Recent changes in heavy metal storage in flood-plain soils of the Lahn River, central Germany

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ORIGINAL ARTICLE

Recent changes in heavy metal storage in flood-plain soils of the Lahn River, central Germany

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Abstract Between 1995 and 2007, the concentrations of Pb and Zn in floodplain soils increased along a 60-km reach of the Lahn River, Germany, suggesting that the storage of some metals in the fluvial system is out of phase with recent declines in the release of metals to the environment. Re-sampling of surface soils to 5 cm along five transects perpendicular to the river indicated that the concentration of Pb increased between 1995 and 2007 along two transects and was statistically unchanged at the other three. The concentration of Zn increased at three of five transects and was statistically unchanged at two transects over the same time period. Between 1995 and 2007, concentrations of Cu were statistically equal along four of five transects and declined at the other transect. The increase in Pb and Zn was greater in a more rural than in a more urbanized reach of the Lahn River. Soil texture and organic matter content had virtually no impact on the concentration of metals. The increase in Pb concentration suggests a lag between the decline in Pb releases to the environment and its movement through the fluvial system. Increased Zn storage may result from the high solubility of the metal and the relative ease with which it moves through the environment. Environmental controls appear to have slowed Cu storage along the Lahn River, but are not yet reflected in Pb and Zn storage.

Keywords Heavy metals · Floodplain metal storage · Recent environmental contamination · Germany

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Introduction

In densely populated, highly industrialized Western Europe, there is a long history of pollution being delivered to and conveyed through fluvial systems. In the watersheds of Germany, arguably the most industrialized nation in Western Europe, heavy metals are among the most studied pollutants. Years before re-unification, the former West Germany began enacting meaningful controls on the discharge of pollutants, including heavy metals, to its surface water systems. Since the end of the Cold War and re-unification of the country, the spread of pollutants from Eastern Europe, whether by air or water, has also been reduced. In spite of considerable effort, rivers in Germany reflect the legacy of centuries of exposure to anthropogenic pollutants. Heavy metals, usually the product of industrial or mining activity, have been discharged to the environment for centuries (Matschullat et al. 1997; Brännvall et al. 1999; Renberg et al. 2001), with the greatest releases occurring from the mid-1800s until the early 1970s (Valette-Silver 1993; Middelkoop 2002). The release of metals to the environment dropped substantially beginning in the early 1970s (Matschullat and Bozau 1996; Schulte et al. 1996; Dämmgen et al. 2000; Scherer et al. 2003; Zerling et al. 2006). The decline accelerated in the early 1990s following the closing of many aged industrial facilities and the installation of modern industrial wastewater treatment facilities in the countries of Eastern Europe (Scherer et al. 2003; Zerling et al. 2006).

Although surface water systems in Germany have become markedly cleaner over the last few decades, large stores of heavy metals remain along rivers. The August 2002 floods along the Elbe River, which affected a large portion of northern Germany, demonstrated that stored metals can be readily remobilized and spread downstream

(Förstner 2003; Krüger et al. 2005; Schwartz et al. 2006). Because of their potential to transport large quantities of heavy metals, rivers in industrial or mined areas of Germany and the Netherlands have received the bulk of attention from researchers. Much, for example, is known about heavy metal pollution in the Elbe River (Brügmann 1995; Förstner 2003; Krüger and Gröngröft 2003; Krüger et al. 2005; Schwartz et al. 2006) and the Rhine River (Dehner 1994; Middelkoop 2002; Wijnhoven et al. 2006).

When stored in floodplain soils or sediments, metals pose little threat to the environment. Concerns arise when they become mobile. The mobility of heavy metals is influenced by parameters such as pH, redox potential, atmospheric oxygen, and the concentration of complexing agents (Zehl and Einax 2005). In doing a risk assessment of metals stored in a particular environment, it is important to ascertain the bioavilability of metals and their potential uptake by biota (Wijnhoven et al. 2006). Heavy metals stored along rivers and streams may also re-enter the environment through erosion. Geomorphically active locations (e.g., channel banks, near-channel floodplains, frequently-flooded low elevation surfaces) have the potential of serving as significant sources of heavy metal pollution (James 1989; Marcus 1989; Leigh 1997; Leece and Pavlowsky 2001). In contrast, those surfaces that are geomorphically "quiet" (e.g., infrequently flooded surfaces, distal floodplains, surfaces protected by levees/high channel banks) may store metals for decades or longer (Foster and Charlesworth 1996; Zhao et al. 1999; Coulthard and Macklin 2003). Locally, channel bank erosion reduces heavy metal concentrations, and thus the risk to biota, but elevates the risk of contamination downstream (Schwartz et al. 2006).

Understandably, most research in Germany has focused on large drainage basins in industrial or mined areas (e.g., Brügmann 1995; Förstner 2003; Schwartz et al. 2006). Less is known about heavy metal pollution in more rural watersheds. Since the mid-1990s the storage and distribution of heavy metals in the Lahn River basin of central Germany had been the focus of my research (Martin 1997, 2000, 2004). A relatively rural watershed, the Lahn River drains an area of approximately 5,000 km^2 at its mouth in the Rhine River south of Koblenz (Fig. 1). Not surprisingly, the aggregate storage of heavy metals (Cu, Pb, Zn) along the Lahn River is less than that noted along waterways such as the Rhine or Elbe, although there are individual sites where metal concentrations approach levels usually found in urbanized watersheds (Martin 2004). Laterally, heavy metal concentrations are at a maximum in near-channel sediments (<100 m from active channel), suggesting that the metals are a fluvial rather than an eolian deposit (Martin 2000). Vertically, the largest stores of metals are found in the upper 15 cm of the floodplain. Below depths of 25 cm the concentrations are virtually identical to concentrations in deeply buried sediments (Martin 1997, 2000). At most sites along the Lahn River, surface samples contain lower concentrations of heavy metals than samples collected between 15 and 20 cm below the surface, evidence of the decline in metal releases to the environment since the early 1970s (Brügmann 1995; Middelkoop 2002; Zerling et al. 2006).

