MODELLING THE OVERLAND TRANSPORT OF LEAD DEPOSITED FROM THE ATMOSPHERE IN THE ELBE CATCHMENT OVER FOUR DECADES (1958–1995)

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Abstract. The Neurotoxin lead has been emitted in large amounts into the environment over decades. To what extent this long-term pollution affects environmental systems is relatively unknown. Despite decreasing atmospheric pollution, soil and freshwater systems still indicate high lead concentrations. This study provides a preliminary estimation of annual overland lead fluxes originating from atmospheric pollution in the Elbe basin in Central Europe during the period 1958–1995. The transport into aquatic systems of lead originally deposited in the soil is assessed. Three pathways from rural areas into the river system were considered: erosion, direct runoff and direct atmospheric deposition. For this purpose, a modified mesoscale empirical–conceptual model for heavy-metal transport was applied. The results indicated that the total lead fluxes decreased after a peak in the 1970s. The emissions into the Elbe and its tributaries due to direct deposition showed a clear decline caused by decreasing atmospheric pollution since the 1970s. On the contrary, overland lead fluxes *via* erosion and direct runoff slightly increased. They were mostly influenced by the hydrometeorological and topographical conditions and less by the intensity of atmospheric input in a given year. Model results showed a steady background accumulation in the soils for the investigation period with a positive temporal and spatial correlation to atmospheric deposition. We conclude that lead-control policies were successful only to a certain degree. In order to reduce pollution by highly sorptive, particle-bound substances such as lead, effort should focus not only on minimizing atmospheric emissions, but also on minimizing soil erosion.

Keywords: atmospheric pollution, direct atmospheric deposition, direct runoff, Elbe catchment, erosion, soil pollution, lead, long-term contamination, modelling

1. Introduction

Nearly all of the lead found in the environment today in soils, river and lake sediments, ocean sediments and ice cores, has an anthropogenic origin. Anthropogenic lead has been emitted into the environment for hundreds of years, but 20th-century

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emission levels of this neurotoxin (for lead's toxic effects see e.g. Lovei, 1997) have been far higher and widespread than at any other time in history,[1] with gasoline combustion by road traffic representing the largest source.

After a steep rise in lead emissions from road traffic from the 1950s through the mid-1970s, reaching an estimated 199,000 t for Europe in 1975 (in the vicinity 400×10^3 t a^{-1} worldwide in 1974–1975, as estimated by Nriagu, 1992), subsequent regulations on gasoline lead content dramatically reduced European emission rates. The history of European gasoline lead-content regulations was reviewed by Hagner (2000). With a gasoline lead content of 0.6 g l^{-1} and ever-growing road traffic, automobile lead emissions rose sharply in Europe until the mid-1970s. Germany was the first in Europe to impose gasoline lead restrictions. Starting in 1972, German production and importation of gasoline with more than 0.4 g Pb l^{-1} was prohibited (EU in 1978), and starting in 1976 the more strict limit of 0.15 g Pb l^{-1} was imposed. In 1983, "unleaded" gasoline (0.013 g Pb l^{-1}) was introduced in Germany. After the introduction of tax incentives for unleaded gasoline in Germany and full availability at all gas stations in the mid-1980s, its market share in this country has increased steadily, approaching full share today. In 1985 and 1987, the EU followed this approach with similar regulation steps EU-wide because observable damage to public health and the environment was claimed (Rat der Europäischen Gemeinschaften, 1987). Similar arguments led to the signing, by nearly all countries in Europe, of the 1998 Aarhus treaty (UN/ECE, 1998), which stipulates the exclusive usage of unleaded gasoline in Europe by the year 2005.

A sharp drop in air-lead concentrations in Europe has resulted, because the mean atmospheric residence time for lead, before the particles which carry it are deposited on the earth surface, is only a few days. In contrast, no corresponding drop has been documented in the lead content of European soils, or of submerged sediments. Lead attaches strongly to sediments, especially those of fine texture, and forms strong complexes with soil organic matter, resulting in long residence times for lead in the terrestrial environment.

In soils, lead accumulates mostly in the humus layer, compounded in metalo-organic sediments, due to its high sorptivity towards clay and humus particles. Its solubility is very limited under most environmental circumstances. Thus, terrestrial plants take up lead mostly from the atmosphere rather than the soil (e.g., Chamberlain, 1983). Lead levels in plant leaves, needles and sprouts have been found to correlate well with atmospheric concentrations for each given plant species (e.g., Toro *et al.*, 1995). Data from the German Umweltprobenbank for different species in the state of Saarland exhibits a decrease with time, which is consistent with dropping atmospheric levels (Hagner, 2002).

In contrast to terrestrial plants, aquatic organisms are influenced mainly by the long-term accumulation of lead in fluvial and marine sediments. For example, Hoebel (1984) found the lead concentration in foraminifera to be spatially correlated to that in the surrounding sediments. Hagner (2002) found no significant trend from 1983 to 1996 in the lead concentration in blue mussels (*Mytilus edulis*) living along

the German North Sea coast, or in the muscle tissue of fish living in the river Elbe. Thus, lead in aquatic sediments, from which it is released only slowly, provides a contaminant source for marine organisms and, through them, also for the human food chain.

Nevertheless, Von Storch and Hagner (2003) found a considerable decreasing trend in lead content in human blood from Germany, to which gasoline lead regulations as well as the elimination of lead in paint, water pipe solder, and food cans has contributed.

The goal of this research is to quantify the annual lead fluxes from terrestrial into aquatic systems in the course of atmospheric lead deposition onto arable land. The study period covers four decades (1958–1995), including the rapid rise of lead consumption as well as its sharp decline due to regulation laws in the beginning of the 1970s. The study focuses on the Elbe river basin upstream of Neu Darchau (an area of 132,000 km^2). The Elbe catchment is a suitable case study due to economic and industrial developments in the second half of the last century. Within this study, the following questions are posed: How high are current lead-contamination levels of soils and aquatic sediments resulting from long-term atmospheric input? Has the decrease of atmospheric lead emissions reduced lead levels in terrestrial soils, lakes and rivers? Is there an adequate method available to estimate diffuse substance fluxes on large scales? To answer these questions, we use the model of overland lead transport METALPOL (Vink, 2002) designed for the considered temporal and spatial scales and adapted to the chemical properties of lead.

2. Methodology and Materials

2.1. Study area: Elbe basin

The Elbe river basin (Figure 1) in central Europe covers an area of an estimated 148, 268 km^2 with a length of 1091 km, and discharges to the North Sea, with a mean annual yield of 22,700 km^2 at Neu Darchau. The basin includes portions in Germany (ca. 96,932 km^2), the Czech Republic (ca. 50,176 km^2), Austria (ca. 920 km^2) and Poland (ca. 240 km^2). The current population within the basin is in the vicinity of 25 million, the largest population centres being Berlin, Hamburg, Prague, Leipzig and Dresden. The fractions of the catchment area covered by agricultural land and forest are estimated to be 55 and 29%, respectively. The Elbe river basin, as a formerly politically divided region, is an appropriate case study of changes in cross-boundary pollution and environmental agreements in the course of economic and political transitions.

