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Geochronology of anthropogenic pollutants in riparian wetland sediments of the Lippe River (Germany)

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Abstract

Anthropogenic pollutants were determined in a dated sediment core, collected from a riparian wetland of the Lippe River (Ruhr district, Germany). The historical trend in heavy metals, polycyclic aromatic hydrocarbons, organochlorines, polychlorinated biphenyls and linear alkylbenzenes as well as more recent contaminants such as industrial additives, organotins, synthetic musks, methyltriclosan and some other compounds were determined for the time period between 1930 and 1986. Emission sources, information on technical production and usage, as well as on the individual pollution pathways, with appropriate environmental stability, were considered in the interpretation of the sediment contamination over the past ~50 years.

Contaminants were analysed and interpreted according to two different criteria: (a) the origin of the main contaminants as related to mining and industrial activities as well as municipal sewage and agricultural effluents and (b) the pollution history. Due to a significant appearance of formerly missing contaminants in sediments deposited since 1970, we suggest classifying contaminants as either common (predating 1970) or modern (postdating 1970).

In summary, the study provided a comprehensive reconstruction of the pollution history of the Lippe River system.

1. Introduction

Anthropogenic contaminants reach the fluvial environment by different emission pathways. Besides atmospheric deposition, the major proportion of contamination can be attributed to direct or indirect anthropogenic discharge of noxious substances by municipal, industrial and agricultural sources. The municipal input includes particulate matter derived from sewage sludge as well as waste water from household effluents and surface and street runoff (Kolpin et al., 2002; Takada et al., 1997). Numerous organic constituents of municipal effluents occur as the result of careless or incorrect usage of chemical products, (excessive) usage of detergents, personal care products, paints, varnish and other technical compounds as well as of the application and disposal of pharmaceuticals in our daily routine. Besides municipal effluents, industrial discharge also represents an important pollution source in riverine systems (Di Corcia et al., 1999; Kjeller and Rappe, 1995; Sanders et al., 1992). Industrial sewage and waste water contains a wide spectrum of noxious substances including synthesis products, corresponding by-products and production wastes, as well as

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contamination as a result of incomplete combustion (Bruns et al., 1997; Kaplan et al., 1997; Volkman et al., 1997).

As a third principal emission source, intensive agricultural activities discharge numerous pollutants, e.g., organic and inorganic fertilizers, herbicides and insecticides (Schwarzbauer et al., 2001; Venkatesan et al., 1999; Zhang et al., 1999). The agricultural input has to be characterized as a diffuse source emission reaching the aquatic environment either by surface runoff or by the interaction of the riverine system with corresponding contaminated groundwater. Further non-point source emissions can be attributed to shipping activities discharging, for example, fuel contaminants or constituents of anti-fouling paint like tributyl tin (TBT; Bence et al., 1996; Poppe et al., 1988, 1991). Besides the permanent emissions described, short-term, catastrophic contamination also occurs as the result of single incidents including, e.g., industrial accidents and disasters during careless transport and storage of chemicals. In summary, a wide spectrum of different specific anthropogenic pollutants and man-made chemicals reach the riverine environment from various different sources.

The environmental fate of anthropogenic pollutants depends on their chemical and physical behaviour in the aquatic system. In the river system, water-soluble (hydrophilic) components predominantly accumulate in the aqueous phase and are consequently transported rapidly as a mobile fraction, whereas more hydrophobic (lipophilic) contaminants tend to be enriched in the solid phase. The particulate matter is then deposited according to hydrological and sedimentological conditions. Therefore, associated lipophilic compounds are transferred into the sediments, as a more immobile fraction. Because of more anaerobic conditions, the sedimentary compartment shows an enhanced environmental stability for many lipophilic contaminants of geogenic, biogenic and anthropogenic origin, accumulated in and incorporated into riverine sediment deposits.

Based on these processes, environmental investigations on fluvial systems focus on the particle-bound contaminants. Besides the lateral transport by cycles of temporary deposition and subsequent erosion, the long-term storage of contaminated particulate matter in undisturbed sediments is of major interest (Takada et al., 1994, 1997). In the case of undisturbed periodical or aperiodical sedimentation, for example, during flood events, the accumulated sediment deposits (floodplains and wetlands) can act as ecological archives. Dating of these sediment layers by radiological analyses in combination with quantitative chemical analyses reveals a detailed record of the riverine load histories for preserved particle-bound contaminants (Catallo et al., 1995; Kähkönen et al., 1998). Hence, fluvial sediment deposits, in particular on floodplains and riparian wetlands, can act as the "memory of the river" (Klös and Schoch, 1993a).

In the past, numerous studies have been performed on dated sediment systems in order to reconstruct historical inputs of organic and inorganic contaminants. Most of these investigations have analysed contaminated sediment cores derived from two different depositional areas: coastal zones as the final sedimentation area of riverine particulate matter (e.g., Fox et al., 2001; Venkatesan et al., 1999; Winkels et al., 1998; Latimer and Quinn, 1996; Gustafsson et al., 2001) and lacustrine systems (e.g., Reiser et al., 1997; Van Metre et al., 1997; Sanders et al., 1992; Eisenreich et al., 1989).

In contrast, geochronological studies of riverine or riparian sediments have been rarely reported (Winkels et al., 1998). Furthermore, it must be noted that the major proportion of these geochemical studies dominantly focussed on pre-selected organic and inorganic contaminants such as heavy metals or priority organic pollutants (Keith and Telliard, 1979). Examples include polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs; Gevao et al., 2000; Latimer and Quinn, 1996; Van Metre et al., 1997; Sanders et al., 1993,), synthetic detergents (Reiser et al., 1997) and chlorinated hydrocarbons (Winkels et al., 1998; Eisenreich et al., 1989). However, the documentation of a wide range of river-specific contaminants from various emission sources in dated riverine sediment cores is quite rare.

Therefore, this study was performed to produce a more comprehensive reconstruction of the pollution history of a riverine system. Based on an earlier, preliminary investigation (Heim et al., 2003), a sediment core derived from a riparian wetland of the Lippe River (Germany) was examined by means of radiological and organic geochemical analysis. Additionally, several inorganic contaminants were analysed. In the present work, time-resolved concentration profiles of a variety of source specific substances are discussed in detail in order to gain a deeper insight into contamination vs. time trends and, consequently, the pollution history of the Lippe River system.

2. Materials and methods

2.1. Sampling location and samples

A sediment core from a floodplain of the Lippe River, a tributary of the Rhine River (Germany), was taken in October 2001 (see Fig. 1). The sampling location was characterized as an undisturbed sediment deposit with periodical/aperiodical sedimentation (Klös and Schoch, 1993a).

The core of 166 cm length was divided into 4-cm segments. The fresh material was placed in solvent-cleaned glass flasks and stored at 4 °C in the dark. Prior to the organic, inorganic and radiometric analyses, the layer samples were subdivided into several aliquots. The