The present study was undertaken to assess recent changes in heavy metal concentrations along a 60-km reach of the Lahn River between Marburg and Wetzlar. Samples were collected from 50 sites along five transects that had been sampled in 1994 and 1995 (Martin 1997). In addition, the geographic coordinates of sample sites were recorded using a hand-held GPS unit in order to permit future monitoring of heavy metal storage. The objectives of the study are to (1) ascertain whether the concentration of heavy metals at the 50 sites has changed since 1994/1995, (2) look at the geographic pattern of any changes in metal concentrations along the transects, and (3) evaluate the effect of organic matter content, grain size, and distance from the active channel on heavy metal concentrations and determine whether changes occurred since the earlier samples were collected. By updating the inventory of heavy metal concentrations begun over a decade ago, this study provides a picture of short-term change in heavy metal storage along part of a rural river system and examines how metals travel through a watershed over time. The findings may also be useful in gauging the effectiveness of environmental controls that have reduced the emission of heavy metals to the environment since the early 1970s.

Study area

From headwaters in the rural uplands north of Marburg, the Lahn River flows southward through a broad valley between Marburg and Giessen, then turns westward towards Wetzlar. The floodplain for nearly all of the study area is wide, reaching a maximum width of about 2.5 km just downriver of Giessen. The watershed is 70% agricultural land, 16% forested land, and 14% urban land (Jöckel 1981), a stark contrast to the more urban watersheds that have been the focus of most research on heavy metal storage in Germany and adjacent countries. The floodplain of the Lahn River is cultivated or grazed, whereas uplands remain largely forested. Downstream from Giessen the Lahn River watershed becomes progressively more urbanized. At the downstream end of the study area is Wetzlar, well-known for its optical industry, but also an historical center of heavy industry (e.g., smelting, steel).

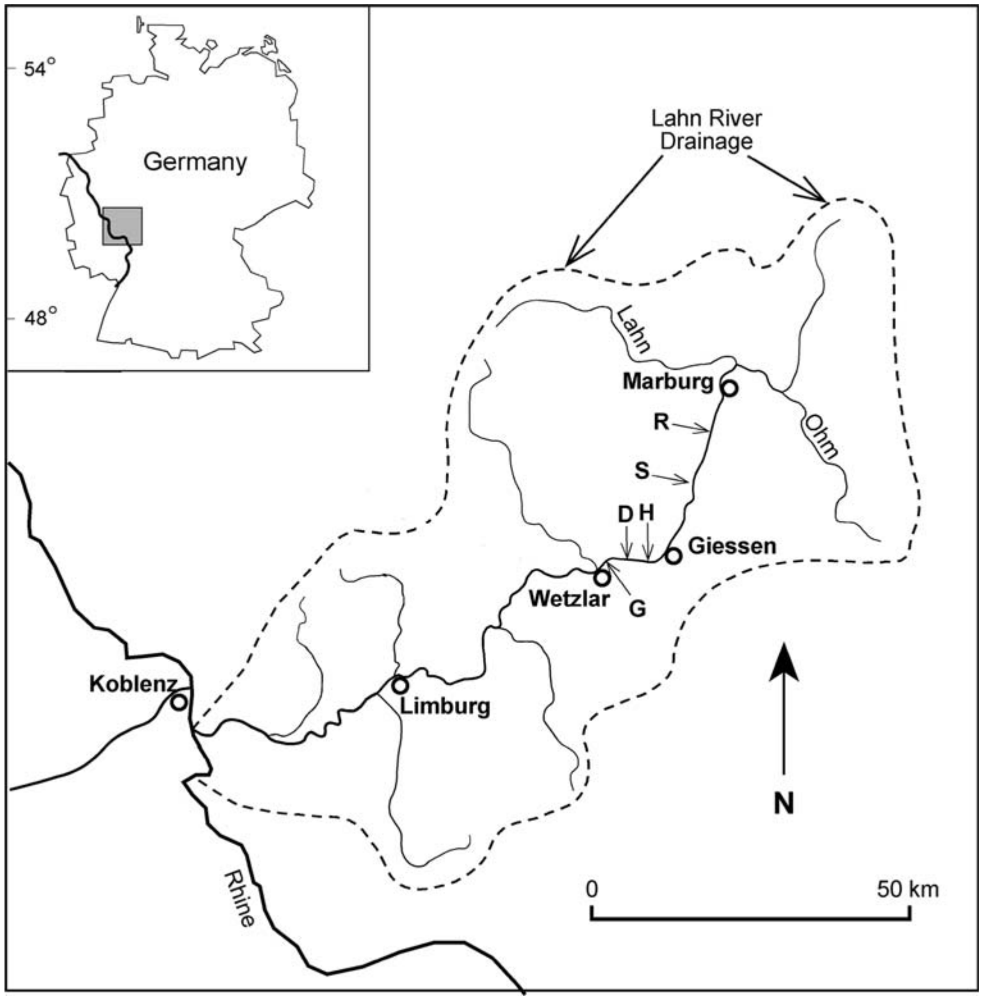

Fig. 1 Study reach of the Lahn River between Marburg and Wetzlar, Germany. Study transects are: *D* Dorlar, *G* Garbenheim, *H* Heuchelheim, *R* Roth, *S* Sichertshausen

As a consequence of channelization in the mid-1800s, flow of the river is sluggish for much of the year, although higher precipitation and snowmelt often increase discharge during the winter. Overbank flow for a week or two is common between January and March, eroding the channel locally and depositing fine sands on point bars and near-channel surfaces. Examination of aerial photographs taken between 1935 and 1995, coupled with considerable field experience in the Lahn River basin since 1995, indicate that most reaches of the channel have been stable for some time. The presence of meander scars in the study reach suggests, however, that historical lateral migration was common (Martin, 2000). Between Marburg and Wetzlar, the Lahn River flows in late Holocene alluvium. The floodplain of the Lahn River is underlain by black, organic-rich silt that accumulated over the last 1,000 years (Mäckel 1969; Houben 2003), presumably as a result of erosion on surrounding hillslopes when they were cleared of forest cover for agriculture and timber (Rittweger 2000; Kalis et al. 2003; Rommens et al. 2006; Hoffmann et al. 2007). In the vicinity of the Lahn River, this black silt reaches a thickness of up to 2 m (Bos and Urz 2003; Houben 2003; Kalis et al. 2003). Soils typically have an A/AC/C profile, a mean pH of 5.2, and a clayey silt texture.