2.2. Contamination pathways

Lead deposited from the atmosphere to the earth surface may reach a stream *via* any one of the following pathways: 1) overland transport and delivery to a stream

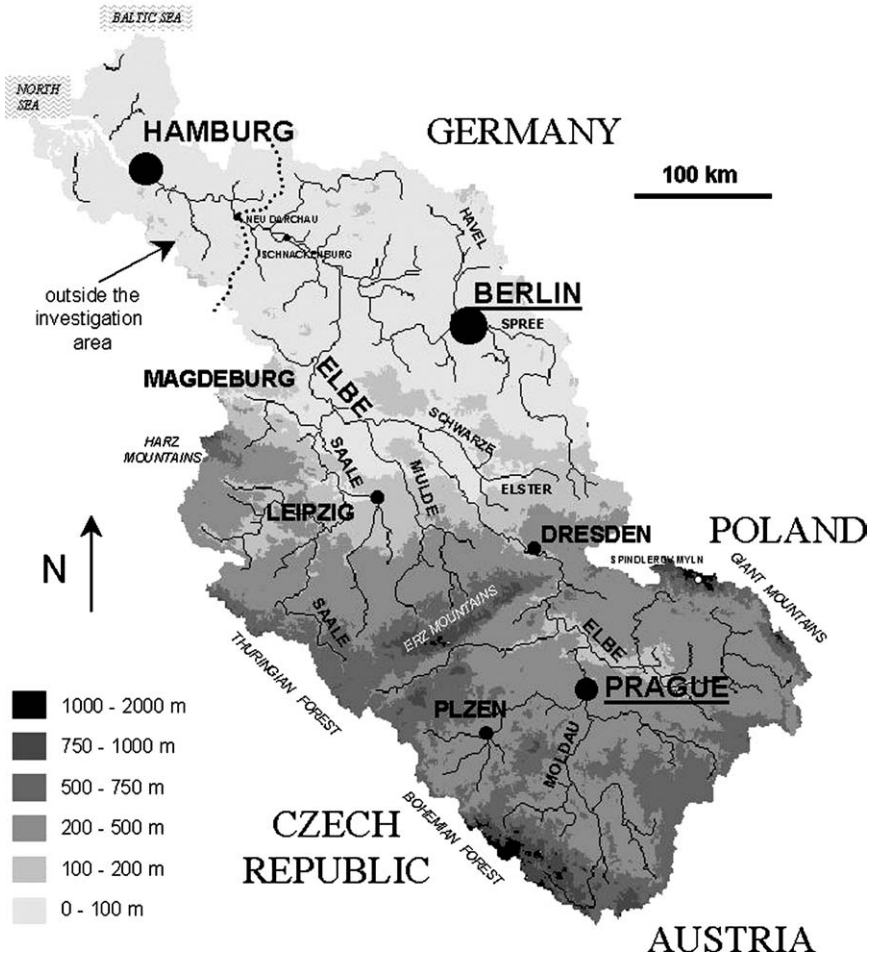

Figure 1. The Elbe river catchment.

channel of sediment particles to which lead compounds are bound; 2) horizontal transport by surface runoff and interflow of lead in dissolved form; and 3) direct deposition of lead-carrying atmospheric particles onto a stream or lake surface.

The availability of lead in the soil compartment for pathway (2) is limited by its low mobility. Even though lead compounds deposited from the atmosphere (lead salts and organic lead complexes) do show significant solubility, they are transformed into mainly insoluble compounds (carbonates, sulphates, or phosphates) in the terrestrial and aquatic environments (e.g., Alloway, 1995). Consequently, leaching of lead from the upper soil to deeper soil zones and groundwater is negligible (e.g., Andreae, 1993; Fahrenhorst, 1993) under most soil conditions. As a simplifying assumption, we model lead as an immobile, inert, particle-bound tracer. This assumption is deemed valid under most conditions, except in the presence of low

pH values, which increase the solubility of lead compounds and may lead to significant horizontal solute lead transport by interflow (Andreae, 1993; Bauer *et al*., 1988) as considered in pathway (2).

2.3. The modelling approach

This study addresses the transport of atmospheric lead into the Elbe stream network (*via* direct deposition and *via* overland transport from arable land). Other important sources of lead in the streams, such as industrial, agricultural, and urban discharges, are not considered. The spatial resolution used is 1 km^2, and the temporal resolution is 1 year.

The distributed rates of atmospheric lead deposition over the Elbe basin, at $0.5^\circ \times 0.5^\circ$ resolution that are used in this study as model input, are the results of computer simulations for 1958–1995 described by Von Storch *et al*. (2003). Bilinear interpolation was used to obtain a distribution for our 1km $\times$ 1 km grid.

Based on the simulated annual atmospheric lead deposition, the annual lead fluxes into the Elbe stream network were calculated using a modified version of the mesoscale model for heavy-metal transport METALPOL (Vink, 2002). It is designed for catchments larger than 500 km^2 and runs with a spatial resolution of 1 km^2. METALPOL was originally developed for the operationalisation of the EU Water Framework Directive to simulate the environmental transport of heavy metals from their emission sources throughout the catchment and to its outlet. It describes the river basin as a series of related compartments transferring heavy-metal emissions (direct and indirect, point and diffuse sources) into river loads, as a function of soil types, runoff, land use and hydrogeology.

For the aim of this study, METALPOL was divided into four sub-models (Schulte-Rentrop, 2003): 1) erosion, 2) direct runoff, 3) direct atmospheric deposition and 4) soil-mass balance.

The raster-based model was constructed in such a way that the amount of transported substance leaving each cell reaches the surface water (Elbe river and tributaries) in the timestep of 1 year.

2.3.1. *Erosion Pathway Model*

We followed the four-step methodology of Behrendt *et al*. (2000) and Vink (2002): In *step one*, the potential long-term soil erosion in the Elbe basin is calculated using the Universal Soil Loss Equation (USLE) (Wischmeier and Smith, 1978 as described in Vink, 2002). In *step two*, a "sediment-delivery ratio" (SDR) is multiplied by the results of step one, in order to account for the sediment that is eroded but does not reach a stream channel because of retention and sedimentation processes. The SDR is the ratio between the mass of sediment delivered to the stream channels and the total sediment mass removed from its original location within a year. The combination of the USLE and SDR model provides an estimate of the long-term sediment delivery to the channels. The rate of sediment delivery

to channels in any given year will in general differ from this long-term estimate, and is a function of that year's hydrometeorological conditions. In *step three*, an annual hydrological coefficient is used to estimate sediment delivery to channels in each particular year (see also Rogler and Schwertmann, 1981).