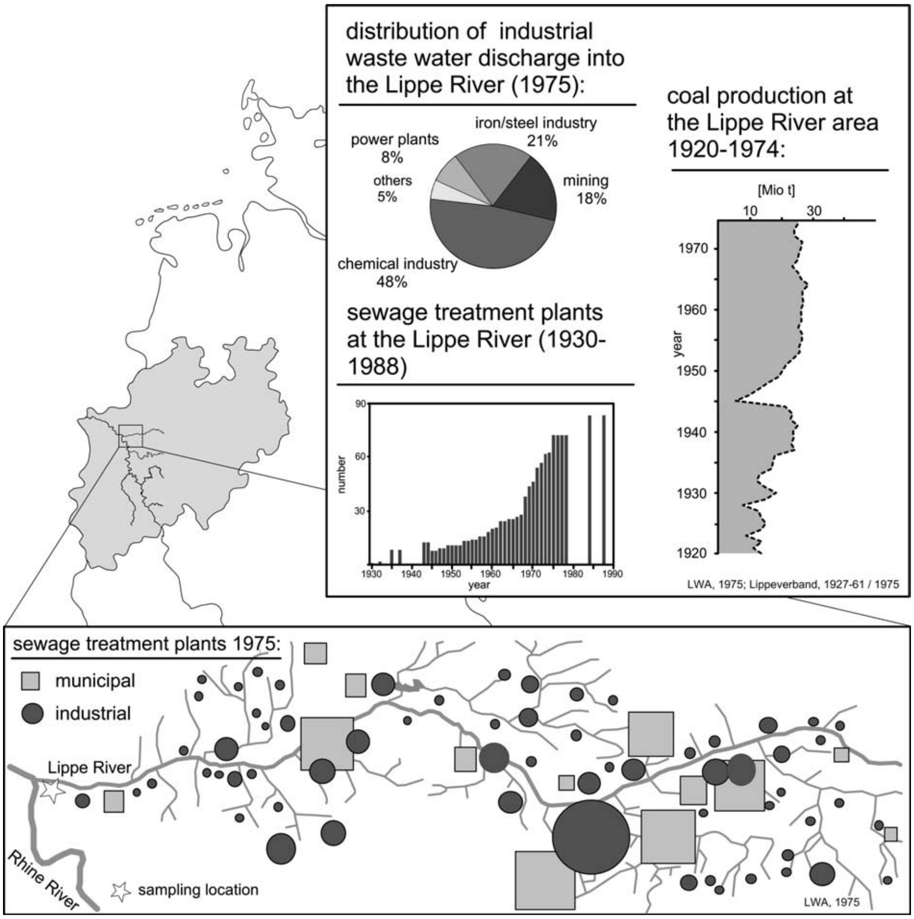

Fig. 1. Map of sampling location at the Lippe River (Ruhr District, Germany). (a) Exemplary distribution of waste water supply (LWA 1975), coal production at the time period of 1920–1974 and number of sewage treatment plants at the Lippe River (1930–1988) and (b) industrial and municipal sewage treatment plants at the Lippe River, indicated by the recorded waste water in proportionate symbol size (Lippeverband, 1975).

sediment was characterized as loamy fine sand (Fig. 2) with distinct bedding and with evident colour variation among the layers.

2.2. Radiometric dating methods

The chronology of the sediment core was determined using ^{210}Pb and ^{137}Cs dating methodology (Bollhöfer et al., 1994). Forty samples, representing the top 166 cm, were analysed using a Canberra n-type γ-spectrometer. Since considerable amounts of excess ^{226}Ra were observed (see below), the equilibrium activity of ^{210}Pb and ^{226}Ra produced by detrital materials was determined via the ^{234}Th activity. Within the limits of error, a constant value for ^{234}Th is observed for the core, the weighted average being 1.25 ± 0.03 dpm/g.

2.3. Organic geochemical analysis

2.3.1. Extraction

Approximately 5 g of each layer sample were extracted by a sequential solvent extraction procedure performed with a high speed dispersion device (Ultra Turrax, T25, IKA, Stauffen, Germany). The extraction conditions were as follows: dispersion time of 3 min at 16,000 rpm for five times with 30 mL solvent, respectively. The solvents used were: first extraction step – acetone, second and third extraction step – acetone/hexane (1:1, v:v), fourth and fifth extraction steps – hexane. Each extraction step was followed by centrifugation at 4000 rpm, and separation and combining of the organic extracts. The extract was then concentrated to a volume of approx. 5 mL and dried over anhydrous

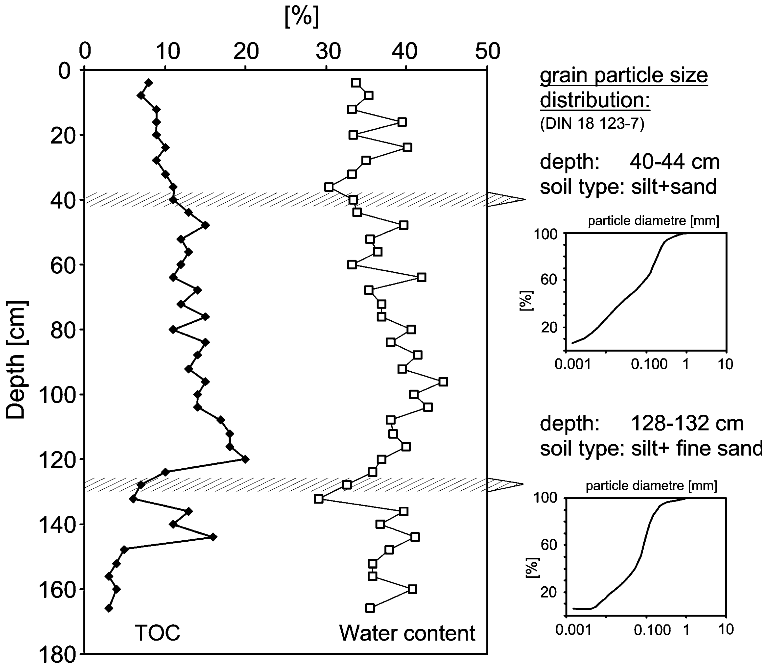

Fig. 2. Petrogenic data for the investigated sediment core of the Lippe River wetland (TOC, total organic carbon).

granulated sodium sulfate. After a second concentration step, down to a volume of 1 mL, 50 mg of activated copper powder was added to remove sulfur. After a short ultrasonic agitation and a reaction time of 16 h, the raw extract was concentrated to a volume of approx. 0.5 mL by rotary evaporation at room temperature and subjected to a liquid chromatographic fractionation.

Since mono-, di- and trialkyltin compounds are not extracted by the procedure mentioned above, a second extractive derivatisation was applied to the sediment samples. Dry pre-extracted sediment residues (1–2 g) were acidified by mixing with 1.5 mL of 10% aqueous hydrochloric acid. After 0.5 h, the pH of the slurry was adjusted to 4 with 10% aqueous sodium hydroxide and a sodium acetate/acetic acid buffer solution. One mL of a 10% aqueous sodium tetraethylborate solution and 45 mL of hexane/acetone (67:33, v:v) were added. Extraction and separation were performed with the high dispersion device. The procedure was repeated three times and the combined extracts were prepared for chromatographic fractionation as described below.

2.3.2. Fractionation

Fractionation of the raw extracts was performed by column chromatography (Baker, 2 g silica gel 40 μm). Six fractions were obtained by using solvent-mixtures of *n*-pentane and dichloromethane as eluant, according to Schwarzbauer et al. (2000). The extraction conditions were as follows: first fraction: 5 mL *n*-pentane, second fraction: 8.5 mL *n*-pentane/dichloromethane (95:5; v:v), third fraction: 5 mL *n*-pentane/dichloromethane (90:10; v:v), fourth fraction: 5 mL *n*-pentane/dichloromethane (40:60; v:v), fifth fraction: 5 mL dichloromethane and sixth fraction: 5 mL methanol.

An aliquot (50 μL) of an internal standard solution containing 5.8 ng/μL fluoroacetophenone, 6.0 ng/μL d_{36}-hexadecane and 5.1 ng/μL d_{10}-anthracene was added to each fraction. Thereafter, the volume was reduced to 50–100 μL by careful evaporation at room temperature. All extracts were analysed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC/MS).

2.3.3. Gas chromatographic analysis

The gas chromatographic analyses were carried out using a GC 8000 series gas chromatograph (Fisons Instruments, Wiesbaden, Germany), equipped with a 25 m × 0.25 mm i.d. × 0.25 μm df SE-54 fused silica capillary column (CS Chromatographie Service, Langerwehe, Germany) and connected to a flame ionisation detector. Chromatographic conditions were as follows: 270 °C injector temperature; 300 °C detector temperature; 1 μL split/splitless injection at 60 °C, splitless time 60 s, 3 min isothermal, then programmed at 3 °C/min to 300 °C, hydrogen carrier gas velocity 40 mL.

