

## Heavy metal storage in near channel sediments of the Lahn River, Germany

Charles W. Martin\*

*Department of Geography, Kansas State University, 118 Seaton Hall, Manhattan, KS 66506-2904, USA*

Received 4 August 2003; received in revised form 14 January 2004; accepted 15 January 2004

Available online 2 March 2004

### Abstract

Heavy metal pollution in urban, industrial, and mined watersheds of Europe is well documented, but less is known about metal contamination in agrarian watersheds or those with no history of mining. Along a 75-km reach of the Lahn River, central Germany, near-channel flood-plain sediments (<5 m from the active channel) have mean concentrations of Cd, Cu, Pb, and Zn that exceed background values. Vertically, metal concentrations are highest at 15 or 20 cm below the flood plain. Although mean metal concentrations in the watershed are below mean values found in more industrial watersheds of western Europe, individual near-channel sites along the Lahn River have metal concentrations approaching those found in more urbanized drainage basins. Several sites along the Lahn are “excessively contaminated” with Cd and “moderately/strongly” contaminated with Cu, Pb, and Zn. Metal concentrations are generally higher and more variable downstream from metal-producing locations and in the vicinity of industrial facilities. Topographic and geomorphic factors appear to have minimal influence on near-channel metal concentrations. The elevated concentrations of metals in geomorphically sensitive channel banks and near-channel sediments raise the possibility of future metal pollution in the Lahn River watershed even as metal emissions to the environment decline.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Heavy metals; Sediment contamination; Flood plains; Germany

### 1. Introduction

The fall of the Berlin Wall in 1989 ushered in a period of dramatic change in Germany. Forces unleashed by the disintegration of the Soviet Union profoundly changed the political, economic, and social landscape of Europe. But more than just the human landscape was altered. With the closing of many aged industrial structures in Eastern Europe, emissions of

heavy metals such as Cu, Cd, Pb, and Zn fell dramatically (Matschullat and Bozau, 1996; Schulte et al., 1996; Dämmgen et al., 2000). As a result, the air and water of eastern European countries and their neighbors are much cleaner today than they were in 1990.

Despite the lowering of emissions, substantial stores of heavy metals remain in river valley sediments of Europe. In the 2002 summer, the catastrophic Elbe River floods in Europe underscored the extensive contamination problems that exist in flood plains of many major rivers (Förstner, 2003). The topic of heavy metal pollution in sediments of Euro-

\* Tel.: +1-785-532-3416; fax: +1-785-532-7310.

E-mail address: [cwmgeog@ksu.edu](mailto:cwmgeog@ksu.edu) (C.W. Martin).

pean rivers has received the attention of many scientists. Much work to date has focused on more industrial parts of Europe, such as the Rhine River of Germany and the Netherlands (Middelkoop, 2000, 2002; Dehner, 1994) or the Elbe River of Germany (Brüggemann, 1995). Others have documented storage of heavy metals in mined drainage basins of Europe (Bradley and Cox, 1986; Macklin and Dowsett, 1989; Hudson-Edwards et al., 1999; Coulthard and Macklin, 2003). Fewer researchers have looked at metal levels in agrarian drainage basins or basins that have little or no history of mining activity. Among the exceptions is previous work along the Lahn River in central Germany (Martin, 1997, 2000).

Metals stored in flood plains and channel sediments have the potential to serve as future sources of pollution. The degree to which they become a source of pollution depends on factors such as the proximity of contaminated sediments to the active channel (lateral and vertical) and the intensity of geomorphic activity along the river. When channel banks or low

elevation surfaces have high metal concentrations, or the river is geomorphically active, the storage of metalliferous sediments may be brief, posing a threat of metal pollution downstream (James, 1989; Marcus, 1989; Leece and Pavlowsky, 1997; Hudson-Edwards et al., 1999; Zhao et al., 1999). In contrast, if metal concentrations are spread more widely and evenly across the flood plain, are present on higher topographic positions, or the river is geomorphically quiet, metalliferous sediments may remain stored for decades or centuries (Meade, 1982; Foster and Charlesworth, 1996; Miller, 1997; Hudson-Edwards et al., 1999; Zhao et al., 1999; Coulthard and Macklin, 2003). As Leece and Pavlowsky (2001) noted, metal concentrations are often highest on lower flood-plain surfaces where the sedimentation rate is at a maximum. In short, sources of metal pollution may remain long after the production and release of metals to the environment has slowed or ceased.

Previously, Martin (1997, 2000) examined the vertical and lateral concentrations of heavy metals in

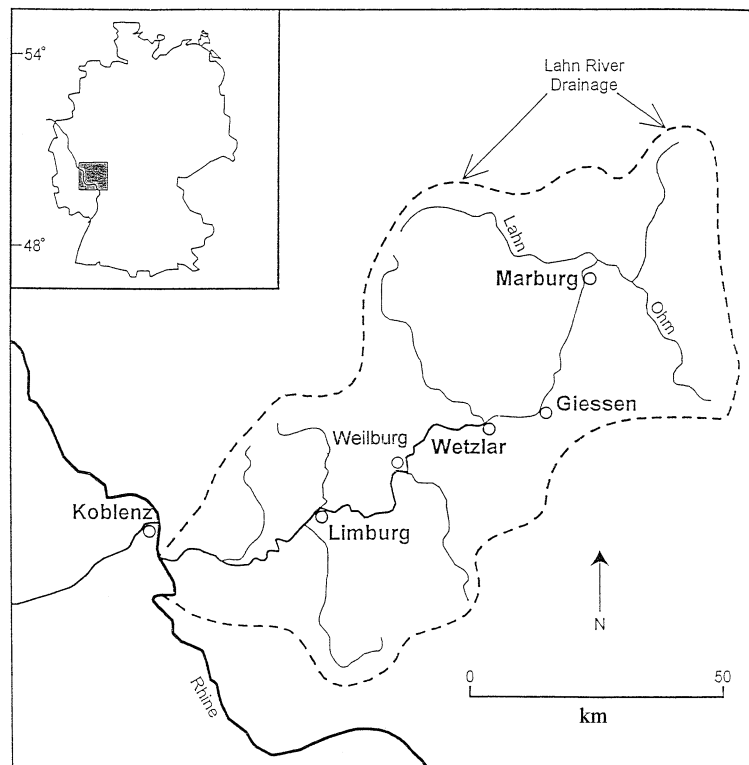


Fig. 1. The Lahn River drainage basin, west-central Germany.