For an estimation of the lead mass contained in the estimated sediment mass delivered to the channels, it is necessary to consider that the lead concentration in eroded sediments is higher than the average concentration in the topsoil. This lead "enrichment" of the eroded sediment is a result of the higher fraction of fine particles, such as clay, to which lead is strongly sorbed. Fine soil particles are more easily detached and more easily transported away, leaving coarser soil particles behind. In *step four*, an "enrichment ratio" (ER) is used to estimate the lead concentration in eroded sediment.

These four computational steps are applied to each model cell i at each annual timestep t, *via* Equation (1):

$$\mathrm{Pb}^{\uparrow}_{\mathrm{eros}_{i,t}} = \mathrm{SL}_i \cdot \mathrm{SDR}_i \cdot H_{i,t} \cdot \mathrm{ER}_i \cdot [\mathrm{Pb}]_{i.t-1} \cdot f_1 \tag{1}$$

where $\mathrm{Pb}^{\uparrow}_{\mathrm{eros}_{i,t}}$ is the rate of lead mass removal by erosion from cell i (delivered to a stream channel) in year t [t a^{-1}], SL_i the long-term potential soil mass loss rate by erosion from cell i [t a^{-1}], SDR_i the sediment delivery ratio in cell i [non-dimensional], $H_{i,t}$ the hydrologic coefficient for cell i and year t [non-dimensional], ER_i the enrichment ratio for cell i [non-dimensional], $[\mathrm{Pb}]_{i.t-1}$ the lead concentration in the upper soil zone in cell i in year $t-1$ [mg kg^{-1}], f_1 the units conversion factor.

2.3.2. *Direct Runoff Pathway Model*

Lead's solubility under most environmental conditions (except under low pH values) is limited; hence, only a small fraction of the lead in soil will dissolve into the soil water that is retained in the soil's pores. Nevertheless, soil water contains a sufficient concentration of lead that direct runoff (horizontal surface and subsurface runoff) represents a pathway for lead transport into stream channels. The mass of lead carried by runoff depends on the lead concentration in the soil material and on the runoff volume.

The solute transport in the upper soil *via* direct runoff was determined with the concept of partitioning coefficient (K_d) in METALPOL.

The volume of direct runoff yearly available for solution and transport was derived with a water-balance model based on Kwadijk (1993) and an empirical runoff coefficient calibrated for the Elbe drainage area. The water balance model works on a monthly timestep.

The equation for determination of the lead fluxes along the fast runoff pathway is:

$$\mathrm{Pb}^{\uparrow}_{\mathrm{fast}_{i,t}} = \frac{1}{K_{\mathrm{d}_i}} \cdot [\mathrm{Pb}]_{i,t-1} \cdot Q_{\mathrm{fast}_{i,t}} \cdot A_i \cdot f_2 \tag{2}$$

where $\mathrm{Pb}^{\uparrow}_{\mathrm{fast}_{i,t}}$ is the rate of lead mass removal by fast runoff from cell i (delivered to a stream channel) in year t [t a^{-1}], $[\mathrm{Pb}]_{i,t-1}$ the lead concentration in the upper soil zone in cell i in year $t-1$ [mg kg^{-1}], K_{d_i} the partition coefficient of lead in cell$i$ [l kg^{-1}], $Q_{\mathrm{fast}_{i,t}}$ the rate of fast runoff in cell$i$ in year$t$ [m^3 a^{-1}], A_i the surface area of cell i [km^2], f_2 the units conversion factor.

2.3.3. *Direct Atmospheric Deposition Model*

The mass of lead deposited directly from the atmosphere into the stream channels and lakes of the Elbe network over a year depends on the mass of lead deposited from the atmosphere in that year and on the extent of the water surface (Equation (3)):

$$\mathrm{Pb}^{\downarrow}_{\mathrm{ddepos}_t} = \overline{\mathrm{Pb}}^{\downarrow}_{\mathrm{depos}_t} \cdot A_{\mathrm{waterbody}} \tag{3}$$

where $\mathrm{Pb}^{\downarrow}_{\mathrm{ddepos}_t}$ is the rate of lead mass delivered to a stream channel of the Elbe network by direct atmospheric deposition onto a water surface in year t [t a^{-1}], $\overline{\mathrm{Pb}}^{\downarrow}_{\mathrm{depos}_t}$ the average rate of atmospheric lead deposition over the basin in year t [t a^{-1} km^{-2}], $A_{\mathrm{waterbody}}$ the total extent of water surface in the investigation area [km^2].

To determine the entire water surface in the catchment, the CORINE landcover database was used in combination with the methodology of Behrendt and Opitz (2000).

2.3.4. *Soil-Mass Balance Model*

The overland transport of lead into streams (as a result of erosion and direct runoff) depends on the lead concentration in the soil compartment. Due to the large sorption surface area and distinct polarity of clay and organic matter, the soil compartment forms a sink for substances such as lead and other heavy metals. As a consequence, the soil plays an important role in the storage, release and further transport of heavy metals. The soil-mass balance is the centre in METALPOL combining input variables (atmospheric deposition and the lead content stored from the last timestep) and output variables (erosion, direct runoff) according to the physico-chemical properties of the soil:

$$[\mathrm{Pb}]_{i,t} = [\mathrm{Pb}]_{i,t-1} + f_3 \cdot \frac{\mathrm{Pb}^{\downarrow}_{\mathrm{depos}_t}}{\mathrm{SOILMASS}} - f_4 \cdot \frac{\mathrm{Pb}^{\uparrow}_{\mathrm{eros}_{i,t}} + \mathrm{Pb}^{\uparrow}_{\mathrm{fast}_{i,t}}}{A_i \cdot \mathrm{SOILMASS}} \tag{4}$$

where $[\mathrm{Pb}]_{i,t}$ is the lead concentration in the soil in cell i and year t [mg kg^{-1}], $[\mathrm{Pb}]_{i,t-1}$ the lead concentration in the soil in cell i and year $t-1$ [mg kg^{-1}], $\mathrm{Pb}^{\uparrow}_{\mathrm{eros}_{i,t}}$ the lead input *via* erosion out of cell i and year t into the river [t a^{-1}], $\mathrm{Pb}^{\uparrow}_{\mathrm{fast}_{i,t}}$ the lead input *via* direct runoff out of cell i and year t [t a^{-1}], $\mathrm{Pb}^{\downarrow}_{\mathrm{depos}_t}$ the atmospheric

lead deposition in year t [μg m^{-2} a^{-1}], SOILMASS the mass of the upper soil per cell, constant value [70,000 t], f_3, f_4 are the units conversion factors.

In the first timestep (year 1958), the lead concentration in the soil is initialized with background soil concentrations gathered by Vink (2002) for the study area.

2.4. DATA

For each 1-km^2 grid cell, METALPOL requires geographical and meteorological input data. Data on precipitation, air temperature and sunshine duration were gathered for 53 stations of German Weather Service (DWD) and the Czech Hydrometeorological Institute (CHMI) for the period of investigation with daily resolution. For the application in the water balance (part of submodel 2) which works on a monthly timestep, these data sets were aggregated to monthly values. They were then interpolated onto the 1-km^2 grid using Thiessen polygons for precipitation and sunshine duration, and by polynomial regression for air temperature (Schulte-Rentrop, 2003).