2.3.4. Gas chromatographic mass spectrometric analysis

GC/MS analysis was performed on a Finnigan Trace MS mass spectrometer (Thermoquest, Egelsbach, Germany) linked to a Mega Series HRGC 5160 gas chromatograph (Carlo Erba, Milan, Italy) which was equipped with a 45 m × 0.25 mm i.d. × 0.25 μm df SE 54-CB fused silica capillary column (CS Chromatographie Service, Langerwehe, Germany). Chromatographic conditions were as follows: 270 °C injector temperature, 1 μL split/splitless injection at 60 °C, splitless time 60 s, 3 min isothermal, then programmed at 3 °C/min to 300 °C, helium carrier gas velocity 40 mL. The mass spectrometer was operated in the electron ionisation mode (El$^+$, 70 eV) with a source temperature of 200 °C, scanning from 35 to 700 amu at a rate of 0.5 s/decade with an inter-scan of 0.1 s. Identification of the individual compounds was based on comparison of EI mass spectra with reference mass spectra database libraries (Nist'98/Wiley/NBS, 4th Ed., electric version).

Acidic compounds in the polar fraction (sixth fraction) were methylated prior to analysis by adding a fresh diazomethane solution and subsequent re-concentration. Quantitative data were obtained by integration of specific ion chromatograms extracted from the total ion chromatogram (TIC). External four point calibrations with authentic reference compounds were used for quantification. Recoveries were determined by spiking pre-extracted sediment samples with a mixture of reference compounds and subsequent execution of the extraction after incubation and fractionation procedures as described above. Quantitative data were recovery corrected and reported on a dry matter basis.

2.4. Inorganic analysis

To assess the content of heavy metals, aliquots of approximately 3 g of each sample were subjected to chemical pulping with nitrohydrochloric acid in accordance with DIN 38414, part 7. The concentrations of selected heavy metals (Cu, Cr, Cd, Ni, Pb and Zn) were determined by Atomic Absorption Spectrometry with an ICP-OES, AAS-FIMS or HGA-AAS system (Perkin–Elmer, Optima 2000 DV).

3. Results

To study the historical input of anthropogenic contaminants into the Lippe River system, organic and inorganic geochemical and radiometric investigations were applied to a sediment core of a corresponding riparian wetland. The sampling location was situated on a frequently flooded area at the downstream end of the Lippe River near the confluence with the Rhine River. Therefore, the particle-bound contaminants deposited in this area represent the accumulated load of the emissions discharged to the overall riverine system.

3.1. Radiological dating

3.1.1. Cs-137

From the ^{137}Cs profile of the core [Fig. 3(a)], three time markers can be derived: the beginning of the nuclear weapon tests (1952) in the depth interval from 92 to 96 cm, the culmination of the nuclear weapon tests (1963–1964) in the depth interval from 52 to 56 cm and the Chernobyl reactor accident (1986) in the top 4 cm. This implies, however, that the last 16 years are missing from the core. This may be due to either partial erosion of the sediment or infrequent occurrence or absence of flooding events during the past decade. From the three time markers, a mean sedimentation rate of approx. 2.4 cm/a for the lower 54 cm and approx. 3.6 cm/a for the interval of 54–94 cm can be calculated.

3.1.2. Pb-210/Ra-226

The ^{210}Pb and ^{226}Ra-profile shown in Fig. 3(b) displays a significant excess of ^{226}Ra. A similar profile was

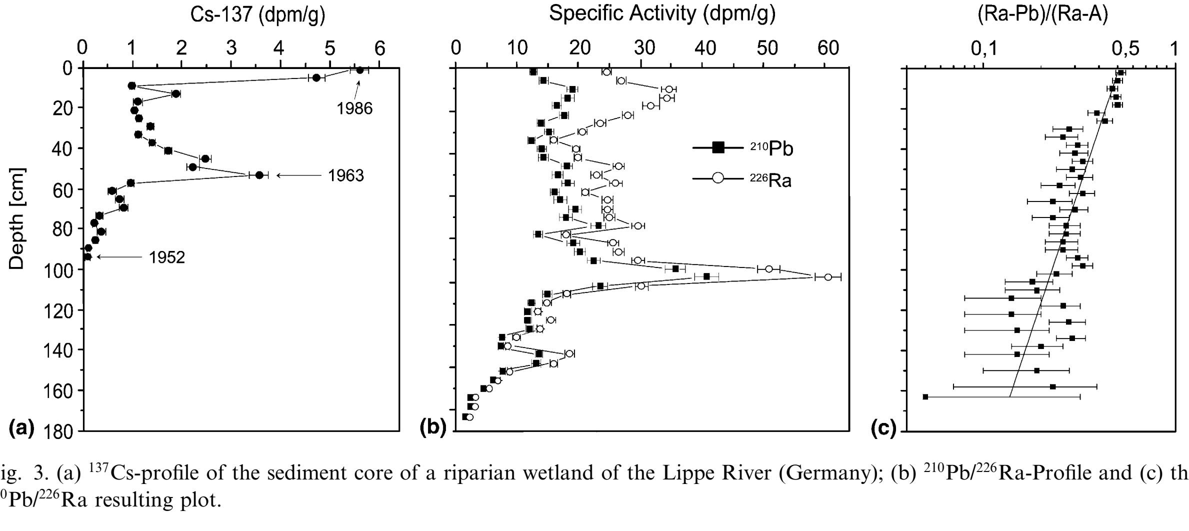

Fig. 3. (a) ^{137}Cs-profile of the sediment core of a riparian wetland of the Lippe River (Germany); (b) ^{210}Pb/^{226}Ra-Profile and (c) the ^{210}Pb/^{226}Ra resulting plot.

observed by Klös and Schoch (1993a) for a sediment deposit from a nearby location of the same river. The authors explain the excess of ^{226}Ra in the sediment by discharge of radium-enriched mine water into the Lippe River, a common feature in mining areas. In comparison, the annual ^{210}Pb deposition from the atmosphere is negligible. This assumption is based on the following estimation: Taking a mean sedimentation rate of 3 cm/a, derived from the ^{137}Cs profile, an atmospheric flux of ^{210}Pb of 0.6 dpm/cm^2/a (Dominik et al., 1981; Hemmerich, 1980) and an average dry bulk density of 0.93 g/cm^3, we arrive at a specific activity of atmospheric (unsupported) ^{210}Pb of approx. 0.2 dpm/g, a value ca. 60 times smaller than the measured value of ^{210}Pb in the top layer. We can thus assume a pure radium excess model for the present study,

$$\frac{^{226}\mathrm{Ra}(z) - {}^{210}\mathrm{Pb}(z)}{^{226}\mathrm{Ra}(z) - A(z)} = \exp\left[-\lambda_{210}\left(t_0 + \frac{m}{r}\right)\right],$$

where ^{226}Ra and ^{210}Pb are the measured specific activities at depth z, A the specific activity of the equilibrium component of both ^{210}Pb and ^{226}Ra, produced by detrital materials, λ_{210} the decay constant of ^{210}Pb, t_0 the age of the top layer, m the cumulative dry mass per unit area and r the mean accumulation rate (Bollhöfer et al., 1994). For $A(z)$, the weighted average of 1.25 ± 0.03 dpm/g was inserted. The plot of the ratio on the left-hand side of the equation versus m is shown in Fig. 3(c). From an exponential fit to the data points, a mean accumulation rate of 3.57 ± 0.27 g/cm^2/a and an age for the top layer of $t_0 = 21 \pm 1$ a was determined. Using the average dry bulk density of 0.93 g/cm^3, a mean sedimentation rate of 3.8 ± 0.3 cm/a was calculated. Since compaction effects are almost negligible for this core, accumulation and sedimentation rate yield identical ages within limits of error.