flood-plain sediments of the Lahn River, west central Germany. That work established that concentrations of Cu, Pb, and Zn are highest within 100 m of the active channel and in the upper 15 cm of flood-plain soils. At distances >100 m from the channel, concentrations are fairly uniform to the valley wall. Likewise, metal concentrations decrease sharply at depths >15 cm below the surface, and by 25 cm the concentrations are virtually identical to those found in deeply buried (>1 m) sediments.

This earlier research demonstrated that the near-channel zone contains the majority of stored metals in the Lahn River flood plain, but provided limited detail on the concentrations of metals immediately adjacent to the channel. The present study examines the near-channel pattern of metal concentrations at 34 sites in a 75-km reach of the Lahn River from Marburg to Weilburg (Fig. 1). The objectives of the study are to (i) inventory the near-channel concentrations of heavy metals in the upper 25 cm of flood-plain soils, (ii) compare near-channel concentrations from the agrarian Lahn River basin with concentrations documented in more urban and industrial basins, and (iii) examine the changes in metal concentrations downvalley from Marburg. This study builds upon previous research in the Lahn valley by providing a detailed look at the along-valley metal concentrations in near-channel sediments and assessing the impact of local industrial concentrations on heavy metal storage in near-channel positions.

## 2. Study area

The Lahn River, a major tributary to the Rhine River, has its headwaters in the rural uplands north of Marburg in west central Germany. Land use in the Lahn watershed is primarily agrarian (70% agricultural, 16% forest, 14% urban), although there are concentrations of industry in Gießen and Wetzlar (Jöckel, 1981). The flood plain of the Lahn, which reaches a maximum width of 2.5 km just downriver from Gießen, is primarily cultivated or used for grazing; hillslopes in the study reach are generally forested. No physical or archival evidence exists of large-scale heavy metal mining in the Lahn River watershed between Marburg and Weilburg. Downstream from Wetzlar, iron was extracted from deep underground

mines in uplands on the north side of the Lahn valley until the early 1980s, but no record exists of heavy metal mining in the reach.

The Lahn River was channelized in the mid-1800s. Consequently, flow during much of the year is sluggish. The exception tends to be in the winter when Atlantic cyclones coupled with snowmelt often result in high discharges and flooding. During the late winter and early spring, near-channel reaches of the Lahn River commonly are submerged for a week or more. Typically, these high water events not only deposit fine sands on point and near-channel bars, but also erode bank and flood-plain sediments at scattered locations. Aerial photographs taken between 1935 and 1995 indicate that most of the Lahn channel has been stable for some time, although numerous swales suggest earlier lateral migration (Martin, 2000). Since 1994, when I began work in the Lahn valley, the channel position has not shifted significantly. Much of the flood plain is underlain by black, organic-rich silt that was eroded from surrounding hillslopes and deposited during the last 1000 years (Mäkel, 1969; Huckriede, 1971; Thiemeyer, 1988). Soils developed in these silts have an A/AC/C profile and a mean pH of 5.2 (standard deviation = 0.5) (Martin, 2000).

## 3. Methods

To evaluate the concentrations of metals in near-channel sediments, samples were collected <5 m from the active channel of the Lahn River. Sites with anthropogenic levees were avoided since the date of levee construction could not always be determined. Topographic maps of the study reach were used to distinguish natural levees from anthropogenic ones. To reduce the possibility of bias from local metal sources, samples were collected away from major roads and railroad lines. Sites were chosen to represent reaches with narrow and wide flood plains. To the extent allowed by access to the river, approximately equal numbers of sites were located on the left and right channel banks. In total, 34 sites were sampled between Marburg and Weilburg.

I extracted cores to a depth of 25 cm, then collected samples from the cores at 5-cm intervals beginning at the surface (0 cm) and ending at 25 cm for a total of five samples from each core. The sampling interval

and maximum sampling depth were based on previous work documenting that metal concentrations peak around 15 cm below the surface, then decline with increasing depth (Martin, 2000). At depths >25 cm, metal concentrations are generally equal to pre-industrial metal values.

Heavy metal concentrations were determined by ALS Chemex Labs, an ISO 9002 registered analytical laboratory in North America. Samples were digested in perchloric, nitric, and hydrofluoric acids, a procedure that results in nearly total recovery of metals (Leece and Pavlowsky, 1997). Metal concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Particle size analysis of samples was done using the pipette method to measure the proportions of clay (<2 µm) and silt (2–63 µm); the proportion of sand was determined by wet sieving. Loss on ignition (LOI) at 430 °C for 24 h was used to measure the percent organic matter content (Davies, 1974).

To assess the anthropogenic enrichment of metals in flood-plain soils and surficial sediments, 18 background samples were collected at a minimum depth of 1 m. Determining the pre-industrial background metal concentrations is problematic (see Birch et al., 2000; Matschullat et al., 2000). Some studies use worldwide average metal values (e.g., Turekian and Wedepohl, 1961) as an estimate of the pre-industrial metal concentrations, whereas others opt to sample presumed pre-industrial sediments to obtain background metal values (e.g., Swennen et al., 1998). The use of worldwide metal values to look at regional or local anthropogenic metal contamination has limitations (Matschullat et al., 2000). In the Lahn valley, sediments at depth of >1 m have pre-industrial concentrations of metals (Martin, 2000). Samples collected between 50 cm and 1 m were also used to determine background metal concentrations in research assessing heavy metal storage in channel bed sediments of the Lahn River (Runkel, 1992; Anonymous, 1994). For those reasons, deeply buried sediments were sampled in order to obtain background metal concentrations. Background samples were collected at slightly more than half of the sites where surface samples were obtained; at the other sites, coarse sand and gravel or a high water table prevented the collection of background samples. In using deeply buried sediments to obtain background metal values, the assumption

is made that the deeply buried and surficial sediments have a similar geologic source. Based on the late Quaternary history of the Lahn valley, this would appear to be a valid assumption (Mäckel, 1969).