Methods

Field notes, topographic maps, and ground-based photography were used to relocate the five transects and 50 sample sites from 1994 and 1995. Because it is channelized and flow tends to be fairly sluggish, the channel of the Lahn River remained stable between 1994 and 2007. Land use in the study area also changed little since the initial sampling. Likewise, no new transportation routes were built in the study reach and suburban sprawl, a rarity in Germany because of strict zoning regulations, was minimal. In short, the physical and human environment of the study area changed little between 1994 and 2007.

Working along transects, cores were extracted to a depth of 5 cm from the same sites where samples had been collected in previous work. Samples were relocated based on field notes and field measurements made with a surveyor's tape in 1994 and 1995. Samples in 1994/1995 and 2007 were positioned across the floodplain at a systematic interval measured from the active channel of the Lahn River. The sampling interval along transects ranged from 25 to 100 m, depending on floodplain width (Martin 1997). At locations where the Lahn valley was wide (e.g., Heuchelheim), the interval was 100 m; where the valley was narrower (e.g., Dorlar), the interval was 25 m. Samples were stored in sterile plastic bags for transport to the geomorphology lab at Justus Liebig-Universität in Giessen. The latitude and longitude of each sample location were recorded using a hand-held GPS unit. Location accuracy as reported on the GPS was 4–7 m.

Once in the lab, samples were split, with half submitted to ALS Chemex Labs, an ISO 9002 registered analytical laboratory in North America, for analysis of heavy metals, and the other half retained for standard soil analyses. To ensure comparability of samples collected in 1994/1995 and 2007, samples were submitted to the same ALS Chemex facility in North Vancouver, Canada, used in previous work and identical laboratory preparation procedures (air drying of samples, screening to 63 μm) were followed. Samples were digested in perchloric, nitric, and hydrofluoric acids (triple-acid digestion), a process that yields near total recovery of metals (Leece and Pavlowsky 1997). Concentrations of Cu, Pb, and Zn were then determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES); the concentrations of Cd were also measured, but the results are omitted because the analytical capabilities for Cd (0.5 mg kg^{-1}) differ little from the Cd concentrations found in surface soils in earlier work (Martin 2000, 2004). Concentrations were measured in mg/kg with an analytical sensitivity of 1.0 mg kg^{-1} for Cu, and 2.0 mg kg^{-1} for Pb and Zn. According to Quality Control data supplied by ALS Chemex, repeated measurement of standards produced coefficients of variation of 1% for Cu, 5% for Pb, and 3.5% for Zn. Analysis of duplicates yielded a mean difference of 1.25 mg kg^{-1} for Cu, 0.75 mg kg^{-1} for Pb, and 5.8 mg kg^{-1} for Zn, with coefficients of variation <4% for all three metals. The coefficients of variation for standards and duplicates noted here are similar to those reported by Leece et al. (2008) for samples analyzed for heavy metals by ALS Chemex. In the geomorphic lab at Justus Liebig-Universität, the proportions of clay (<2 μm) and silt (2–63 μm) were determined on the other half of each sample using the pipette method; the sand percentage was measured through wet sieving. Organic matter content was measured by loss on ignition (LOI) at 430°C for 24 h (Davies 1974). These analyses were carried out by the author.

The surface samples were also compared to background samples to evaluate the degree of anthropogenic enrichment. Background values, which represent pre-industrial age (pre-1750 AD) metal concentrations, were obtained from deeply buried sediments (0.85–1.15 m) collected within 5 m of the Lahn River channel. As noted by Martin (2004), ascertaining non-anthropogenic, or background, metal concentrations is problematic, but sediments collected at a depth of ca. 1 m in the study area can be assumed to reflect pre-industrial concentrations of metals (Martin 2000).

Metal concentrations were compared to standards contained in the German Federal Soil Protection Act (*Bundes-Bodenschutzgesetz [BbodSchG]* of 1998 and the German Federal Soil Protection and Contaminated Sites Ordinance (*Bundes-Bodenschutzverordnung [BbodSchV]* of 1999. These federal acts set standards for various contaminants above which some remediation action is required. When a "precautionary value" is exceeded, the natural soil functions are said to be at risk. A higher level of concern is attached to the "trigger value". It represents a concentration above which an investigation of the soil should be undertaken to evaluate the extent and magnitude of the contamination.

Results

Given the post-1989 reduction in metal releases to the environment, the lack of a broad decline in heavy metal storage in the study reach between 1994/1995 and 2007 is surprising (Table 1). For Cu, the mean concentration in the 2007 samples (27.4 mg kg^{-1}) was not significantly different than the concentration in 1994/1995 (28.8 mg kg^{-1}). The concentration of Cu in 2007 was higher at 22 sites

Table 1 Summary descriptive statistics for soil samples

	Cu	Pb	Zn
1995 (n = 50)			
Mean (SD)	28.8 (7.3)	**42.0** (8.4)	**123.0** (37.6)
Range	18– 53	30– 68	78–278
2007			
Mean (SD)	27.4 (7.2)	**44.3** (8.1)	**137.5** (43.7)
Range	17– 59	26–70	77–352
Precautionary Value	40.0	70.0	150.0
Trigger Value	N/A	200.0	N/A
Background (n = 35)			
Mean (SD)	22.9 (12.7)	26.6 (23.3)	84.1 (43.8)
Range	11–82	12–136	42–246

Mean concentrations shown in bold are statistically different (P = 0.05). Standard deviations (SD) shown in parentheses. The "Precautionary Values" and "Trigger Values" are published in the German Federal Soil Protection Act (*Bundes-Bodenshutzgesetz*) of 1998

(44%), lower at 23 sites (46%), and identical at 5 sites (10%). The mean concentration of Cu in 2007 was greater than the mean background value (22.9 mg kg^{-1}), evidence that there is minor anthropogenic enrichment of Cu in upper floodplain soils of the Lahn valley. At several individual sample sites the degree of contamination exceeded German Federal Standards. The "precautionary value" for Cu (40 mg kg^{-1}) was exceeded at two sites in 2007, down from four sites in 1994/1995. There is no "trigger value" for Cu.