Topography, pedology and land-use data covering the Elbe catchment were obtained from the United States Geological Survey (USGS-EROS, 1996), *Bundesanstalt für Geowissenschaften und Rohstoffe* (BGR, 1997) and Statistisches Bundesamt (1997), respectively, as described in Vink (2002). The pedological data were taken from the BUEK 1000 soil map (BGR, 1997) containing the main soil-type classifications (so-called "Leitböden"), texture (fractional composition of clay and silt) and organic-matter content.

The atmospheric lead-deposition rates were estimated from the computer simulations of regional climate, atmospheric emissions and atmospheric transport for 1958–1995, at a spherical resolution of 0.5°, by Von Storch *et al.* (2003). Bilinear interpolation was used in order to establish values for our 1-km^2 grid. The atmospheric emissions used in that study were based on the estimates by Pacyna and Pacyna (2000) for the reference years 1955, 1965, 1975, 1985, 1990 and 1995, which accounted for all major lead sources, namely, road traffic, non-ferrous metal manufacturing, stationary fuel combustion, iron and steel production, cement production, waste disposal, and miscellaneous sources. Road transport represented by far the largest source, accounting for about 50% of the total European emissions in 1955, 75% from the mid-1970s through the mid-1980s, and 69% in 1995. Linear interpolation between reference years was used to make emission estimates for all intermediate years.

Estimated lead emissions from road traffic in Europe totalled about 31×10^3 t in 1955, nearly quadrupling to 119×10^3 t in 1975. As a result of gasoline lead content reductions, road traffic emissions have henceforth declined to about 19.5×10^3 t in 1995, despite the continued rise in gasoline consumption.

To simulate lead transport in the atmosphere and its annual rates of local deposition, Von Storch *et al.* (2003) first generated climate reconstructions for the European region with a spatial and temporal resolution of 0.5° and 1 h, respectively

(see also Feser *et al*., 2001) for 1958–1995. The hourly values of local temperature and wind direction and speed were then used to drive a Lagrangian model of atmospheric particle transport and deposition (Costa-Cabral, 1999; Von Storch *et al*., 2003).

For its application in METALPOL, this data set was adjusted to the required spatial resolution of 1 km^2 by bilinear interpolation. Resulting deposition estimates for the Elbe basin for 1958, 1965, 1975, 1985, 1990 and 1995 are presented in Figure 2. Deposition rates reached a peak in 1975 (with an average of 28.3 mg m^{-2} for the basin), when emission rates were also maximal, given that the average residence time for lead in the atmosphere is only a few days. By 1980, deposition rates abated drastically except for the region in vicinity of Dresden/Freiberg in Saxony. In this area, lead-manufacturing and lead-recycling industries were maintained and expanded in the 1980s. By 1995, emissions across the Elbe basin were much lower than at any other time in the study period (2.1 mg m^{-2} on average), remaining somewhat higher over the Czech Republic portion than over the German portion.

3. Results

3.1. Temporal variation of lead loads and contributions of the three pathways

The overall trend in total simulated lead load (Figure 3), peaking in the mid-1970s and decreasing thereafter, reflects the trend in direct deposition onto water surfaces (Figure 3). In turn, direct deposition mimics the trend in total emissions to the atmosphere (Figure 2). The maximum simulated load occurred in 1977 (179.52 t) and the lowest in 1991 (85.55 t). Over the entire period, the total estimated load of lead contaminating the Elbe river amounted to 5000.39 t (direct deposition: 2020.93 t or 0.655 g per m^2 water surface; erosion: 1842.43 t or 26.29 mg m^{-2}; direct runoff: 1137.03 t or 16.23 mg m^{-2}). A 5-year running average showed that overland lead fluxes maintained an increasing trend throughout the study period, despite the decreasing atmospheric deposition.

The considerable year-to-year variability displayed in Figure 3 is determined largely by corresponding variability in annual precipitation and runoff.

The percentage contribution by each of the three considered pathways changed over time (Figure 4). While direct deposition represented the most important pathway up until the mid-1980s, by the 1990s it had become the least important, while erosion then contributed over half of the total load to channels.

The continued rise in contribution by erosion reflects the increase in mean lead concentration of the soil (20.91 ppm in 1958 up to 21.73 ppm in 1995; see also Section 3.3, Figures 7 and 8), and the rise in the contribution by direct runoff is also a consequence of higher soil concentration.