## 4. Results

### 4.1. Mean metal concentrations

Mean near-channel metal concentrations are markedly higher than background concentrations for Cd, Cu, Pb, and Zn (Table 1); the background values reported here are comparable to those noted by Runkel (1992) and Knoblich and Sanner (1992) for the upper Lahn River. Sediments are especially enriched in Cd and Zn relative to background levels. Metal concentrations peak at depths of 15 or 20 cm, then decline toward the surface. Although not examined in this study, metal concentrations generally decline rapidly at depths >25 cm, then vary little below 40 cm (Martin, 2000).

In order to assess the degree of contamination, metal concentrations were converted to Index of Geoaccumulation ( $I_{geo}$ ) values (Table 2), then assigned contamination levels (Table 3) based on standards established for the Lahn River basin (Anonymous, 1994). The  $I_{geo}$  is a widely used index of heavy metal pollution in Europe (Förstner and Müller,

Table 1  
Near-channel metal concentrations and standard deviations with depth, Marburg to Weilburg

| Depth (cm) | n  | Metal concentrations (S.D.) in ppm |                |                |                  |
|------------|----|------------------------------------|----------------|----------------|------------------|
|            |    | Cd                                 | Cu             | Pb             | Zn               |
| 0          | 34 | 1.07<br>(0.89)                     | 45.0<br>(11.4) | 61.8<br>(18.2) | 239.5<br>(69.8)  |
| 5          | 34 | 1.13<br>(0.68)                     | 48.2<br>(13.4) | 68.4<br>(24.7) | 245.2<br>(79.4)  |
| 10         | 34 | 1.31<br>(0.82)                     | 51.9<br>(16.4) | 71.9<br>(23.4) | 258.8<br>(90.2)  |
| 15         | 34 | 1.46<br>(0.96)                     | 54.0<br>(18.0) | 78.0<br>(31.2) | 266.4<br>(96.9)  |
| 20         | 34 | 1.50<br>(1.0)                      | 54.3<br>(19.9) | 75.6<br>(25.3) | 259.4<br>(100.9) |
| Background | 18 | 0.08<br>(0.19)                     | 28.1<br>(18.2) | 42.2<br>(33.5) | 106.6<br>(68.2)  |

Table 2

Near-channel Index of Geoaccumulation ( $I_{\text{geo}}$ ) and contamination level with depth, Marburg to Weilburg

| Depth (cm) | $I_{\text{geo}}$ and contamination level <sup>a</sup> |           |             |           |
|------------|---|-----------|-------------|-----------|
|            | Cd  | Cu        | Pb          | Zn        |
| 0          | 3.16 (SC)   | 0.09 (MC) | −0.03 (SLC) | 0.58 (MC) |
| 5          | 3.24 (SC)   | 0.19 (MC) | 0.11 (MC)   | 0.62 (MC) |
| 10         | 3.45 (SC)   | 0.29 (MC) | 0.18 (MC)   | 0.69 (MC) |
| 15         | 3.60 (SC)   | 0.36 (MC) | 0.30 (MC)   | 0.74 (MC) |
| 20         | 3.64 (SC)   | 0.36 (MC) | 0.26 (MC)   | 0.69 (MC) |

<sup>a</sup> SLC (slightly contaminated); MC (moderately contaminated); SC (strongly contaminated).

1981). Near-channel sediments are “strongly contaminated” with Cd and “moderately contaminated” with Cu and Zn at all depths. With the exception of surface samples (0 cm), which are “slightly contaminated,” sediments are “moderately contaminated” with Pb. Because they are calculated using the background values obtained from the study reach, the  $I_{\text{geo}}$  values reported here should be regarded as specific to the study reach. For example, the designation “moderately contaminated” in the Lahn River valley could be produced by a different mean metal concentration than the same  $I_{\text{geo}}$  designation in the Rhine River valley if the background metal values for the two drainage basins are different. The degree of Cd contamination is noteworthy given that samples collected on more distal parts of the floodplain revealed low levels of Cd in the surface soil and floodplain sediments (Martin, 1997, 2000).

Although the  $I_{\text{geo}}$  values for the Lahn valley indicate anthropogenic enrichment of metals in near-channel sediments, the mean metal concentrations are generally less than those documented in more urban drainage basins of Germany such as the Rhine (Japenga et al., 1990; Dehner, 1994; Wolterbeek et al., 1996) and Elbe (Brügmann, 1995). Along the Elbe

Table 3

Index of Geoaccumulation ( $I_{\text{geo}}$ ) for Lahn River sediments

| $I_{\text{geo}}$ | Class | Contamination level                  |
|------------------|-------|--------------------------------------|
| <0               | 1     | Uncontaminated/Slightly contaminated |
| 0–1              | 2     | Moderately contaminated              |
| 1–3              | 3     | Moderately/Strongly contaminated     |
| 3–5              | 4     | Strongly contaminated                |
| >5               | 5     | Extremely contaminated               |

Table 4

Maximum near-channel metal concentrations with depth, Marburg to Weilburg

| Depth (cm) | Metal concentrations (ppm) |      |      |       |
|------------|----------------------------|------|------|-------|
|            | Cd                         | Cu   | Pb   | Zn    |
| 0          | 2.0                        | 69   | 108  | 386   |
| 5          | 2.5                        | 77   | 148  | 412   |
| 10         | 4.0                        | 91   | 130  | 464   |
| 15         | 4.5                        | 100  | 196  | 494   |
| 20         | 5.0                        | 100  | 136  | 470   |
| Background | 0.08                       | 28.1 | 42.2 | 106.6 |

River in northern Germany, mean Cd, Cu, Pb, and Zn values in near-channel positions are  $2\text{--}4 \times$  the values found in the Lahn River valley (Brügmann, 1995). Similarly, along the Rhine River in the Netherlands, mean Cd values are  $\sim 10 \times$ , and Zn values  $5 \times$ , the mean concentrations in the Lahn valley (Japenga et al., 1990). The vertical trend of lower metal concentrations at the surface than in the subsurface noted in this study is consistent with trends reported elsewhere in Germany and the Netherlands (Middelkoop, 2000; Gocht et al., 2001).