The sedimentation rate compares well with the caesium-derived sedimentation rate for the depth interval from 54 to 94 cm, but is significantly larger than the caesium-derived rate for the upper 50 cm. In addition, the ^{210}Pb age of the top layer is somewhat higher than the one indicated by the ^{137}Cs profile. It is possible that the discharged mine water is not only enriched in radium but also transports particle-bound ^{210}Pb in variable concentration. This would then be an additional, hardly quantifiable source of ^{210}Pb in the sediments, which results in a systematic uncertainty in the ^{210}Pb ages. It should be noted, however, that age discrepancies between the two clocks never exceed five years. We thus conclude that the ^{137}Cs time markers should be more reliable, but that the derived ^{210}Pb/^{226}Ra chronology can be useful for coarse age estimations below 54 cm.

3.2. Inorganic geochemical analysis

The inorganic contamination of the sediment core was assessed by a determination of selected heavy metals. According to the screening programme of the ICPR (International Commission for the Protection of the Rhine), the elements cadmium, nickel, chromium, lead, copper and zinc were analysed (ICPR, 1996). The vertical concentration profiles are shown in Fig. 4, including a corresponding time scale.

The concentration profiles of all elements analysed exhibited similar trends, but on different concentration levels. Lead, copper and zinc occurred in significantly higher concentrations than cadmium, nickel and chromium, with values ranging from 95 to 400 µg/g for Pb, from 56 to 430 µg/g for Cu and from 517 to 2373 µg/g for Zn. These data correspond to values measured for

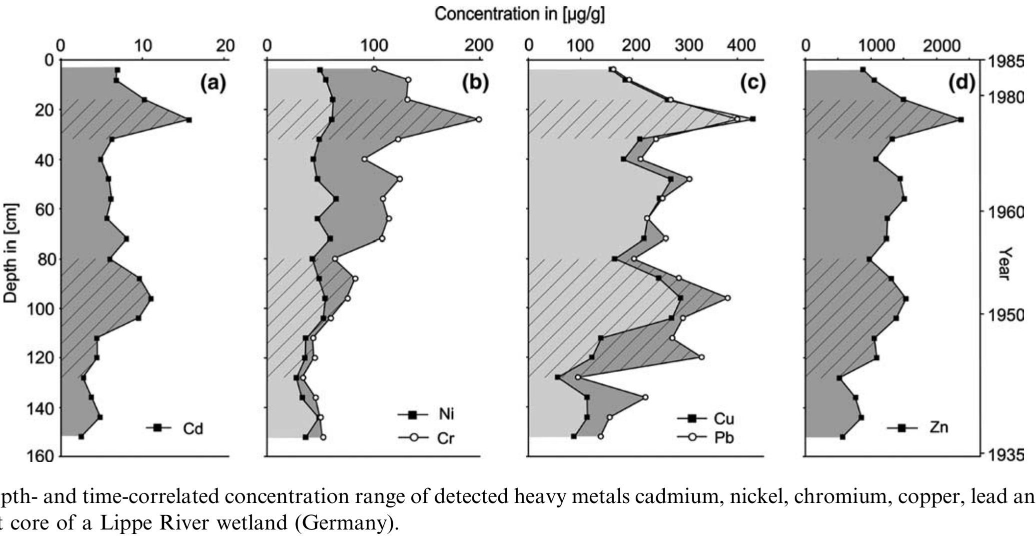

Fig. 4. Depth- and time-correlated concentration range of detected heavy metals cadmium, nickel, chromium, copper, lead and zinc, in a sediment core of a Lippe River wetland (Germany).

other study areas on the Lippe River, which are highly influenced by industrial emissions (Poppe et al., 1991). Lower concentrations were determined for Cd (2.7–15.7 μg/g), Ni (28–62 μg/g) and Cr (34–199 μg/g). With respect to the concentration trends, two significant maxima at a depth of approx. 25 cm and between 88 and 115 cm were observed for most of the metals, as indicated by the hatched areas in Fig. 4. These horizons correspond to sedimentation periods from 1975 to 1980 and from 1945 to 1955, respectively.

In detail, most of the concentration profiles reveal increasing values from the bottom of the core up to a depth of 100 cm, reaching a first maximum there. Subsequently, the values decrease to a fairly constant level at a depth between ±80 and ±30 cm. The averaged values in this zone are: Cd ±6 μg/g, Ni ±50 μg/g, Cr ±85 μg/g, Cu ±180 μg/g, Pb ±240 μg/g and Zn ±1100 μg/g. A second concentration maximum was observed at a depth of approx. 25 cm. In the top layers of the sediment core, the concentrations decrease to values similar to those in the 30–80 cm zone. These trends are best developed in the concentration profiles of lead, copper, zinc and cadmium (Fig. 4).

3.3. Organic geochemical analyses

Detailed GC/MS screening analyses were performed to identify a wide range of persistent lipophilic organic compounds representing the organic contamination of the sediment samples. In addition to a large proportion of biogenic compounds, numerous anthropogenic substances including, for example, chlorinated aromatics, constituents of personal care products, plasticizers and further industrial additives as well as artificial food ingredients (e.g., preservatives) were identified. For quantitative analysis, numerous substances were selected according to different selection criteria: (i) source specifity, (ii) fluvial origin and (iii) appropriate environmental stability. Only a minor proportion of the organic contaminants fulfilled all three criteria. Furthermore, only lipophilic (hydrophobic) compounds were considered in order to avoid misinterpretation as a result of vertical transport of the contaminants associated with pore water. Such vertical transport processes are impeded in particular by strong interactions of compounds with particulate matter.

For most of the substances the riverine origin was confirmed by a recently reported investigation of surface sediments derived from a longitudinal profile of the Lippe River (Kronimus et al., 2004). Also, the attribution of the individual contaminants to different emission sources, in particular municipal, industrial and agricultural effluents, was established (LWA, 1983, 1987, 1991). Furthermore, contaminants derived from superposed emission sources were considered, e.g., polycyclic aromatic compounds. In the following sections, the quantitative results for contaminants and the corresponding concentration profiles obtained for the dated sediment layers are presented in detail.

3.3.1. Polycyclic aromatic compounds

Polycyclic aromatic compounds (PACs) are common environmental pollutants derived either from fossil fuels or as atmospheric contaminants as a result of incomplete combustion processes (pyrogenic sources; Volkman et al., 1997; Kaplan et al., 1997). Quantitative results for the PACs are presented as concentration profiles in Fig. 5(a)–(c) or are listed in Table 1.

The concentration of the representative pyrogenic PAC benzo[a]pyrene ranged between 81 and 11061 ng/g, with only a few significant concentration maxima [Fig. 5(a)]. The profile shows slowly increasing concentrations from the bottom of the core up to a depth of 120 cm. Subsequently, a significant maximum at a depth of 102 cm and a second maximum value at 86 cm are recorded. Above this level the concentrations decrease to an average of ±1400 ng/g.

Benz[a]anthracene and benzo[x]fluoranthene (x = b,k) were detected at elevated concentrations, 280–19,920 ng/g and 417–36,116 ng/g, respectively [Fig. 5(b) and (a)]. The concentration profile of benzo[x]fluoranthene (x = b,k) is very similar to the one of benzo[a]pyrene. In contrast, the concentration profile of benz[a]anthracene exhibited a broad maximum between 120 and 60 cm depth rather than two distinct but narrow maxima.

With respect to further PACs in the sediment core (see Table 1), concentration profiles very similar to the one of benz[a]anthracene were detected for most of the substances. This group of PAHs include acenaphthylene, anthracene, chrysene, fluoranthene, phenanthrene, fluorene and pyrene. Only for perylene, the distribution within the sediment core resembled those of benzo[a]pyrene and benzo[x]fluoranthene (x = b,k).