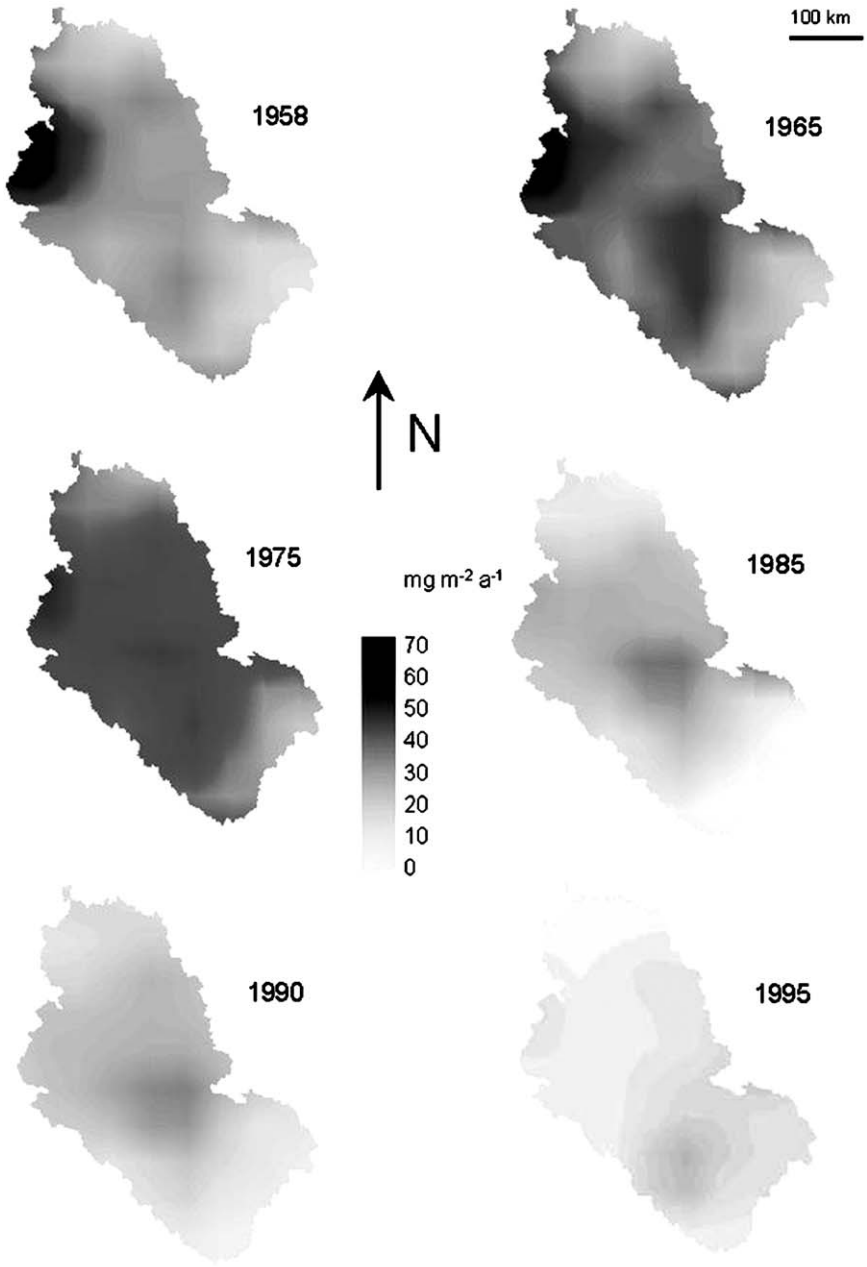

Figure 2. Lead depositions rates for the years 1958 (average of 15.7 mg m^{-2}), 1965 (average, 19.4 mg m^{-2}), 1975 (average, 28.3 mg m^{-2}), 1985 (average, 13.0 mg m^{-2}), 1990 (average, of 9.1 mg m^{-2}), and 1995 (average, of 2.1 mg m^{-2}). Values were estimated by linear interpolation onto the 1-km^2 grid, of the simulated deposition values at 0.5° scale from Von Storch *et al*. (2003).

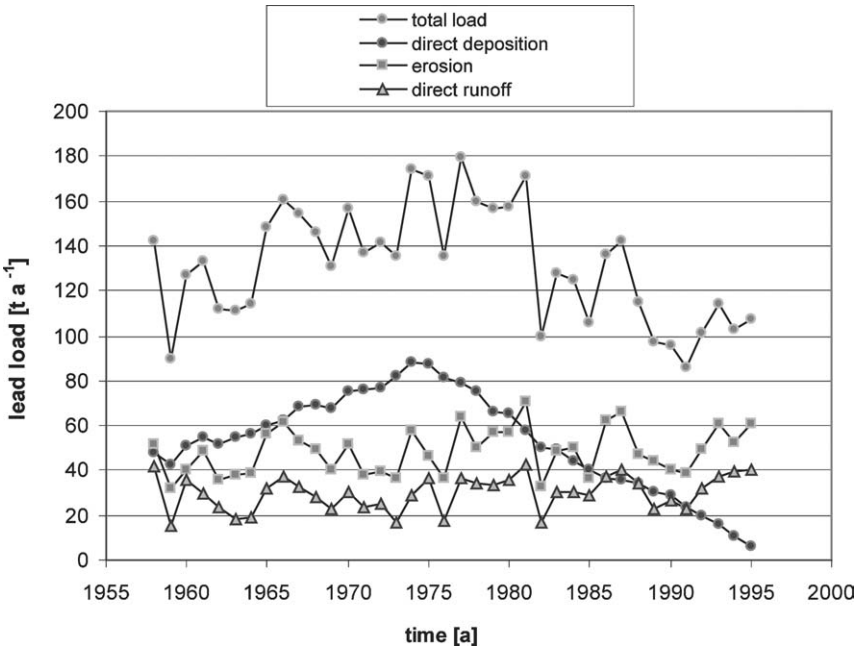

Figure 3. Simulated lead loads *via* the three pathways considered during the study period.

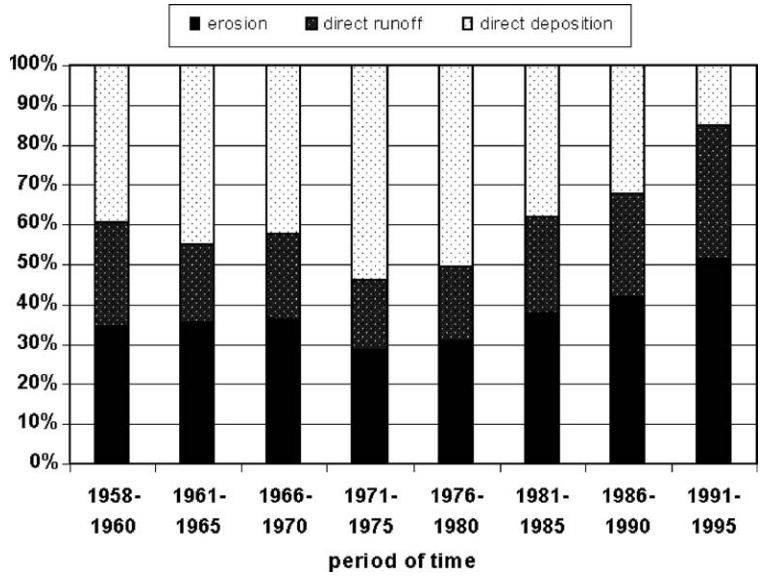

Figure 4. Percentage contribution of the three pathways considered during the study period.

3.2. SPATIAL DISTRIBUTION OF LEAD DEPOSITION AND OVERLAND LEAD FLUXES

The regions of highest atmospheric lead pollution and deposition were situated in the east and in the centre of the catchment (Harz mountains and Erz mountains, respectively) as well as the congested urban areas such as Berlin and Prague (see also Figure 2). These areas were highly contaminated due to metal-manufacturing, metal-producing industries (established for decades in the Harz and Erz mountains) as well as rising gasoline combustion and automobile ownership (see also Von Storch *et al*., 2003).

There is no obvious relationship between the extent of atmospheric lead deposition and spatial distribution of overland lead fluxes, as can been seen from Figures 5 and 6. The soil (see also Section 3.3) acts as a buffer and storage compartment because of lead's high sorptivity and low solubility. Thus, the soil releases overland lead fluxes according to the geography: The spatial variation of particle-bound lead