#### 4.2. Maximum metal concentrations

The mean metal concentrations afford a broad assessment of the extent of metal contamination in the study reach, but obscure the degree of contamination present at individual near-channel sites. In order to assess metal concentrations at individual sites of the study reach, maximum concentrations for each metal for each depth were identified (Table 4). The

Table 5

Near-channel Index of Geoaccumulation ( $I_{\text{geo}}$ ) and contamination level for maximum near-channel metal concentrations, Marburg to Weilburg

| Depth (cm) | $I_{\text{geo}}$ and contamination level <sup>a</sup> |              |              |              |
|------------|---|--------------|--------------|--------------|
|            | Cd  | Cu           | Pb           | Zn           |
| 0          | 4.06 (SC)   | 0.71 (MC)    | 0.78 (MC)    | 1.27 (MC/SC) |
| 5          | 4.38 (SC)   | 0.87 (MC)    | 1.22 (MC/SC) | 1.36 (MC/SC) |
| 10         | 5.06 (EC)   | 1.11 (MC/SC) | 1.04 (MC/SC) | 1.54 (MC/SC) |
| 15         | 5.23 (EC)   | 1.24 (MC/SC) | 1.63 (MC/SC) | 1.63 (MC/SC) |
| 20         | 5.38 (EC)   | 1.24 (MC/SC) | 1.10 (MC/SC) | 1.56 (MC/SC) |

<sup>a</sup> MC (moderately contaminated); MC/SC (moderately/strongly contaminated); SC (strongly contaminated); EC (excessively contaminated).

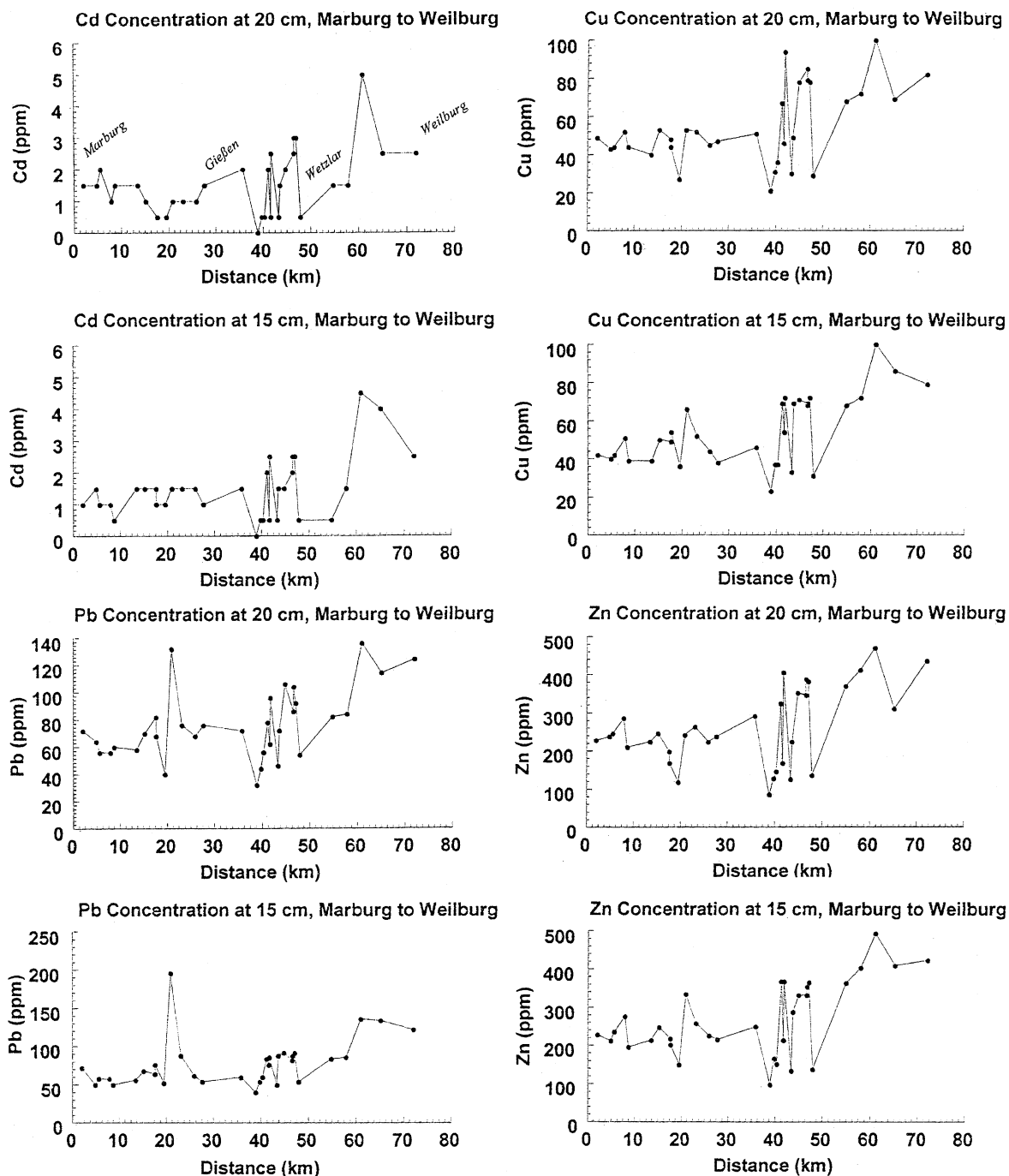


Fig. 2. Downstream changes in Cd, Cu, Pb, and Zn concentrations at depths of 15 and 20 cm, Marburg to Weilburg. Location of Marburg, Gießen, Wetzlar, and Weilburg shown in left, upper figure.



