) are usually at a higher level and have a lower potential risk to the environment (class II). These soil units are normally used agriculturally. A hazard to the environment may arise from the soil unit along the River Grane (location 603) if land use changes (class III). If mobilisation of heavy metals is to be prevented in the future, a decrease in the buffering capacity of the top soil, for example, by the destruction of the natural layering, must be avoided. No hazard to the environment is expected from a soil unit in the northern part of the sub-area (Fig. 3). The total heavy-metal concentrations are below BW III and no mobile fraction of heavy metals was detected in the pH$_{const}$ experiment. This soil unit is, therefore, assigned to class I. Some smaller areas could not be classified because no pH$_{const}$ investigations were carried out on samples from those soil units. Comparing the maps in Figs. 2 and 3 it can be noted that the assessment of contaminated areas on the basis of pH$_{const}$ analyses and pedological information gives a more detailed picture of the risk to the environment than assessment on the basis of total heavy-metal concentrations. In the study presented here, the extent of heavy-metal contamination of the floodplains of the Harz Mts. and the area around the northwest end of the Harz Mts. is characterised and the environmental hazard arising from this contamination can be assessed.

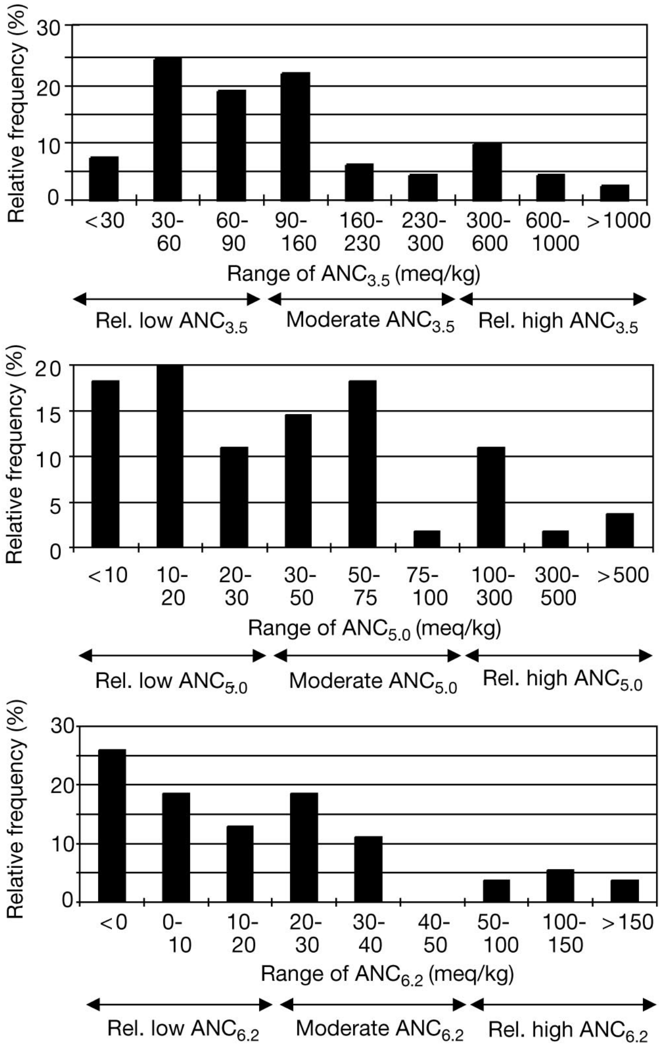

**Fig. 4**
Frequency distribution and classification of the $ANC_x$ data

## Conclusion

This survey of heavy-metal contamination of floodplain soils in a large study area (12.5 $km^2$) of the Harz Mts. demonstrates that it can be carried out in several steps. Evaluation of available information provides targets for mapping the soils of the selected area contaminated with heavy metals. In addition, a rapid photometric field test will yield soil units for heavy-metal analysis. Using the classification system of Eikmann and Kloke (Eikmann and Kloke 1993), the soil units of the study area can be initially assessed on the basis of total heavy-metal content. The heavy-metal contamination in the study area can be further assessed by conducting $pH_{const}$ experiments to determine heavy-metal mobility. The contaminated soil units are then classified on the basis of the pedological data and the results of the $pH_{const}$ experiments to obtain a better assessment of the contaminated areas than the assessment based on total heavy-metal loads.

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