In contrast to Cu, the concentrations of Pb and Zn showed marked change between 1994/1995 and 2007. The mean concentration of Pb in 2007 was 44.3 mg kg^{-1}, significantly greater ($P = 0.05$) than the mean concentration of 42.0 mg kg^{-1} in 1994/1995. It also exceeds the background concentration of 26.6 mg kg^{-1}, evidence that anthropogenic Pb is stored in the five transects. At 33 of 50 sites (66%), the Pb concentration in 2007 was greater than it had been in 1994/1995. At 14 of 50 sites (28%), the Pb concentration decreased between 1994/1995 and 2007, and at 3 sites (6%) it remained unchanged between the two dates. Despite the increase, no site in 2007 exceeded the 200 mg kg^{-1} "trigger value" for Pb concentration set out by the German Federal pollution guidelines, and only one site equaled the "precautionary value" of 70 mg kg^{-1}, the same as in 1994/1995.

For Zn, the mean concentration in 2007 of 137.5 mg kg^{-1} was significantly higher ($P = 0.05$ level) than the mean concentration of 123.0 mg kg^{-1} in 1994/1995. The mean concentration was also greater than the background value of 84.1 mg kg^{-1}. In 2007, the Zn concentration was higher than it had been in 1994/1995 at 38 of 50 sites (76%) and lower at 12 of 50 sites (24%). No site had the same concentration in 2007 and 1994/1995. German Federal guidelines do not specify a "trigger value" for Zn, but do list a "precautionary value" of 150 mg kg^{-1}. This value was exceeded at 10 sites in 2007, up from 7 sites in 1994/1995.

In order to assess the geographic pattern of changes in metal storage between 1994/1995 and 2007, results were grouped by transect location. The Roth and Sichertshausen transects are located in a predominantly agrarian area between Marburg and Giessen, the Heuchelheim, Dorlar, and Garbenheim transects in a more urbanized reach between Giessen and Wetzlar. Given the more urbanized nature of the river downstream from Giessen, it is reasonable to assume that higher concentrations of heavy metals have been released to the downstream reach of the Lahn River. Earlier work (Martin 1997) found that the mean metal concentrations at Dorlar and Heuchelheim were similar to those upstream at Roth and Sichertshausen, although the Garbenheim transect, which is located closest to Wetzlar, had the highest mean values of Pb and Zn.

Comparison of 2007 and 1994/1995 data verifies the aforementioned overall increase in Pb and Zn concentrations between the two periods (Table 2). There are six instances where the 2007 mean concentration was statistically different than the 1994/1995 mean concentration, and in five of them the 2007 values exceeded the 1994/1995 value. The majority of the overall increase in metal storage between the two sample periods resulted from the increased storage of Pb and Zn at Roth and Sichertshausen, the two upstream and more rural transects. At the three downstream, and less rural,

Table 2 Descriptive statistics for five sample transects

	Cu	Pb	Zn
Roth ($n = 7$)			
1995			
Mean (SD)	26.8 (3.7)	**39.7** (2.7)	**118.6** (30.8)
Range	23–34	36–44	94–184
2007			
Mean (SD)	28.1 (4.6)	**45.3** (4.3)	**137.1** (35.8)
Range	24–35	40–52	105–201
Sichertshausen ($n = 9$)			
1995			
Mean (SD)	28.4 (3.9)	**39.3** (7.0)	**120.4** (24.7)
Range	23–34	30–48	92–158
2007			
Mean (SD)	29.5 (6.1)	**43.4** (7.2)	**146.4** (35.8)
Range	19–38	32–56	93–197
Heuchelheim ($n = 10$)			
1995			
Mean (SD)	32.1 (5.7)	42.0 (8.1)	120.6 (21.4)
Range	25–44	30–60	78–158
2007			
Mean (SD)	28.1 (7.4)	41.8 (7.9)	121.2 (22.9)
Range	17–46	26–57	77–167
Dorlar ($n = 11$)			
1995			
Mean (SD)	**29.1** (8.1)	37.8 (6.3)	114.7 (49.4)
Range	22–52	32–54	84–260
2007			
Mean (SD)	**24.8** (5.4)	38.9 (4.8)	120.2 (37.2)
Range	19–39	32–48	96–227
Garbenheim ($n = 13$)			
1995			
Mean (SD)	27.2 (10.4)	48.8 (9.8)	**136.0** (47.5)
Range	18–53	34–68	88–278
2007			
Mean (SD)	27.3 (9.9)	50.8 (8.8)	**158.6** (61.2)
Range	21–59	41–70	117–352

Concentrations in mg kg^{-1}. Concentrations shown in bold are statistically different ($P = 0.05$). Standard deviations (SD) shown in parentheses transects an increase in metal concentrations between the two samples periods was less apparent (Table 2). Although the overall storage of metals appears to have increased more in upriver than in downriver transects, the maximum single-site concentrations for all three metals were noted for both sample periods at near-channel positions along the Garbenheim transect. In addition, that transect had the highest mean concentrations for Pb and Zn in 1994/1995 and 2007. In short, the upstream transects of Roth and Sichertshausen displayed the greatest increase in metal concentrations between the two sample periods, but the downstream transect at Garbenheim had the highest overall storage of heavy metals among the five transects. Copper concentrations varied at the five transects between 1994/1995 and 2007, but the mean concentration was statistically different only at the Dorlar transect.