highest maximum concentrations, which are present at depths of 15 or 20 cm, are  $4\text{--}5 \times$  the background values, evidence of substantial anthropogenic enrichment at individual near-channel sites. The maximum values shown in Table 4 were converted to  $I_{\text{geo}}$  values to determine the degree of metal contamination (Table 5). Individual sites are “strongly” or “excessively contaminated” with Cd and generally “moderately/strongly contaminated” with Zn, Pb, and Cu. The maximum Cd, Pb, and Zn values frequently exceed the “Probable Effect Level” (PEL), defined by the U.S. Environmental Protection Agency (EPA) as the level above which metals have the potential to produce toxic biological effects (Christensen and Juracek, 2001).

The site with the highest metal concentrations is directly opposite an industrial complex north of Gießen. Concentrations of Pb are particularly high there, with the highest concentration of Pb in the study reach (196 ppm) and three of the five highest Pb concentrations measured at this site. In contrast, Cd, Cu, and Zn concentrations at the site are only slightly above the concentrations at other sites between Marburg and Gießen. Sites with notably high metal concentrations are also present between Gießen and Wetzlar and at the lower end of the study reach between Wetzlar and Weilburg.

#### 4.3. Downstream metal trends

Downstream changes in near-channel metals for the 75-km study reach were examined by plotting the concentrations of Cd, Cu, Pb, and Zn at depths of 15 and 20 cm, the depths that have the highest mean metal concentrations, against the distance downstream from Marburg (Fig. 2). With the exception of one site (21 km) where Cu, Pb, and Zn concentrations were high, metal concentrations varied little between Marburg (0 km) and Gießen (31 km), but then increased and displayed significantly more variation downstream from Gießen. Generally, the highest metal values were found downstream from Gießen, suggesting that the city served as a source of metals. Although the highest Pb concentrations in the study reach are upstream from Gießen (21 km), the maximum Cd, Cu, and Zn concentrations are present between Wetzlar and Weilburg.

#### 4.4. Metal concentrations and sediment characteristics

Although high metal concentrations are often associated with fine-textured, organic-rich sediments (e.g., de Groot et al., 1982; Horowitz, 1985; Bubb and Lester, 1996), other studies report, at best, a weak relationship between metal concentration and fine-textured, organic-rich sediments (e.g., Leenaers et al., 1988; Taylor, 1996; Leece and Pavlowsky,

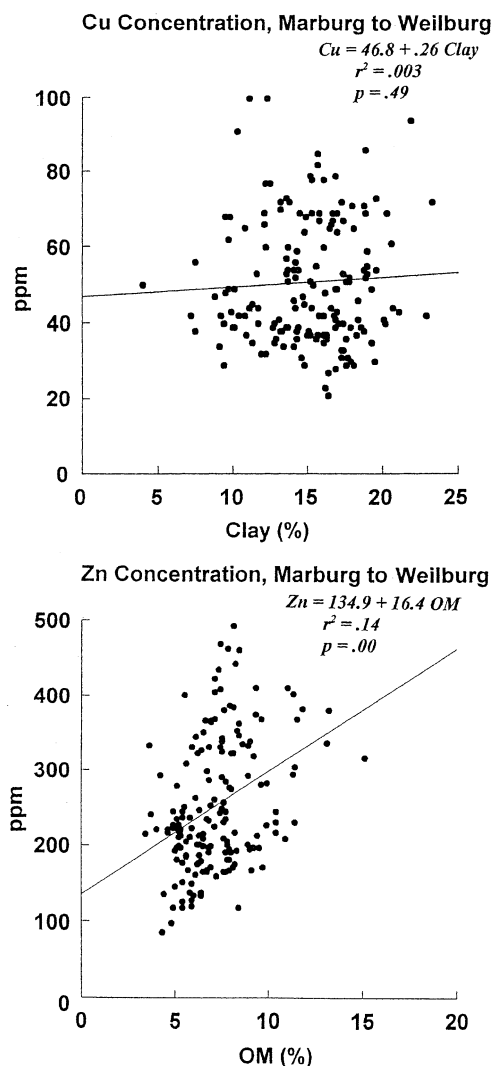


Fig. 3. Scatter plots and best-fit bivariate regression of metal concentrations with percent clay and percent organic matter content (OM %) for all samples.

1997). Previous work in the Lahn valley noted a weak relationship between metal concentrations and sediment texture and organic matter content (Martin, 2000). This appears to hold true for near-channel sediments, as well. Between Marburg and Weilburg, Cu has the highest  $r^2$  value (0.003) with percentage clay (Fig. 3), although the value is not statistically significant; the concentrations of the other metals have no relationship to the percentage of fine sediments. Organic matter content has a marginally stronger effect on metal concentrations. Zinc has the highest  $r^2$  value (0.14) with organic matter content for the near-channel samples between Marburg and Weilburg. Although weak, the relationship is statistically significant at the 0.01 level.