As common sulfur-containing aromatic compounds, dibenzothiophene and benzo[b]naphtho[2,1-d]thiophenes were determined as illustrated in Fig. 5(c) and (b). Interestingly, the concentration profiles of both contaminants differ significantly. Dibenzothiophene was detected, with concentration values between 66 and 2939 ng/g. The first occurrence at a depth of 152 cm can be attributed to a period around 1940. The concentration profile shows relatively consistent values from the bottom to the top of the core, with two local maxima at a depth of 142 cm and at a depth range between 62 and 38 cm. In contrast, the concentration of benzo[b]naphtho[2,1-d]thiophene is very low in the bottom sediment layers (170–135 cm), but increases rapidly towards a depth of 110 cm, with values up to approx. 4400 ng/g. This high concentration level persists to a depth of 80 cm, followed by a slight decrease towards the top layers with concentrations around 2000 ng/g. Interestingly,

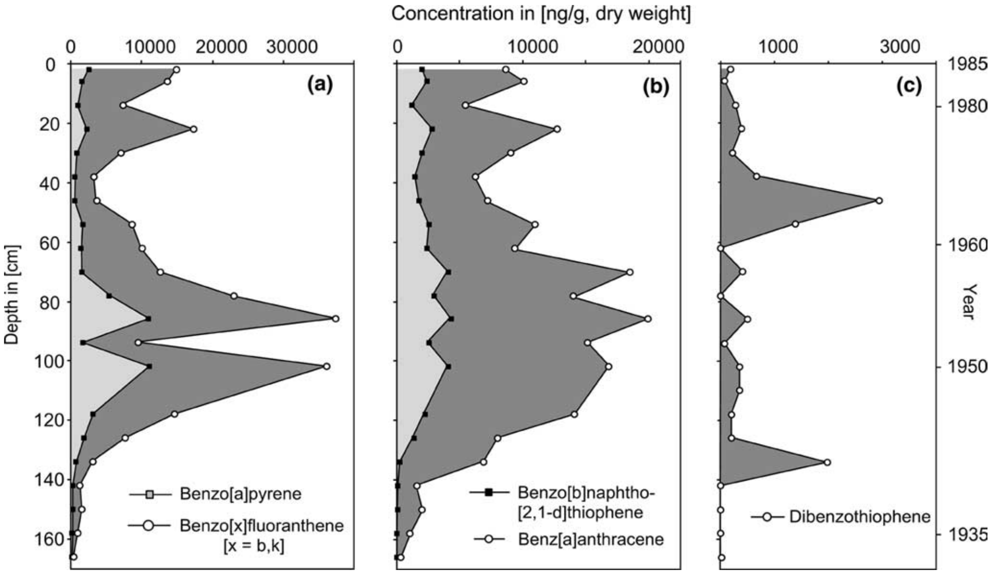

Fig. 5. (a–c) Depth- and time-correlated concentration profiles of PACs benzo[a]pyrene, benz[a]anthracene, benzo[x]fluoranthene (with x = b,k), dibenzothiophene and benzo[b]naphtho[2,1-d]thiophene; determined in dated sediments of a Lippe River wetland (Germany).

acenaphthylene (Table 1) was also detected with a similar concentration profile.

In addition, nitrogen- and oxygen-containing PACs were analysed, comprising dibenzofurane, carbazole and benzocarbazole. Dibenzofurane was found in high concentrations of up to 6000 ng/g, whereas the nitrogen containing compounds occur at a lower concentration level between 10 to 170 ng/g. The concentration profiles of the nitrogen- and oxygen-containing PACs match well the distribution pattern observed for most of the PAHs, e.g., benz[a]anthracene.

3.3.2. PCBs, tetrachlorobenzyltoluenes and polychlorinated aromatic compounds

Polychlorinated biphenyls are well known persistent pollutants ubiquitously distributed in the aquatic environment (Takada and Eganhouse, 1998). Therefore, PCBs as well as their industrial substitutes tetrachlorobenzyltoluenes (TCBT, commercial product Ugilec® 141) were both formerly identified in the Lippe River sediments (Kronimus et al., 2004; Poppe et al., 1991; LUA, 2000).

In this study, seven PCB congeners (PCB 8, 28, 52, 101, 153 and 180) were quantified. Fig. 6(a) illustrates the concentration profiles of the PCBs in sum (ΣPCB), Fig. 6(b) shows the data for the PCB substitute TCBT. The concentration of ΣPCB ranges between 1 and 2632 ng/g. The first occurrence of PCBs was detected at a depth of 150 cm, with very low values. Subsequently, the concentrations increase slowly up to values between 100 and 300 ng/g (38 cm layer). A significant increase in the concentration level up to a maximum of 2632 ng/g was observed between depths 30 and 6 cm, followed by a distinct decrease towards the surface. The concentration ranges of the individual PCB congeners are different. PCBs 8, 28 and 180 occur in concentrations up to 100 ng/g, whereas the congeners PCB 52, 101 and 153 predominate, with concentrations up to 1580 ng/g per individual compound. Nevertheless, all corresponding concentration profiles exhibit similar trends. In contrast to the occurrence of the PCBs, the concentration profile of TCBT shows a continuous increase from its first occurrence at a depth of 70 cm up to the top of the core, with a concentration maximum of 13421 ng/g. These results confirm former data for Lippe River sediments analysed in 1987 and 1989 (Poppe et al., 1991).

Hexachlorobenzene (HCB) represents both industrially derived contamination and agricultural emissions. The concentration profile shows two distinct maxima [Fig. 6(c)] with values between 10 and 6548 ng/g. At the bottom of the core the concentrations are very low, but a significant increase towards a depth of 118 cm was observed. Subsequently, a second local maximum (94 cm) occurs, followed by rapidly decreasing values (±1743 ng/g). Up to the top of the core the concentrations stagnate at values of around 1500 ng/g.

Octachlorostyrene is a very specific industrial pollutant. The emission trend, as revealed by the concentration profile, is similar to HCB. There are two concentration maxima at a depth of 118 and 94 cm (Table 2). In the shallower section there is a decrease

Table 1
Concentration values of PACs, determined in the dated sediment core from the Lippe River wetland (Germany)

Depth (cm)	Acenaphthylene (ng/g)	Acenaphthene (ng/g)	Fluorene (ng/g)	Phenanthrene (ng/g)	Anthracene (ng/g)	Fluoranthrene (ng/g)	Pyrene (ng/g)	Chrysene (ng/g)	Benzo[e]-pyrene (ng/g)	Perylene (ng/g)	Dibenzofurane (ng/g)	Dibenzothiophene (ng/g)	Carbazole (ng/g)	Benzo-carbazole (ng/g)
2	65	1	438	742	387	878	558	6022	3260	984	618	181	54	38
6	92	1	573	1125	515	1245	773	6332	2034	502	1624	71	76	94
14	235	20	514	895	569	1209	640	3078	1484	608	1423	271	90	77
22	255	7	681	943	767	1221	716	7414	3374	947	2050	385	n.q.	n.q.
30	143	3	613	886	450	1021	498	5385	1205	298	1917	223	95	48
38	127	112	766	1533	890	1048	778	4116	795	284	2551	674	156	55
46	480	1462	1447	3256	1881	1806	1467	5136	883	206	6315	n.q.	160	50
54	241	195	1159	2664	1122	2697	1490	6595	2381	542	4096	2939	171	88
62	251	24	585	953	628	1082	637	5119	2120	380	2346	1392	87	53
70	178	2	790	1191	757	1682	993	11110	2210	395	3514	n.q.	86	60
78	334	10	626	1014	868	1743	902	7497	7362	922	2452	414	59	94
86	230	31	878	1401	1197	2129	1192	10574	13156	2223	3880	n.q.	130	92
94	362	10	1253	1490	916	1938	1091	10570	2363	657	5070	505	103	107
102	397	10	817	1304	1135	2536	1115	8592	12119	3000	3259	66	93	90
110	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	2148	537	192	n.q.	349	143	146
118	467	45	1015	1237	1018	2570	828	7376	3754	837	3401	343	113	130
126	203	5	473	612	486	1382	552	4120	1971	479	1522	200	59	n.q.
134	274	95	732	861	882	905	589	4156	824	202	2634	201	107	97
142	14	0	108	283	59	325	174	1284	321	80	667	1978	19	16
150	20	1	100	282	56	353	159	1483	401	85	480	0	0	n.q.
158	11	1	41	121	19	219	58	888	246	47	176	0	11	7
166	3	0	8	19	0	60	10	350	117	28	17	0	6	8

n.q., not quantified.