Laterally across the floodplain, the storage of metals generally decreased with increasing distance from the river, with the greatest change close to the Lahn River channel (Fig. 2). Martin (1997) demonstrated that mean concentrations of Cu, Pb, and Zn were higher within 100 m of the channel than at positions greater than 100 m from the channel. Across the more distal part of the floodplain, metal concentrations in surface soils were generally uniform or decreased slightly. The changes in metal concentrations along the five transects for the 1994/1995 and 2007 data illustrate the rapid decline in metals within the first 10s of meters from the channel. Generally, the concentration of metals was at a maximum closest to the Lahn River and declined by the second sample site along the transect, although the decline was more pronounced for Zn than it was for Cu and Pb. Beyond the second or third sample location, metal concentrations changed little. The decline in concentration with distance from the active channel was most apparent at the Garbenheim and Heuchelheim transects, least apparent at Roth and Sichertshausen.

To assess the strength of the relationship between distance from the channel and metal concentrations, and look for change between the two time periods, a bivariate regression analysis of distance against each metal was done (Fig. 3). For Cu and Zn, the influence of distance was stronger in 2007 than in 1994/1995. The relationship between distance and Pb changed from a direct relationship in 1994/1995 to an inverse one in 2007. The higher y-intercept values in 2007 as compared to 1994/1995 for the three metals suggest additional storage of Cu, Pb and Zn immediately adjacent to the Lahn River valley between 1994/1995 and 2007. Overlap of data points on the y-intercept and at other distances shown in Fig. 3 account for the lack of five discrete data points at all distances from the Lahn River. The highest concentrations at the near-channel location for all three metals are from the Garbenheim transect (see Fig. 2) for both time periods. The concentration of Cu across the floodplain for the two time periods changed most dramatically on the distal part of the floodplain (Fig. 3). In 1995, there were several outliers between 600 and 800 m from the active channel; by 2007, the outliers are gone, reducing the scatter along the best fit line and strengthening the impact of distance on Cu concentrations.

Several studies note that heavy metal concentrations are typically highest in organic-rich, fine-textured sediments (e.g., de Groot et al. 1982; Horowitz 1985; Bubb and Lester 1996). Soils in the study area have a silty-clay texture, with the mean silt plus clay content between 80 and 85% and clay content around 20% (Table 3). The silt plus clay content ranged from 53 to 94% in 1995 and between 63 and 93% in 2007. Organic matter contents averaged 10.9% in 1995 and 10.4% in 2007.

Previous work along the Lahn River found virtually no relationship between the percentage of fine sediments and heavy metal contents (Martin 1997, 2004). Similar to other studies from Germany (e.g., Krüger et al. 2005), there was a relationship between organic matter content and heavy metal concentrations, albeit a very weak one (Martin 2004). For the 1994/1995 and 2007 data, organic matter content, percent clay, and percent silt plus clay explained little of the variation in heavy metal concentrations (Table 4). The highest r^2 values, and the only ones significant at the 0.05 level, appeared in the relationship between Zn and percent silt plus clay in both the 1994/1995 and 2007 data. The relationship between metal concentrations and percent clay was not noticeably different than the relationship to the percent silt plus clay. It is difficult to discern any change in the strength of the statistical relationship between metal content and sediment texture or organic matter content between 1994/1995 and 2007 because the association is so weak. Curiously, the impact of the percent silt and clay on heavy metal concentrations was the opposite of what has been reported in the literature. In both the 1994/1995 and 2007 data, an increase in the silt and clay content was associated with a decline in metal concentrations rather than the expected increase.

Discussion

Re-sampling along five transects perpendicular to the Lahn River revealed that heavy metals are still present in floodplain soils at concentrations above background values. At a small number of sites metal concentrations exceeded the “precautionary value” specified in German federal standards. Along three floodplain transects, storage of Zn in 2007 was statistically greater than it had been in 1994/1995, and along two transects the concentration of Pb increased from 1994/1995 to 2007. Along other transects the concentrations were statistically the same in 2007 and 1994/1995. In contrast, the concentration of Cu was