## 5. Discussion

Heavy metals in flood-plain sediments of the Lahn River are concentrated in near-channel positions, corroborating preliminary findings from previous work in the drainage basin (Martin, 1997, 2000). Vertically, mean values for Cd, Cu, Pb, and Zn are less at the surface than at greater depths, with maximum metal concentrations at 15 or 20 cm; at the surface, values are from 60% (Cd) to 22% (Zn) less than peak concentrations. The decrease in metal concentrations toward the surface reflects the reduction in metal releases to the environment over the last several decades, a trend that has been noted in flood-plain sediments of other drainage basins in Western Europe (Dehner, 1994; Brüggmann, 1995; Middelkoop, 2000; Gocht et al., 2001). Middelkoop (2000, 2002) identified major heavy metal peaks in the early 1930s and 1960s in sediments of the lower Rhine River, the Netherlands. He noted a sharp decrease in metal pollution between 1975 and 1985, followed by a slower rate of decline since 1985. In a survey of water quality across Europe, Vink et al. (1999) found that the concentrations of heavy metals in rivers decreased dramatically between 1980 and 1995. Other studies in central Europe have noted a peak in Pb pollution between 1945 and 1970, corresponding to the increased burning of leaded fuel by automobiles (Brännvall et al., 1999; Renberg et al., 2001). The closure of polluting industries since the 1980s in Eastern

Europe has likewise led to a decline in emissions of metals to the atmosphere (Matschullat and Bozau, 1996; Schulte et al., 1996).

This study confirms previous work in the Lahn basin that metal concentrations decline quickly with increasing distance from the active channel (Martin, 2000), an indication that metals were deposited primarily by fluvial rather than by atmospheric processes. Atmospheric deposition would likely produce a more even distribution of metals across the flood plain, whereas fluvial deposition would tend to concentrate metals close to the active channel where flow velocity drops sharply with the onset of overbank flow. Distal parts of the flood plain are flooded less frequently than are near-channel locations and thus have lower metal concentrations (Brewer and Taylor, 1997; Middelkoop, 2002). Because the maximum metal concentrations are adjacent to the active channel, remobilization of metal-contaminated sediments is possible during flooding. As was demonstrated by the 2002 floods along the Elbe River, contaminated sediments can be dispersed over large areas by floodwaters, coming to rest in flood plains, agricultural areas, and residential zones (Förstner, 2003). Seasonal flooding along the Lahn River typically produces high flows during the winter. These flows, which can persist for several weeks, have the potential to erode near-channel sediments, which, as this study documents, often contain elevated concentrations of heavy metals.

Metal concentrations displayed no systematic variation between Marburg and Gießen. In contrast, downstream from Gießen metal concentrations increased and varied more from site-to-site. Several “hot spots” with anomalously high metal concentrations were identified between Marburg and Gießen, although the sites did not always have high concentrations of all four metals. For example, 21 km downstream from Marburg (Fig. 2), Pb levels approached 200 ppm at 15 cm and 140 ppm at 20 cm; concentrations of Zn and Cu at 15 cm were also elevated, but the Cd concentration was the same as elsewhere in the Marburg to Gießen reach. At the next sample site, 1.5 km downstream, the Cu, Pb, and Zn concentrations were similar to those at other sample sites between Marburg and Gießen, suggesting that the conveyance of metal-rich sediment downvalley has been limited. Downstream from Marburg at a



distance of 61 km, the highest concentrations of Cd, Cu, and Zn, and the second highest concentration of Pb were measured.

Topographically, sites with high metal concentrations are not markedly different than sample sites that have lower metal concentrations, an indication that differences in relief are not controlling metal concentrations, in contrast to what has been noted in some studies (e.g., Brewer and Taylor, 1997; Leece and Pavlowsky, 2001; Middelkoop, 2002). Similarly, valley and flood-plain width, which influence stream power (Magilligan, 1985, 1992; Faulkner, 1998), do not explain the pattern of metal concentrations; between Gießen and Weilburg, where metal concentrations are highly variable, valley and flood-plain width change little. The percentage of clay and the organic matter content of sediments have virtually no effect on metal concentrations. Rather, the sites with high metal concentrations appear to reflect proximity to metal sources, with the highest concentrations generally located close to metal-producing locations (e.g., industrial concentrations, urban concentrations).

The generally higher metal concentrations downstream from Wetzlar suggest that the city, which has a long history of heavy industry, serves as a major point source for heavy metal releases to the environment. The concentrations of all metals, but especially Cd and Zn, are noticeably higher downstream from Wetzlar than upstream from the city. Land use in the Lahn River valley is primarily agrarian both up- and downstream from Wetzlar, and fewer towns exist on valley uplands downstream from Wetzlar than upstream from the city. This suggests that the source of most heavy metals is not the local environment but rather an upstream source, probably Wetzlar. Floodwaters have spread metal-contaminated sediments downstream from the city. Near-channel locations have received the bulk of contaminated sediments because they are inundated most frequently. The along-channel variation in metal concentrations may reflect a fluvial regime that tends to move metals episodically rather than spreading them evenly in a downstream direction. The irregular pattern of metal contamination is similar to that reported by Coulthard and Macklin (2003) in a mined watershed of northern England. As was noted upstream from Wetzlar, metal concentrations downstream from the city decreased toward the

surface, an indication that metal releases to the environment have slowed recently.

## 6. Conclusion

Near-channel sediments in the Lahn River flood plain between Marburg and Weilburg have mean concentrations of Cd, Cu, Pb, and Zn that exceed background metal values for the study reach. Based on the Index of Geoaccumulation ( $I_{geo}$ ), sediments in the upper 20 cm of the near-channel zone are “strongly contaminated” with Cd, “moderately contaminated” with Cu and Zn, and “moderately” or “slightly contaminated” with Pb. Mean metal concentrations along the Lahn River are less than mean values noted along the Elbe and Rhine Rivers, waterways that flow through more industrial parts of Western Europe; but individual near-channel sites along the Lahn have metal concentrations that approach those found along more urbanized watersheds. According to the  $I_{geo}$  index, several Lahn River sites are “excessively contaminated” with Cd and “moderately/strongly contaminated” with the other three metals.