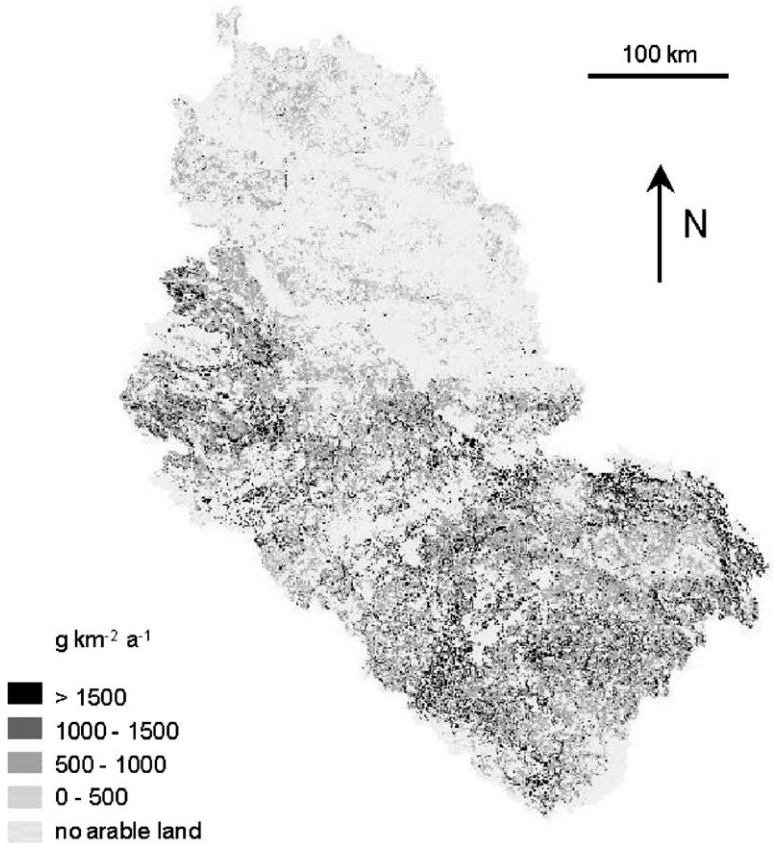

Figure 5. Mean annual lead load to channels *via* erosion from the land surface ($\overline{Pb}^{\downarrow}_{eros_{i,t}}$) for the study period (1958–1995).

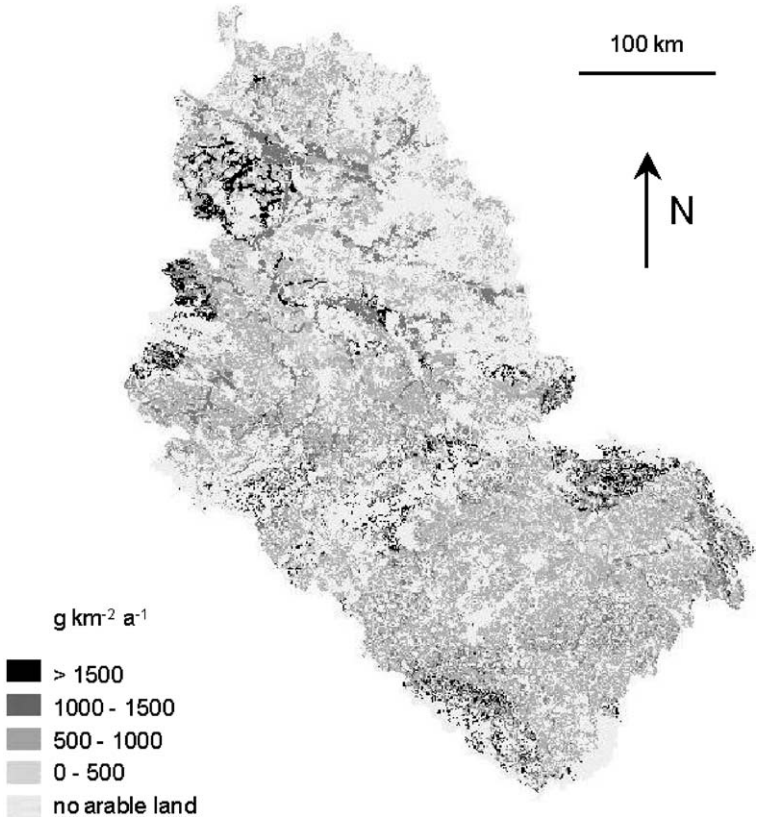

Figure 6. Mean annual lead load to channels *via* direct runoff ($\overline{\mathrm{Pb}}^{\downarrow}_{\mathrm{fast}_{i,t}}$) for the study period (1958–1995).

loads were related to soil erosion. Here, soil texture and topography appeared as the most strongly influencing factors. Regions with highest lead erosion, with more than 10^3 g km^{-2} a^{-1}, were situated in the loess areas of the central Czech Republic and central Germany as well as in the mountain ranges of the catchment (Giant mountains, Harz mountains).

The spatial distribution of solute lead transport varied with the extent of direct runoff and was much less influenced by the spatial distribution of lead deposition. For example, in some regions with high deposition rates (e.g. in the years 1958–1975 adjacent regions southeast of the Harz mountains, Figure 2), amounts of generated direct runoff available for lead solution are relatively low, resulting in generally lower lead loads. And, in some regions with low deposition rates (e.g. 1965, south east of the catchment/CZ, Figure 2), direct runoff generation is strongly developed so that the total lead transport is higher, even at lower soil concentrations. The generation of direct runoff is mostly dependent on precipitation, soil type and terrain inclination. As a result, the main areas of lead fluxes *via*

direct runoff (surface and subsurface runoff) appeared in the mountain ranges of the catchment (Harz mountains, Erz mountains, Giant mountains and Thuringian and Bohemian forest, with more than 10^3 g km^{-2} a^{-1}).

3.3. SOIL CONTAMINATION

Acting as a buffer, soils play a major role in substance transfer from the terrestrial to the aquatic environment. Soil texture (in particular, clay content), and organic matter content largely determine the environmental fate of deposited lead. With the application of the soil-mass balance, the role of the soil as source and sink for lead was incorporated.

During the study period, the mean soil concentration of the Elbe basin showed a steady increase (Figure 7). The accumulation rate varied with the lead-deposition rate. In years with highest atmospheric lead pollution (mid-1970s), accumulation rose steeply. With decreasing air pollution at the beginning of the 1980s the accumulation rates declined accordingly and ceased in the early 1990s. This phenomenon was also observed by Prieler and Anderberg (1996). The lead accumulation stopped at a low lead-deposition rate of 2.8×10^3 g km^{-2} a^{-1}, which was reached in the years 1994 and 1995 in the present study. The mean net accumulation for the whole study period fit well with long-term data (40 years) from Prieler and Anderberg (1996).

The impact of local atmospheric deposition on the spatial distribution of lead accumulation in the Elbe basin is shown in Figure 8. The regions with the highest soil pollution were the Harz mountains and adjacent areas, which are also the regions with by far the highest air pollution in the study area. In addition, the

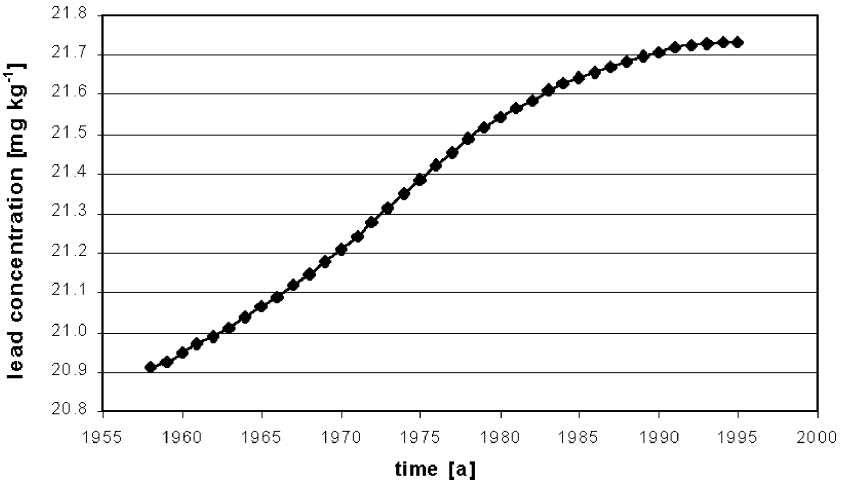

Figure 7. Mean lead concentration of the soils in the study region over the study period (1958–1995).