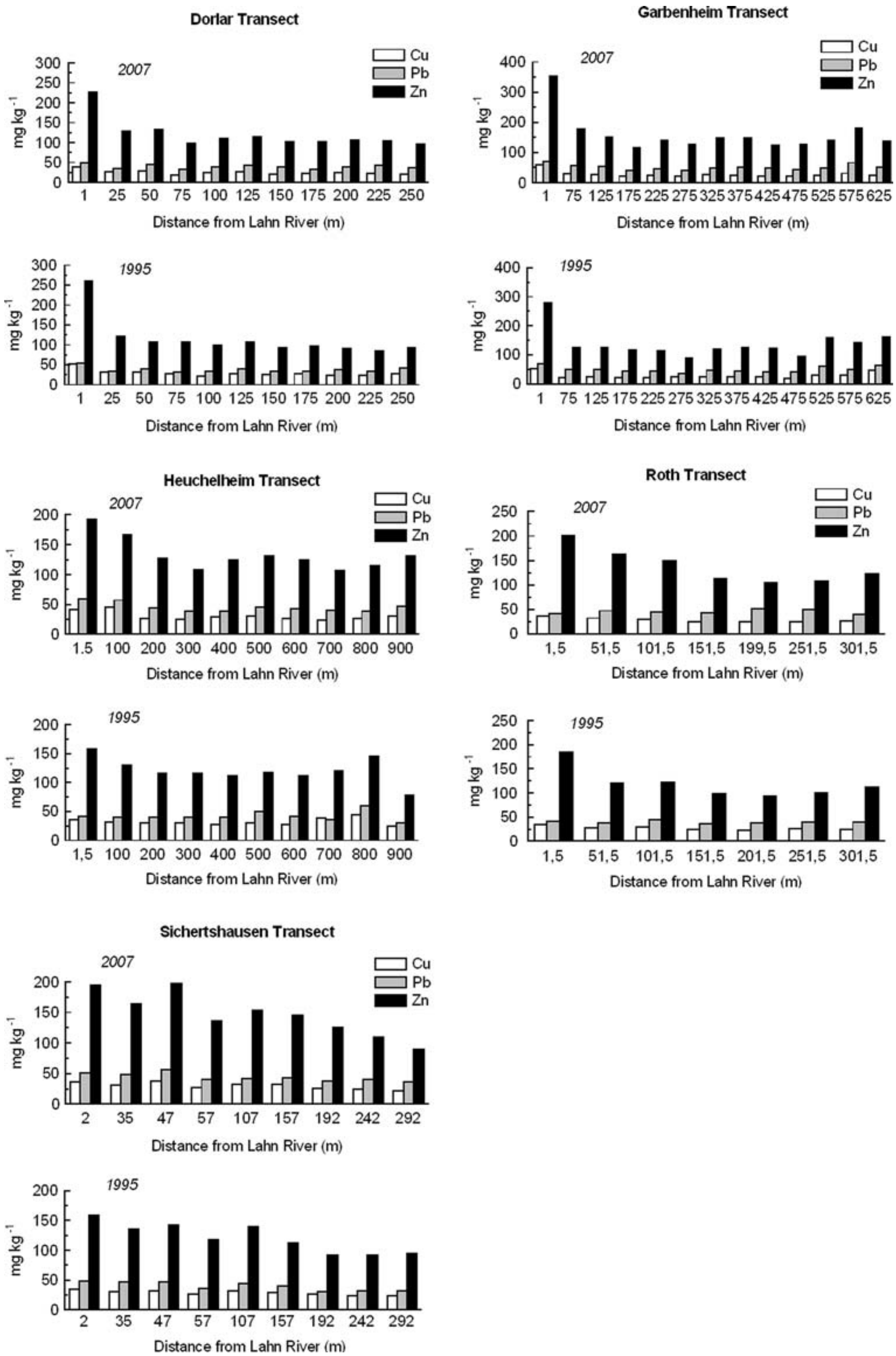

Fig. 2 Comparison of Cu, Pb, and Zn concentrations along five transects for 2007 and 1995

statistically unchanged at four transects and decreased at one transect between 1994/1995 and 2007.

When the results are examined by transect, the greatest increases in heavy metal concentrations between 1994/1995 and 2007 were found not in the more urban, downstream transects (Heuchelheim, Dorlar, Garbenheim), but rather in the upstream, more rural ones (Roth, Sichertshausen). Between 1994/1995 and 2007, the concentrations of Pb and Zn increased significantly at Roth and Sichertshausen; the concentrations of Cu at the two transects also increased, but by an amount that was not statistically significant. One variable that might contribute to the increase in storage is the geomorphology of the transect sites, specifically valley and floodplain width. Both

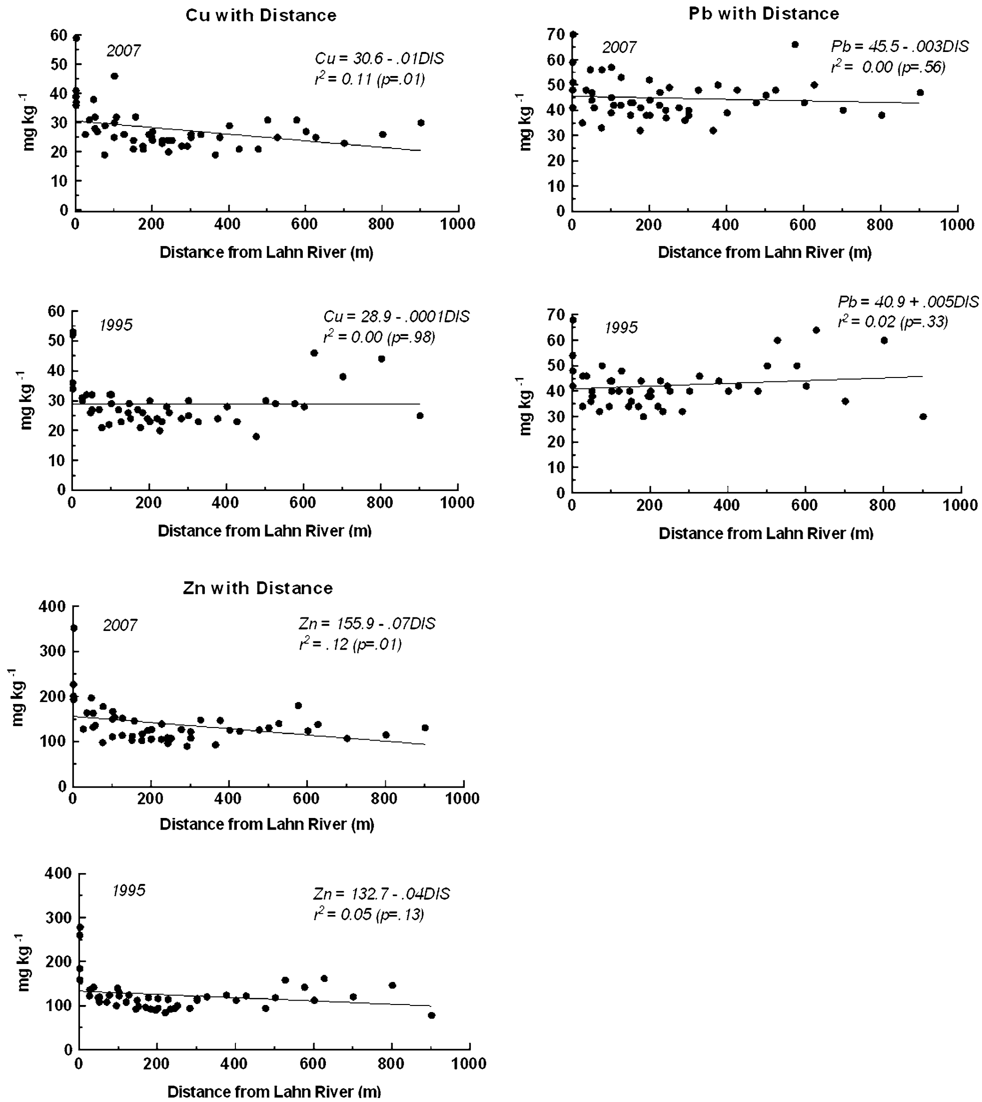

Fig. 3 Influence of distance from the Lahn River channel on concentrations of Cu, Pb, and Zn for 2007 and 1995