Metal concentrations are highest at between 15 and 20 cm below the flood plain. This trend likely reflects the reduction in metal releases to the environment since the early 1970s and agrees with other work done in Western Europe. Near-channel metal concentrations vary little between Marburg and Gießen. Downstream from Gießen, metal concentrations are higher and more variable, possibly reflecting inputs of metals from industrial activity in Gießen and the irregular downstream conveyance of metal-contaminated sediments. Metal concentrations rise sharply downstream from Wetzlar, a city with a long history of heavy industrial activity. The increased variability of metal concentrations between Gießen and Wetzlar and the higher concentrations downstream from Wetzlar echo findings from a more limited study of metals in channel bed sediments of the Lahn River (Jöckel, 1981). Metal concentrations have virtually no statistical relationship to the percentage of clay in sediments. Likewise, the relationship between metal concentrations and the organic matter content of sediments is weak. Rather, metal concentrations are controlled by proximity to potential metal sources.

Given the agrarian landscape of the majority of the study reach, the high concentrations of metals in near-channel sediments demonstrates that even predominantly rural environments have stores of heavy metals. A few point sources are apparently sufficient to elevate metal concentrations above background values in flood-plain soils and sediments. In the Lahn River valley, the location of these metals adjacent to the active channel poses the threat of future metal dispersion downstream. This threat may become more acute under a warmer global climate because warmer surface temperatures are expected to increase flood frequencies and magnitudes (Kwadijk and Rotmans, 1995; Becker and Grünewald, 2003). In contrast, some work suggests that increased flood magnitudes may decrease flood-plain and channel bank contamination through dilution by cleaner sediments (Coulthard and Macklin, 2003). Regardless of the future impact of climate change and despite a marked decrease in the release of contaminants to the environment over the last several decades, the threat of heavy metal pollution persists in the Lahn River, and presumably in other rural drainages, as well, when metals are stored in geomorphically sensitive channel banks and near-channel sediments.

### Acknowledgements

This research was supported by the Alexander von Humboldt Stiftung of Bonn, Germany, in the form of a Research Fellowship. The work was undertaken at Justus Liebig-Universität, Gießen, Germany, during a sabbatical year granted by Kansas State University. I thank Professor Willibald Haffner, my host at the Geographisches Institut in Gießen, for lab and field assistance. Jutta Hempfing and Matthias Schick provided crucial logistical support during my year in Gießen. The heavy metal analysis was funded by the Humboldt Stiftung. Comments and suggestions from Richard A. Marston and an anonymous reviewer greatly improved the manuscript.

### References

Anonymous, 1994. Die Lahn, Ein Fließgewässerökosystem. Regierungspräsidium Giessen, Niederhausen. 218 pp.

- Becker, A., Grünewald, U., 2003. Flood risk in central Europe. *Science* 300, 1099.
- Birch, G.F., Robertson, E., Taylor, S.E., McConchie, D.M., 2000. The use of sediments to detect human impact on the fluvial system. *Environmental Geology* 39, 1015–1028.
- Bradley, S.B., Cox, J.J., 1986. Heavy metals in the Hamps and Manifold Valleys, North Staffordshire, UK: partitioning of metals in floodplain soils. *Science of the Total Environment* 50, 103–128.
- Brännvall, M.L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J., Billström, K., 1999. The Medieval metal industry was the cradle of modern large-scale atmospheric lead pollution in northern Europe. *Environmental Science and Technology* 33, 4391–4395.
- Brewer, P.A., Taylor, M.P., 1997. The spatial distribution of heavy metal contaminated sediment across terraced floodplains. *Catena* 30, 229–249.
- Brüggemann, L., 1995. Metals in sediments and suspended matter of the river Elbe. *Science of the Total Environment* 159, 53–65.
- Bubb, J.M., Lester, J.N., 1996. Factors controlling the accumulation of metals within fluvial systems. *Environmental Monitoring and Assessment* 41, 87–105.
- Christensen, V.G., Juracek, K.E., 2001. Variability of metals in reservoir sediment from two adjacent basins in the central Great Plains. *Environmental Geology* 40, 470–481.
- Coulthard, T.J., Macklin, M.G., 2003. Modeling long-term contamination in river systems from historical metal mining. *Geology* 31, 451–454.
- Dämmgen, U., Lüttich, M., Scholz-Seidel, C., 2000. Atmosphärische Deposition von Cadmium in landwirtschaftliche Nutzflächen in Deutschland. *Landbauforschung Völknerode* 50, 103–131.
- Davies, B.E., 1974. Loss-on-ignition as an estimate of soil organic matter. *Proceedings-Soil Science Society of America* 38, 150–151.
- de Groot, A.J., Zschuppe, K.H., Salomons, W., 1982. Standardization of methods of analysis for heavy metals in sediments. *Hydrobiologia* 92, 689–695.
- Dehner, U., 1994. Das Verteilungsmuster von Schwermetallen in der Rheinaue des Hessischen Rieds. *Geologisches Jahrbuch Hessen* 122, 159–171.
- Faulkner, D.J., 1998. Spatially variable historical alluviation and channel incision in west-central Wisconsin. *Annals of the Association of American Geographers* 88, 666–685.
- Förstner, U., 2003. Geochemical techniques on contaminated sediments—river basin view. *Environmental Science and Pollution Research International* 10, 58–68.
- Förstner, U., Müller, G., 1981. Concentrations of heavy metals and polycyclic aromatic hydrocarbons in river sediments: geochemical background, man's influence and environmental impact. *GeoJournal* 5, 417–432.
- Foster, I.D.L., Charlesworth, S.M., 1996. Heavy metals in the hydrologic cycle: trends and explanation. *Hydrological Processes* 10, 227–261.
- Gocht, T., Moldenhauer, K.M., Püttmann, W., 2001. Historical record of polycyclic aromatic hydrocarbons (PAH) and heavy metals in floodplain sediments from the Rhine River (Hessische Ried, Germany). *Applied Geochemistry* 16, 1707–1721.