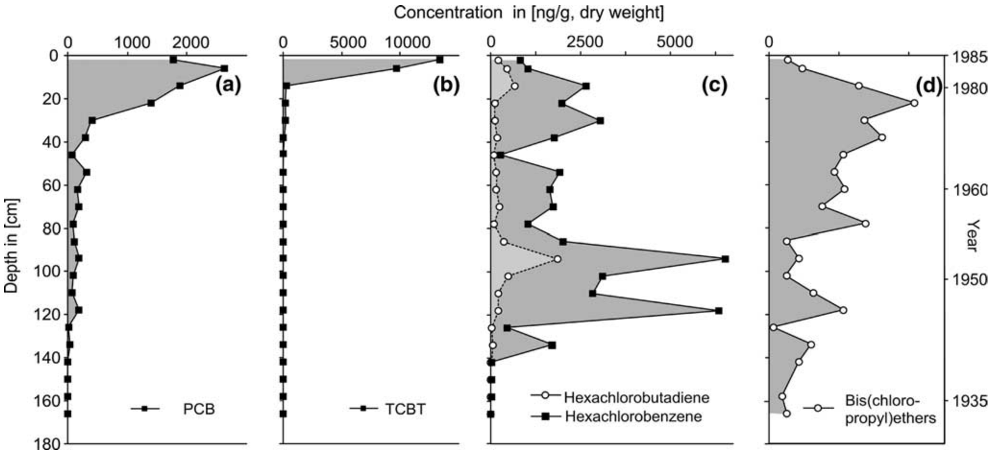

Fig. 6. (a–d) Depth- and time-correlated concentration ranges of industrial markers ΣPCB, TCBT, hexachlorobenzene, hexachloro-1,3-butadiene and bischlorobutylethers (2 isomers) in dated sediments from a Lippe River wetland (Germany).

down to average values of ±280 ng/g between 54 and 14 cm and up to values of ±100 towards the surface layer.

Hexachloro-1,3-butadiene is another representative of emission of industrial origin [Fig. 6(c)]. The concentrations range between 3 and 1863 ng/g with a maximum value at a depth of 94 cm. Below and above this layer, similar average values of ±170 ng/g were detected. Furthermore, a second concentration maximum at a depth of 18 cm is followed by slowly decreasing values towards the top layer.

The compound (1-chloro-2-propyl-2-chloro-1-propyl)ether was the last industrial marker 2, analysed as two isomers. The concentration profile [Fig. 6(d)] exhibits a generally increasing trend from the bottom up to a depth of 22 cm, with concentrations between 7 and 208 ng/g. Subsequently, a significant decrease towards the top of the core was detected.

3.3.3. Linear alkylbenzenes

Linear alkylbenzenes (LABs) are alkylated benzenes with linear C_{10}–C_{14} alkyl chains. As a residue of detergents, LABs reach the river system mainly by way of municipal sewage and waste water. The systematic change in their isomeric composition is used as an indicator for the extent of microbial degradation. For this purpose, two types of isomers are considered: (i) the external isomers (benzene ring attached to the end of the alkyl chain or at the 2- or 3-position) and (ii) the internal isomers (benzene ring attached in the middle of the alkyl chain). The ratio of internal to external isomers (I/E-ratio) has been proposed as an index of the degree of selective microbiological degradation. Thus, higher I/E ratios indicate a higher microbial degradation (Takada and Eganhouse, 1998). The concentration profiles of several C_{10}–C_{13} linear alkylated benzenes were determined as presented in Table 2. As an example, the concentration profiles of the external C_{12}-LABs are represented in Fig. 7(a), together with the calculated I/E-ratios. The concentrations of the isomers (Σ5-C_{12}- and 6-C_{12}-LABs) range between 1 and 62 ng/g. The concentration profile reveals two distinct maxima at a depth of 78 and 14 cm, respectively. Between both maxima concentrations are in the range of approx. 25 ng/g. Much lower concentrations – between the quantitation limit and approx. 5 ng/g – are encountered in the lower part of the profile. The I/E-ratios [black dots in Fig. 7(a)] within the sediment profile range between 0.4 and 0.8 with higher ratios in the deeper layers.

3.3.4. Organotin compounds

In addition to tetrabutyl tin, the key chemical material of butylated organotin compounds, mono-, di- and tributyl tin were also detected. TBT reaches the Lippe River system by way of industrial waste water as well as emissions from anti-fouling agents used in marine paints for shipping and fish cages. The concentration profiles generally reveal an onset of contamination in younger sediment levels above a depth of 62 cm. Increasing values up to a maximum peak at a depth of 6 and 14 cm [Fig. 7(b) and (c)] are followed by significantly lower concentrations in the top layer. The concentrations were found to range between 10 and 1051 ng/g for tetrabutyl tin, 1 and 19 ng/g for TBT, 9 and 130 ng/g for dibutyl tin, and 2 and 310 ng/g for monobutyl tin.

3.3.5. Galaxolide/tonalide

The musk fragrances galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-(g)-2-benzopyrane, HHCB) and tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-tetralin, AHTN) enter fluvial systems mainly by way of municipal emissions. The concentration profiles of both synthetic musks [Fig. 7(d)] exhibit very similar concentration trends with only little variation. Galaxolide and tonalide were not detected in the lower horizons. The

Table 2
Concentration values of quantified compounds with different emission sources: linear alkylbenzenes (LAB), bis(-4-octylphenylamine (Vanlube 81®), organochlorine compounds and limonene, determined in the sediment core of the Lippe River wetland (Germany)

Depth (cm)	ΣC_{10}-LAB (ng/g)	ΣC_{11}-LAB (ng/g)	ΣC_{12}-LAB (ng/g)	ΣC_{13}-LAB (ng/g)	Bis(4-octyl-phenylamine) (ng/g)	Octachloro-styrene (ng/g)	Limonene (ng/g)	Dichloro-carbazole (ng/g)	Pentachloro-butadiene (ng/g)	Dichloro-benzene (ng/g)	Trichloro-benzene (ng/g)
2	17	77	85	55	149	89	8	16	47	88	21
6	23	94	99	67	9	106	11	32	81	175	28
14	37	154	158	103	1	294	14	8	262	282	64
22	38	132	115	63	0	259	13	n.q.	181	248	40
30	24	56	65	35	1	342	7	0	396	95	26
38	31	112	82	45	0	213	11	0	584	211	47
46	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	1	0	406	224	22
54	19	28	18	10	0	208	19	0	454	153	43
62	n.q.	n.q.	n.q.	n.q.	0	97	12	0	82	113	43
70	22	22	33	26	0	93	7	0	27	47	37
78	12	29	67	47	0	50	10	0	83	110	42
86	49	66	126	83	0	131	12	0	307	174	146
94	54	87	203	154	0	776	11	0	218	211	294
102	32	113	192	109	0	443	6	0	98	76	116
110	40	33	45	19	0	202	7	0	106	83	18
118	19	12	17	10	0	639	5	0	14	18	5
126	6	2	1	1	0	31	2	0	17	6	2
134	21	13	5	1	0	81	9	0	7	49	11
142	1	1	1	0	0	2	2	0	9	3	2
150	2	1	1	0		2	3	0	2	5	2
158	1	1	1	0	0	1	2	0	1	0	1
166	0	0	0	0	0	1	1	0	0	0	0

n.q., not quantified.