Table 3 Summary particle size and organic matter statistics for soil samples

	SiCl	Cl	OM
1995 (n = 50)			
Mean (SD)	80.8 (9.5)	20.9 (5.2)	10.9 (3.4)
Range	53–94	11–30	4.3–17.5
2007			
Mean (SD)	85.4 (7.4)	19.2 (4.7)	10.4 (2.1)
Range	63–93	11–33	6.3–15.9

Silt plus clay (SiCl) and clay (Cl) given as percentages. Organic matter (OM) shown as percentage organic matter content. Standard deviations (SD) shown in parentheses

have been shown to influence stream power (Magilligan 1985; Faulkner 1998), and therefore the relative transport versus deposition of metal-laden sediments. In this reach of the Lahn River valley, floodplain width does not appear to play a role in explaining metal concentrations as Roth and Sichertshausen have relatively narrow floodplains restricted by anthropogenic levees, yet realized an increase in Pb and Zn storage between 1994/1995 and 2007.

One possible source for the elevated Pb and Zn in surface soils is a background rich in the two iments col-lectedat a depth of ca. 1m in themetals. As Table 1 indicates, the background samples for Pb ranged from 12 to 136 mg kg^{-1}, suggesting at least one site where the non-anthropogenic concentration of Pb was several times the mean value in surficial samples. Likewise, the maximum value of Zn in the background samples was 246 mg kg^{-1}, a value that exceeded the mean concentrations of Zn in the 1995 and 2007 samples. A closer look reveals that the background concentrations of Pb and Zn at virtually every site were markedly lower than the mean concentrations found in surface soils. At twenty-nine of thirty-five background sites the Pb concentration was $\leq$30 mg kg^{-1}, well below the mean surficial value of 42.0 mg kg^{-1} in 1995

Table 4 Relationship between metal concentrations and percent clay (Cl), silt plus clay (SiCl) and percent organic matter (OM)

	n	r^2	*P*
2007			
Cu = 23.4 + 0.21 Cl	50	0.02	0.35
Cu = 43.5 − 0.19 SiCl	50	0.04	0.18
Pb = 48.2 − 0.21 Cl	50	0.01	0.41
Pb = 55.7 − 0.13 SiCl	50	0.01	0.39
Zn = 151.2 − 0.71 Cl	50	0.006	0.59
Zn = 289.8 − 1.8 SiCl	50	0.09	0.03
Cu = 26.2 + 0.11 OM	50	0.001	0.82
Pb = 40.3 + 0.39 OM	50	0.009	0.49
Zn = 132.6 + 0.48 OM	50	0.0004	0.88
1995			
Cu = 21.8 + 0.34 Cl	50	0.06	0.09
Cu = 38.6 − 0.12 SiCl	50	0.03	0.27
Pb = 39.8 + 0.11 Cl	50	0.004	0.64
Pb = 55.4 − 0.17 SiCl	50	0.04	0.19
Zn = 120.5 + 0.12 Cl	50	0.0003	0.91
Zn = 227.3 − 1.29 SiCl	50	0.11	0.02
Cu = 25.9 + 0.26 OM	50	0.015	0.39
Pb = 34.9 + 0.64 OM	50	0.07	0.07
Zn = 120.6 + 0.22 OM	50	0.0004	0.89

and 44.3 mg kg^{-1} in 2007. At only three of the thirty-five background sites was the Pb concentration ≥50 mg kg^{-1}. For Zn, 32 of the 35 background samples had concentrations <120 mg kg^{-1}, below the 1995 and 2007 mean Zn concentrations of 123 mg kg^{-1} and 138 mg kg^{-1}, respectively. Only seven background samples had Zn concentrations >100 mg kg^{-1}.

Rather, the elevated Zn and Pb concentrations appear to derive from anthropogenic sources. Historically, the combustion of leaded gasoline, a practice that continued in parts of Western Europe, including Germany, into the mid-1990s, was a major source of Pb released to the environment. Once in the atmosphere, Pb would have been distributed across the landscape by local and regional winds. Whereas heavy metals such as Cu and Zn commonly derive from site-specific industrial discharges (Scherer et al. 2003), Pb originates from diverse locations, although high concentrations close to urban and paved areas would be expected. Simply put, Cu and Zn are primarily point source contaminants, Pb is a non-point source contaminant. In contrast to other metals, which were released directly to waterways, Pb-contaminated sediments have migrated from dispersed sources to surface water systems in a slow, episodic process lasting years. This would explain why Pb levels in the Lahn valley increased between 1994/1995 and 2007 even though Pb releases to the environment have declined since the early 1970s (Renberg et al. 2001; Middelkoop 2002; De Vleeschouwer et al. 2007). Additional storage of Pb in floodplain soils continues several decades after the decline in Pb releases to the environment because Pb-contaminated sediments are slowly being transported from numerous sources to surface water systems.

Sediments rich in Zn also continue to be conveyed through and deposited in the study reach, with accumulations greater in the agrarian upper reaches than in the urban downstream sections. Common anthropogenic sources of Zn to the environment include metal works, battery production, and automobile tires (Charlesworth and Lees 1999; Tobin et al. 2000), all of which would seemingly be more plentiful in the urbanized and industrial lower reaches of the study area than in the more rural upper reaches. The explanation for the Zn increase in the agrarian upper reaches of the Lahn River valley between 1994/1995 and 2007 may lie in the relative mobility of Zn. In comparison to the other metals examined here, Zn is relatively soluble, and thus likely to be transported in the soluble phase (Charlesworth and Lees 1999; Gocht et al. 2001). This higher solubility means that geomorphic processes (e.g., sediment erosion, transport, and deposition) are relatively less important in moving Zn than they are in transporting other metals. Because Zn is relatively mobile, it can be deposited by groundwater table fluctuations. Typically, the water table in the study area is about 1.5 m deep, but during the winter often rises to the surface and contributes to surface flow and standing water on the floodplain. Those processes may bring Zn to surface soils.