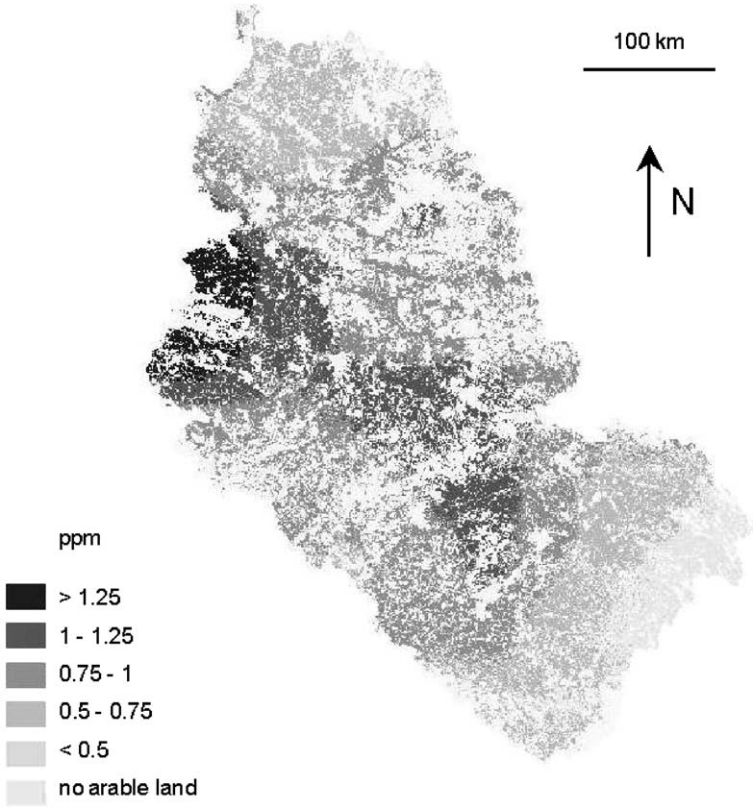

Figure 8. Lead accumulation in the soils of the Elbe catchment over the study period (1958–1995).

Erz mountains showed high lead-accumulation rates. Areas with the lowest lead deposition and lowest soil pollution accordingly were situated the southeast and northwest of the catchment. In comparison to the lead background contents of the soils (ranging from 11.5 mg kg^{-1} in Land Brandenburg to 31.8 mg kg^{-1} in Land Thuringia; Vink, 2002) the accumulation rates were relatively low and did not reach critical values (e.g. precaution values, see German Federal Soil Protection Aid and Ordinance (BbodenschV), Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, 1999).

It should be pointed out that the information gained with METALPOL is valid only for the present scales as well as only for the pathways studied and lead inputs considered. Lead fluxes and lead accumulation are assumed to vary widely according to the spatial and temporal resolution of interest. As a result, elevated concentrations following fertilizer applications, industrial dumps or forestal interception etc., which present a local high-risk problem, were not reflected in this study and should be considered in studies conducted at higher resolutions.

TABLE I
Comparison of model results with literature data (t a^{-1})

Period	Vink (2002) 1983–1995	This study 1983–1995	Vink and Behrendt (2001)[a] 1993–1997	This study 1993–1995	Vink *et al.* (1999) 1992–1995	This study 1992–1995
Direct runoff	11	32.5	5.5	39.0	87.3	37.3
Erosion	73	50.6	67.4	58.0	87.3	55.9
Lead load from arable land	84	83.1	72.9	97	87.3	93.2
Direct deposition	26	28.9	8.8	11.0	41.4	13.2
Total load	110	112.0 (Δ = 1.8%)	81.7	108 (Δ = 31.7%)	128.7	106.4 (Δ = 17.3%)

[a]As described by Vink (2002).

4. Comparison with Other Studies on Heavy Metals

This work represents one of the first long-term studies on heavy-metal transport on the river-basin scale. Unfortunately, only few studies are available for model validation at temporal and spatial scales considered. The contribution of the different lead pathways into the River Elbe is compared to the results of Vink (2002, using the same model METALPOL), Vink *et al.* (1999, using METALPOL in its preliminary stages) and Vink and Behrendt (2001; model MONERIS, in Vink, 2002) (Table I). Although these studies offer the only available possibility for model validation, the comparability is limited since they cover different periods and use different input variables and data sets.

A first comparison was made between the present model results and measurements at the gauging station near Schnackenburg available for the period 1984–1995 (Elbe 474 km; in Vink, 2002) (Figure 9). The comparability is limited to the temporal patterns and does not imply the absolute values of the data sets. The present study considers only atmospheric deposition and overland transport as lead source for the entire basin. However, measurements are locally restricted observations and contain point information concerning the total lead sources throughout the catchment as well as complex interactions between lead input, sedimentation, retention and transport processes. Nevertheless, some comparisons between model results and measurements are admissible since the major contribution to the entire lead loads in the Elbe basin is represented by erosion and direct runoff processes (70% for 1985–1999) as estimated by Vink (2002). Thus, it can be assumed that the measurements reflect at least the temporal development of the three pathways considered. In view of these restrictions, it can be stated that the present study could reconstruct the dynamics of lead fluxes in the Elbe river fairly well (Figure 9).

Furthermore, literature data were compared with model results to validate the simulated fluxes in the individual pathways (Table I). Lead emission estimates *via* the three pathways for the Elbe basin are available from *Vink* (METALPOL, 2002),