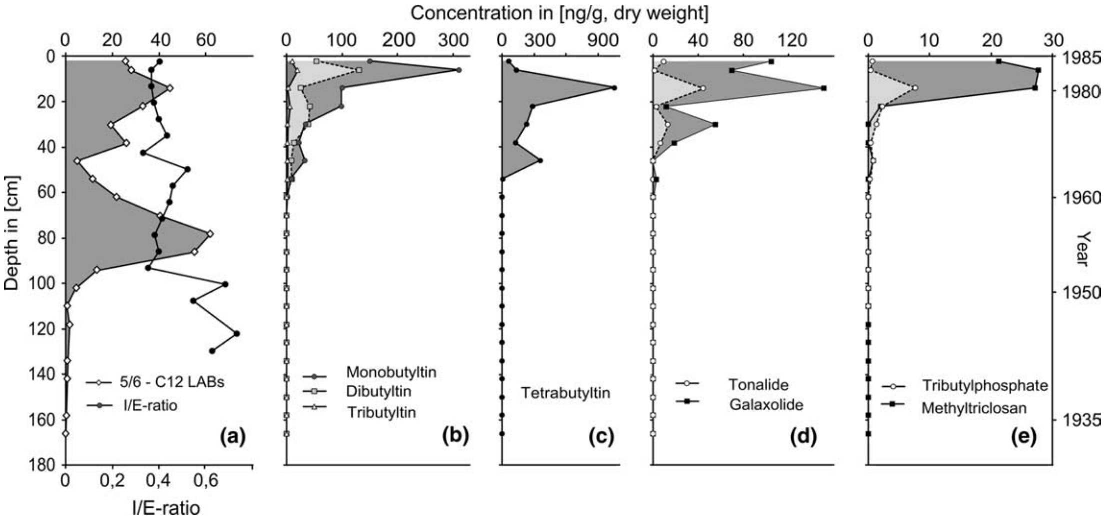

Fig. 7. (a–e) Depth- and time-correlated concentration ranges of LABs, organotin compounds, synthetic musks, tributylphosphates and methyltriclosan, determined in dated sediments of a Lippe River wetland (Germany).

first occurrences of both compounds were encountered at a depth of 54 cm, with concentration levels increasing towards the top. The maximum values were determined in the 14 cm layer, with 151 and 44 ng/g, respectively.

3.3.6. Methyltriclosan

Methyltriclosan is a rarely reported contaminant in riverine sediments. It enters the fluvial environment via municipal effluents. The concentrations in the sediment core range between 1 and 28 ng/g. The first occurrence of methyltriclosan was detected at a depth of 46 cm, with very low values [Fig. 7(e)]. A concentration maximum is reached at a depth between 14 and 6 cm.

3.3.7. Tributylphosphate

The last anthropogenic marker compound analysed in this study was tributylphosphate (TBP). TBP enters the aquatic environment via municipal as well as industrial sewage effluent. The concentration trend illustrated in Fig. 7(e) shows a great similarity with that of methyltriclosan. The first occurrence of TBP was detected in the 54 cm layer, followed by low concentrations up to 1 ng/g without any significant variation. Towards the top layers (14 cm), rapidly increasing concentrations, up to 7.8 ng/g, were observed.

4. Discussion

A combination of radiological and geochemical analyses of a sediment core derived from a riparian wetland of the Lippe River was used to determine the deposition and emission periods of individual contaminants. The layers of the sediment core cover a sedimentation period from 1935 to 1986. Given appropriate environmental stability, the concentration profiles detected for inorganic and in particular organic compounds thus reflect the emission of the contaminants to the corresponding riverine system. Consequently, variations in riverine contamination loads were reflected in the sediment core by way of varying concentrations.

The Lippe River contains an extensive catchment area with numerous municipal, industrial and agricultural emission sources. With the beginning of mining activities in the Lippe River area around 1900, the waste water discharge increased significantly. Because of obvious damage caused to the environment, sewage treatment plants were installed from 1930. Altogether, 83 municipal and industrial sewage treatment plants were put into service until 1988 (Fig. 2; LWA, 1989). Nevertheless, extensive investigations into the organic and inorganic content of the waste water discharge into the river did not start until the 1980s. Documentation and specific environmental data are very rare prior to 1980. Therefore, the interpretation dates determined in this study are based on more or less coherent contemporary documents such as reports on water quality, published by several water authorities (e.g., Lippeverband) and the Environmental Agency of North-Rhine Westphalia (LUA-NRW). Nevertheless, concentration values of the investigated components are comparable with data published earlier (e.g., Klös and Schoch, 1993a,b).

In the following sections, the time-correlated concentration profiles are discussed with respect to the main pollution sources (industrial, municipal and agricultural emissions) in order to provide a comprehensive view on the pollution history of the Lippe River.

4.1. Mining activities

The pollution discharge of numerous heavy metals and specific organic compounds in this area could be attributed to mine-water drainage and sewage water from coking plants and mining industry, as documented already by numerous former studies (e.g., LWA,1982,1987,1991; LUA, 2000; Lippeverband, 1975; Klös and Schoch, 1993a,b; see Fig. 2).

Heavy metals are biologically and chemically non-degradable, and therefore their persistence reveals not only their ecological and ecotoxicological relevance but characterizes them as stable marker species. Significant maximum concentrations of all heavy metals investigated were correlated to an emission time between 1945 and 1955. This pollution trend can be associated with increasing mining activities after the Second World War and related mine water drainage. The results and evaluations are consistent with results published by Klös and Schoch (1993a). Decreasing heavy metal contaminations and a reduction in pollution levels in the 30–80 cm layers corresponding to 1955 and 1975 were correlated with: (i) the stepwise closure of Pb/Zn-mines, (ii) the reduction of mine water contributions derived from the coal mining industry (Klös and Schoch, 1993a) and (iii) the increased river development and new sewage treatment plants (LWA, 1991). Furthermore, high concentrations for the sedimentation period from 1975 to 1980 were associated with renewed increase of mining waste water and industrial sewage discharge, as well as increasing car traffic and rising discharge by heat generation and production of electricity (Klös and Schoch, 1993a).

However, anthropogenic emissions can also be traced to sources other than mining. This can be reflected in more detail by way of specific organic marker compounds. Most of these compounds have entered the list of priority pollutants due to their biological and chemical persistence (Takada and Eganhouse, 1998). This reveals not only their ecological and ecotoxicological relevance but characterizes them as stable marker substances.

Polycyclic aromatic compounds are common constituents of fossil fuels. Due to the intensive usage of petroleum, coal and oil related products; these compounds are released in high amounts into the aquatic environment. Additionally, PACs enter the aquatic system and corresponding floodplains after formation during incomplete combustion processes and subsequent atmospheric deposition (Sanders et al., 1993). Perylene and benzo[a]pyrene were analysed as representative PAHs of pyrogenic origin (Volkman et al., 1997). But, there was no clear assignment, based on fingerprints of significant PAHs, to allow an obvious statement regarding their origin (fossil fuel or atmospheric input).

Generally, all PACs exhibit concentration profiles with only minor variations. A significant accumulation was observed within the time period between 1947 and 1960. This contamination trend exhibits a strong similarity to those of the mining-derived heavy metals, as described above. Thus, a close correlation of the PAC emission with mining activities in particular with the coal mining industry can be inferred. Another contamination source of PACs in the sediments is a refinery, situated close to the sampling location. Decreasing contamination trends in PAC contaminations are attributed to improved sewage treatment plants (Lippeverband, 1975).

Further indicators of mining activities are polychlorinated biphenyls (PCBs), due to their extended usage in hydraulic oil in the mining industry (Poppe et al., 1991). The variety of their technical applications (e.g., in capacitors, transformer oils and high-pressure lubricants) and resulting emission sources lead to a distinct correlation of PCB contamination with local mining activities. In the 1980s the mining industry substituted PCBs gradually with tetrachlorobenzyltoluenes (TCBT, commercial product, Ugilec$^{®}$ 141). But the ecotoxicological behaviour of TCBTs is very similar to PCBs (Poppe et al., 1991). Because of their toxicity, persistence and bioaccumulation TCBTs have been included into the list of priority pollutants and their use has also been restricted since 1990.