The highest concentrations of Cu and Zn were adjacent to the active channel (Figs. 2, 3). At distances greater than ca. 100 m from the channel concentrations of Cu and Zn changed little across the floodplain. The clustering of Cu and Zn adjacent to the Lahn River supports fluvial deposition of sediments and attached contaminants. Fluvial deposition occurs during overbank flow as sediments and attached pollutants accumulate adjacent to the channel when overland flow velocity drops. As shown in the bivariate regression plots and r^2 values, the effect of distance on Cu and Zn concentrations increased between 1994/1995 and 2007. That this relationship is stronger for the 2007 data than for the 1994/1995 data suggests an increase in the importance of fluvial processes bringing metal-laden sediments to the floodplain. In contrast, the distribution of Pb across the floodplain was relatively uniform in both the 1994/1995 and 2007 samples, evidence of a source other than fluvial processes (possibly airborne deposition) that spreads Pb across the floodplain. Since 1995 the Pb levels in eolian sediments likely declined as leaded gasoline was phased out and polluting industries of Eastern Europe were shuttered (Matschullat and Bozau 1996; Schulte et al. 1996; Dämmgen et al. 2000).

The greatest change in the influence of distance on metal concentrations between the two time periods occurred with Cu. The decrease in scatter around the best-fit line for Cu between 1995 and 2007, especially between 600 and 800 m from the channel, may reflect the deposition of cleaner sediments on or the erosion of Cu-contaminated sediments from the more distal parts of the floodplain, the uptake of Cu by vegetation, or the downward migration of Cu in the soil. Given the location on the distal part of the floodplain, fluvial erosion of metal-laden sediments or deposition of cleaner sediments is unlikely. It is also possible that the 1995 Cu trend in Fig. 3 reflects an eolian component of Cu deposition on the more distal parts of the floodplain, accounting for the scatter between 500 and 900 m from the channel. By 2007, perhaps because of a reduction in emissions from Eastern Europe, this eolian component had decreased in importance, and the Cu trend reflected mainly fluvial deposition of the metal.

The impact of organic matter content and soil texture on metal concentrations was minimal for the 2007 samples just as it had been for the 1994/1995 samples. The distribution of Cu, Pb, and Zn in the study reach was, at best, weakly related to the percentage of silt plus clay. Organic matter was also unrelated to metal concentrations along the five sample transects. The findings suggest that metals were not preferentially attracted to fine-textured and organic-rich soils.

Conclusions

In aggregate, the mean concentrations of Pb and Zn in samples from the five transects increased significantly between 1994/1995 and 2007, whereas the mean concentration of Cu for the two time periods was statistically the same. Between 1994/1995 and 2007, Zn concentrations increased at 76% of the 50 samples sites while Pb concentrations rose at 66% of the sites. In contrast, the Cu concentrations increased at only 44% of the sites while decreasing at 46% of the sites. Increases in Pb and Zn were greatest in the more rural upstream transects between Marburg and Giessen, although the transect with the highest concentrations of Pb and Zn is found in an urbanized reach of the river upstream from the industrial city of Wetzlar. Three transects displayed a statistically significant increase in Zn between the time periods, two had a significant increase in Pb, and one showed a significant decrease in the concentration of Cu. As outlined in German federal standards, the “precautionary value” for Cu was exceeded at two sites, the value for Pb at one site, and the value for Zn at ten sites in 2007.

The increase in Pb concentrations post-1994/1995 suggests a lag between the decline in Pb releases to environment in the early 1970s and conveyance of Pb-contaminated sediments to and through the Lahn River basin. Gradually, and intermittently, Pb-contaminated sediments are being transported by overland flow to the Lahn River, then either stored in or conveyed through the drainage basin. Because Pb concentrations increased along three of the five transects, it appears that storage was the dominant process between 1994/1995 and 2007. The increase in Zn concentrations during the same period is potentially explained by the high solubility of the metal. It can be brought to the Lahn River floodplain either in solution by surface or groundwater, or attached to sediment particles. That mean concentrations increased significantly at three of the five transects suggests that Zn continues to move through and be stored in the Lahn valley.

In the two decades since the Berlin Wall came down, ultimately leading to the dismantling of many aged, polluting industrial facilities in Eastern Europe, the water and air in Western Europe has become cleaner. Nonetheless, stores of heavy metals remain along German rivers, even in drainage basins such as the Lahn River that are removed from the larger industrial concentrations of the country. The overall similarity in concentration of Cu in the floodplain of the Lahn River between 1995 and 2007 and the decline in Cu concentration along several transects provide evidence that environmental controls instituted decades earlier are having some effect. In contrast, the increase in the concentrations of Pb and Zn over the same time period indicates that metals in floodplain sediments of the Lahn River have not responded uniformly to decreases in metal inputs to the environment. In the case of Pb and Zn, it appears that these two metals move from their source areas to surface water systems more slowly or by different methods than does Cu, and as a result their concentrations have increased in the Lahn River valley between 1995 and 2007. Ultimately, floodplain soils will become cleaner as a consequence of reduced metal emissions to the environment, but the reduction in metal concentrations may well vary by metal type. Lead appears to be one contaminant whose concentration in floodplain soils is out-of-phase with the decline in Pb releases to the environment. It will take time for Pb-contaminated sediments to move to, and finally through, surface water systems. Until then, Pb concentrations in floodplain soils will likely remain higher than the decades-long reduction in Pb releases to the environment would suggest.

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