- Horowitz, A.J., 1985. A Primer on trace metal-sediment chemistry. Geological Survey Water-Supply Paper 2277 (Reston, VA, 115 pp.).
- Huckriede, R., 1971. Über jungholozäne, vorgeschichtliche Löß-Umlagerung in Hessen. *Eiszeitalter und Gegenwart* 22, 5–16.
- Hudson-Edwards, K., Macklin, M.G., Taylor, M.P., 1999. 200 years of sediment-borne heavy metal storage in the Yorkshire Ouse basin, NE England, UK. *Hydrological Processes* 13, 1087–1102.
- James, L.A., 1989. Sustained storage and transport of hydraulic gold mining sediment in the Bear River, California. *Annals of the Association of American Geographers* 79, 570–592.
- Japenga, J., Zschuppe, K.H., de Groot, A.J., Salomons, W., 1990. Heavy metals and their micropollutants in floodplains of the river Waal, a tributary of the river Rhine, 1958–1981. *Netherlands Journal of Agricultural Science* 38, 381–397.
- Jöckel, R., 1981. Geochemische Untersuchung der Lahnsedimente im Hinblick auf Ihre Belastung durch Schwermetalle. Diplomarbeit, Fachbereich Geowissenschaften und Geographie der Justus Liebig-Universität. Gießen, Germany.
- Knoblich, K., Sanner, B., 1992. Zur Schwermetallbelastung der Lahn zwischen Gießen und Wetzlar. *Zeitschrift für Angewandte Geowissenschaften (Gießen)* 11, 47–57.
- Kwadijk, J., Rotmans, J., 1995. The impact of climate change on the River Rhine: a scenario study. *Climate Change* 30, 397–425.
- Leece, S.A., Pavlowsky, R.T., 1997. Storage of mining-related zinc in floodplain sediments, Blue River, Wisconsin. *Physical Geography* 18, 424–439.
- Leece, S.A., Pavlowsky, R.T., 2001. Use of mining-contaminated tracers to investigate the timing and rates of historical flood plain sedimentation. *Geomorphology* 38, 85–108.
- Leenaers, H., Schouten, C.J., Rang, M.C., 1988. Variability of the metal content of flood deposits. *Environmental Geology and Water Sciences* 11, 95–106.
- Mäkel, R., 1969. Untersuchen zur jungquartären Flußgeschichte der Lahn in der Gießener Talweitung. *Eiszeitalter und Gegenwart* 20, 138–174.
- Macklin, M.G., Dowsett, R.B., 1989. The chemical and physical speciation of trace metals in fine grained overbank flood sediments in the Tyne River, north-east England. *Catena* 16, 135–151.
- Magilligan, F.J., 1985. Historical floodplain sedimentation in the Galena River basin, Wisconsin and Illinois. *Annals of the Association of American Geographers* 75, 583–594.
- Magilligan, F.J., 1992. Thresholds and the spatial variability of flood power during extreme floods. In: Phillips, J.D., Renwick, W.H. (Eds.), *Geomorphic Systems*. Elsevier, Amsterdam, pp. 373–390.
- Marcus, W.A., 1989. Regulating contaminated sediments in aquatic environments: a hydrologic perspective. *Environmental Management* 13, 703–713.
- Martin, C.W., 1997. Heavy metal concentrations in floodplain surface soils, Lahn River, Germany. *Environmental Geology* 30, 119–126.
- Martin, C.W., 2000. Heavy metal trends in floodplain sediments and valley fill, River Lahn, Germany. *Catena* 39, 53–68.
- Matschullat, J., Bozau, E., 1996. Atmospheric element input in the eastern Ore Mountains. *Applied Geochemistry* 11, 149–154.
- Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background—can we calculate it? *Environmental Geology* 39, 990–1000.
- Meade, R.H., 1982. Sources, sinks, and storage of river sediments in the Atlantic drainage of the United States. *Journal of Geology* 90, 235–252.
- Middelkoop, H., 2000. Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands. *Geologie en Mijnbouw/Netherlands Journal of Science* 74, 411–428.
- Middelkoop, H., 2002. Reconstructing floodplain sedimentation rates from heavy metal profiles by inverse modelling. *Hydrological Processes* 16, 47–64.
- Miller, J.R., 1997. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. *Journal of Geochemical Exploration* 58, 101–118.
- Renberg, I., Bindler, R., Brännvall, M.-L., 2001. Using the historical atmospheric lead-deposition record as a chronological marker in sediment deposits in Europe. *Holocene* 11, 511–516.
- Runkel, M., 1992. Untersuchungen zur Sorption und Desorption von Schwermetallen an Lahnsedimenten und zur Beurteilung der Gefährdung der Lahn durch Schwermetalle. PhD thesis, Fachbereich Chemie, Philipps-Universität, Marburg, Germany.
- Schulte, A., Balazs, A., Block, J., Gehrman, J., 1996. Entwicklung der Niederschlags-Deposition von Schwermetallen in West-Deutschland: 1. Blei und Cadmium. *Zeitschrift für Pflanzenernährung und Bodenkunde* 159, 377–383.
- Swennen, R., van der Sluys, J., Hindel, R., Brusselmans, A., 1998. Geochemistry of overbank and high-order stream sediments in Belgium and Luxembourg: a way to assess environmental pollution. *Journal of Geochemical Exploration* 62, 67–79.
- Taylor, M.P., 1996. The variability of heavy metals in floodplain sediments: a case study from mid-Wales. *Catena* 28, 71–87.
- Thiemeyer, H., 1988. Bodenerosion und holozäne Dellenentwicklung in hessischen Lößgebieten. *Rhein-Mainische Forschungen* 105, 1–174.
- Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin* 72, 175–192.
- Vink, R., Behrendt, H., Salomons, W., 1999. Development of the heavy metal pollution trends in several European rivers: an analysis of point and diffuse sources. *Water Science and Technology* 39, 215–223.
- Wolterbeek, H.Th., Verburg, T.G., van Meerten, Th.G., 1996. On the 1995 flooding of the rivers Meuse, Rhine, and Waal in the Netherlands: metal concentrations in deposited river sediments. *Geoderma* 71, 143–156.
- Zhao, Y., Marriott, S., Rogers, J., Iwugo, K., 1999. A preliminary study of heavy metal distribution on the floodplain of the River Severn, UK, by a single flood event. *Science of the Total Environment* 243/244, 219–231.