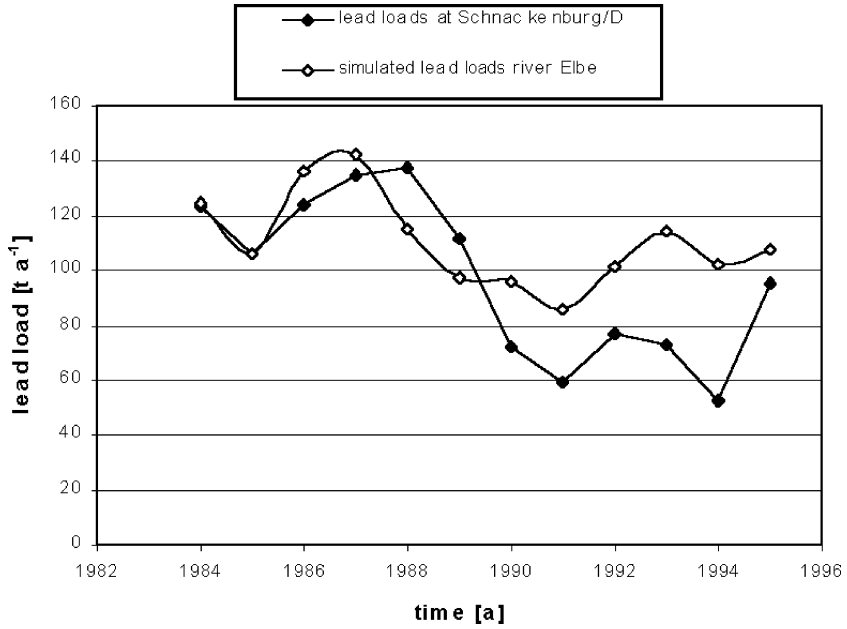

Figure 9. Measurements of lead loads at the gauging station Schnackenburg/Germany (as described by Vink, 2002) and simulated total lead emissions (direct deposition, erosion, direct runoff) with METALPOL.

Vink and Behrendt (MONERIS, 2001, in Vink, 2002) and *Vink et al*. (preliminary version of METALPOL, 1999).

The results concerning the total loads (overland transport and direct deposition) and the overland transport itself proved to be in the same order of magnitude. According to Vink (2002), discrepancies from 30 to 50% are acceptable in transport modelling on the river-basin scale. In this context, the discrepancies found (1.8–31.7%) are in an admissible range. The comparison shows that, although the total lead loads were relatively similar, the contribution of the three pathways shows some large differences. Generally, this is due to the fact that the present work included only atmospheric deposition as lead input. Vink (2002), Vink and Behrendt (2001) and Vink *et al*. (1999) additionally considered lead contamination *via* fertilizer and manure application. Furthermore, the result that the particle-bound lead loads considered in the present work were lower than the estimation of Vink (2002), is due to lower soil erosion rates (1.1 t ha^{-1} a^{-1} – this study, 1.57 t ha a^{-1} – Vink, 2002). The discrepancies concerning direct deposition rates are due to the different input data of the compared studies. In contrast to the annually varying deposition rates derived with atmospheric-transport models and climate reconstructions, Vink (2002), Vink and Behrendt (2001, in Vink, 2002)) and Vink *et al*. (1999) assumed emission factors which were interpolated over several years. The largest differences can be detected in the direct runoff pathway. The results are generally higher than

those from Vink (2002), Vink and Behrendt (2001) and Vink *et al*. (1999) and as reported by Alloway (1995). One reason for the large differences is assumed to be the use of Thiessen polygons for interpolation of meteorological data. This technique, which is widely applied on large scales, led to uncertainties in the water balance, especially in those regions with high lead deposition and high elevations (mountain ranges of the catchment). Vink (2002) states that the direct runoff pathway is generally overestimated by METALPOL in comparison to other studies. With respect to Vink (2002), this may be due to the different model approaches applied in the studies: In METALPOL, the Kd-concept is implemented in the direct runoff submodel, while in other studies, the calculation was made with estimated/measured concentrations in the drainage and surface runoff. In Vink and Behrendt (2001, transport model MONERIS), the direct runoff pathway was modelled through a constant emission factor that was lower than the mean lead concentration in the direct runoff determined in this study and assumed to be representative (1.5 μg l^{-1} compared to 4.9 μg l^{-1}).

The temporal trends of the individual contamination pathways (Figure 3) were confirmed by the long-term heavy-metal-transport studies of Vink (2002) for the Elbe catchment over the period 1983–1999 and Behrendt (1993) for the Rhine basin over the period 1973–1987. Both authors found a rising or more or less constant contribution of erosion and direct runoff pathways for lead in the river networks and study periods.

A validation of the spatial distribution of the main lead input was impossible due to lack of comparable data. The analysis of sediment cores as conducted by Prange *et al*. (1997) for three sites along the Elbe river would be a possible method to reconstruct local lead pollution. A more dense and more representative measurement network would be required.

5. Conclusions

The lead fluxes found and their spatial and temporal dynamics were in reasonable agreement with literature data except for the overland pathway direct runoff, which was overestimated by this model. The problem of estimating heavy-metal emissions *via* surface and subsurface runoff cannot be solved since there is no method available to measure these heavy-metal fluxes (see also Vink and Peters, 2003). For an accurate pollution survey by indirect diffuse sources in large river basins such as the Elbe, future research should focus on developing measurement and modelling techniques to determine overland fluxes on large scales. The present work achieved a preliminary estimation of long-term contamination of the Elbe basin originating from atmospheric lead pollution. The lead pollution of the Elbe river declined in the course of lead-control policies. Nevertheless, the overland transport poses a long-term risk since those fluxes were apparently not influenced by decreasing atmospheric deposition. They depended mainly on hydrometeorological, topographical and pedological factors. As a result, regions at high pollution risk

were the areas with high precipitation and steep slopes, which are prone to high erosion rates and intense direct runoff. Furthermore, the steady accumulation of lead in the soils (resulting from its high sorptivity and low solubility, and negligible biodegradation of this metal) led to persistently high lead fluxes in the form of erosion and direct runoff. A decline in lead contamination *via* overland transport cannot be expected in the near future. Therefore, controlling pollution of the adjacent aquatic systems by particle-bound, highly sorptive toxic substances is strongly linked to reducing soil pollution and soil erosion.

This study indicates that the sustainable protection of environmental systems and human life against harzadous pollutants is a multi-faceted task. Even though lead-control policies significantly decreased atmospheric pollution, lead has not simply vanished out of the environment. This study underscores the fact that the contamination with persistent, highly sorptive substances remains a danger long after pollution-control measures have been implemented. Today's soils and sediments have inherited the former reckless lead consumption. For this reason, materials from maintenance dredging and capital dredging operations sometimes have to be handled as harzadous waste, and the persistently high concentrations in marine and freshwater organisms resulting from bioaccumulation in the food chain (see Hagner, 2002) represent a long-term risk to human health. As a result, human health on the one hand has significantly benefitted from decreasing atmospheric pollution (see Von Storch *et al*., 2003; Von Storch and Hagner, 2003) but on the other hand still may be imperilled to a certain degree.

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Note

1. To gain historical perspective, consider the measurements out in remote ice cores in central Greenland (Hong *et al*., 1994), far away from emission sources. Confirmed by isotopic analysis to be of anthropogenic origin (Rosman *et al*., 1995), lead contents in these ice cores rose steadily during the last centuries: ancient Greek and Roman lead smeltering (2–3 pg g^{-1}), Middle Ages and Renaissance (4 pg g^{-1}), the Industrial Revolution (10 pg g^{-1}), and 50 pg g^{-1} in the 19th century. In the 1960s, 100 pg g^{-1} was reached, and in 1984, levels rose to 150 pg g^{-1}, reflecting the use of lead as antiknock additive in gasoline in Europe and North America.

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