The substitution of PCBs by TCBTs is clearly reflected in the sediment core [Fig. 6(a) and (b)]. The first appearance of TCBT coincides with the decrease in PCB concentrations since the mid 1970s. However, the contamination history of PCBs, i.e., their distribution within the sediment core differs significantly from that of the mining markers discussed above. In particular, the sharp increase in concentrations since 1975 is interpreted as a superimposition of further emission sources.

4.2. Industrial emissions

Further halogenated compounds identified in the sediment core specifically reflect the influence of industrial activities on the pollution level of the Lippe River in time. In detail, Cl_2- to Cl_6-benzenes, octachlorostyrene, hexachloro-1,3-butadiene and bis(chloropropyl)ethers were quantified. A distinct association with emissions derived from industrial areas situated at the lower river section has already been proposed by Kronimus et al. (2004).

Chlorinated benzenes are key precursors for the industrial production of colours, pesticides, rubber products and disinfectants. Additionally, HCB was used for a long time as a pesticide. Octachlorostyrene is a specific by-product of the production of magnesium, as well as a by-product of the technical production of chlorine (Kaminski and Hites, 1984). Hexachloro-1,3-butadiene is used in rubber production, as hydraulic liquid, solvent and as a by-product of the technical synthesis of volatile chlorinated compounds like tetrachloroethene (Booker and Pavlostathis, 2000). Bis(chloropropyl)ethers represent by-products of the technical synthesis of epichlorhydrin, used for the production of epoxy resins and disinfectants. The concentration profile of the individual chlorinated compounds reveals different emission histories.

For the chlorinated benzenes, a very similar distribution within the sediment core is observed as for some PAHs, e.g., benzo[a]pyrene. An elevated large scale industrial activity related to these compounds can be deduced for the time between 1947 and 1955. We attribute the decrease in contamination towards the top layers to a reduction of emissions as a result in more efficient sewage treatment plants [Fig. 1(a) and (b)] as well as a modified array of products. The concentration profile of HCB [Fig. 6(c)] and all lower chlorinated benzenes (Table 2) suggests the dominance of industrial sources responsible for the contamination as contrasted to agricultural emission derived from pesticide usage. It should be noted that the contamination level of 1,4-dichlorobenzene was elevated in the time period between 1975 and 1980, comparable with concentration levels determined for Rhine River sediments 1982/1983. The extensive use of 1,4-dichlorobenzene as an odorous ingredient of toilet cleaners contributed additionally to the contamination via municipal sewage effluents (LWA, 1987, 1989).

The vertical distribution of octachlorostyrene agrees very well with that of the chlorinated benzenes, reflecting a similar industrial source and usage. With respect to hexachlorobutadiene and its de-chlorinated congener pentachlorobutadiene, slight differences within the contamination history were observed. Concentrations of hexachlorobutadiene maximize in a narrow time interval around 1955. A second maximum was detected near the top of the core. The concentration and correlated contamination profile of bis(chloropropyl)ethers reflect a different load history. The emissions increased continuously from 1945 to 1978, but were significantly reduced thereafter. The recently decreasing pollution level is probably due to improved sewage treatment processes.

Apart from chlorinated compounds, butyl tin compounds also reflect the contribution of industrial effluents to the contamination of the Lippe River system. Tributylated tin compounds enter the aquatic environment due to its migration from anti-fouling paints. Sources of di- and monobutylated tin compounds are municipal and industrial waste water, sewage sludge and landfill leaks (Fent and Hunn, 1991). The production and usage in particular of TBT has been restricted in Germany since 2001. The major contribution to the contamination of the Lippe River system can be attributed to an organotin-consuming and -producing industrial plant (Kronimus et al., 2004). All butylated tin compounds are dominated by tetrabutyl tin, the synthetic precursor for the preparation of all lower butylated substances. This pattern was confirmed as a typical industrial signature of riverine contamination, e.g., by Poppe et al. (1991).

Butyl tin compounds were detected in the core layers representing an input time since approx. 1970. This observation agrees well with the initiation of a large scale production in the area investigated. The concentration profile reveals a significant increase in the upper layers until approx. 1980. However, thereafter a sharp decrease in the top layer was observed corresponding to a similar contamination trend in all other industrial markers.

4.3. Municipal effluents

As one of the most important pollution sources of riverine systems, municipal effluents have been considered in this study by analysis of linear alkylbenzenes (LABs), limonene, methyltriclosan, synthetic musk fragrances, TBP and phosphate-based flame retardant. All compounds are known constituents of effluents of sewage treatment plants (Takada and Eganhouse, 1998 and references therein) and were previously identified in surface sediments from the Lippe River (Kronimus et al., 2004). Interestingly, some of these compounds occur exclusively since 1970.

LABs are raw materials for the industrial production of linear alkylbenzenesulfonates (LASs), the most widely used anionic surfactants. Large-scale production and usage of LAS type detergent started in the early 1960s as biodegradable substitutes for the non-biodegradable tetrapropylene-based alkylbenzenesulfonate (ABS). In the sediment core from the Lippe River floodplain, alkylbenzenes with linear C_{10}–C_{13}-alkyl chains were detected since 1950 [Fig. 7(a)], with rapidly increasing concentrations until 1960, representing the ABS/LAS-substitution (Reiser et al., 1997). The subsequent decrease in contamination has to be attributed to improved sewage treatment techniques in the time period until 1960 in this region. In order to avoid misinterpretations due to degradation processes affecting these more biodegradable compounds, the I/E-ratios approach (see Section 3.1) was applied. The calculated ratios indicate a slowly increasing degradation towards the bottom of the sediment core [Fig. 7(a)]. Hence, using the more stable internally substituted isomers for concentration profiles, a realistic view of the contamination history was achieved.

As further municipal contaminants, synthetic musk fragrances, galaxolide (HHCB) and tonalide (AHTN) were determined. They are used widely in soaps, cosmetics and laundry detergents (Rimkus et al., 1997). Also methyltriclosan, the methylated metabolite of triclosan, commonly used as an antibiotic or disinfectant in personal care products, is regarded as a common environmentally stable sewage effluent indicator (Lindström et al., 2002; Kronimus et al., 2004). In addition, tris(chloropropyl)phosphates (TCPP), belonging to the group of technical flame retardants and mainly used in polyurethane foams and discharged by municipal effluents, were determined. TBP can be assigned to both municipal and industrial effluents, because of its usage as plasticizer and additive in cellulose-varnish as well as a constituent during cellulose production, and, to a minor extent, as solvent for rare earths (Fries and Püttmann, 2001).

In contrast to common contaminations like heavy metals, PACs and LABs, we classify butylated tin compounds, synthetic musk fragrances, methyltriclosan, TBP, TCPP and some chlorinated compounds as "modern contaminants" [Fig. 7(b)–(e), Table 2]. They first occur in the sediment layers corresponding to 1975. Subsequently, sharply increasing concentrations levels were determined with compound-specific variations towards the top layer. With respect to their increasing production rates and usage, their reduced concentration in the top layer implies an enhanced elimination as the result of improved sewage treatment processes.

4.4. Miscellaneous

Further contaminants detected in the sediment core could not be definitely attributed to individual emission sources, because the knowledge about their environmental occurrence and behaviour is limited. Examples include the high viscosity lubricant bis(-4-octylphenylamine; Vanlube 81®), 3,6-dichlorocarbazole and limonene. The quantification of limonene revealed a uniform concentration profile, which cannot be attributed to any other contamination history discussed so far. In contrast, the occurrence of 3,6-dichlorocarbazole, formerly not described as an environmental contaminant, exhibits great similarity to more modern sewage marker compounds (see Table 2).

5. Conclusions

Based on geochemical analyses applied to a dated sediment core derived from a riparian wetland of the Lippe River, numerous specific substances were analysed quantitatively. These substances show vastly different contamination histories. For the most important emission sources, information on technical production and usage as well as on the pathways of the individual pollutants was discussed.

Contamination related to mining activities was characterized by concentration profiles of specific heavy metals, PCBs and selected PACs. Maximum mining discharge was observed for the time interval between 1945 and 1955. Subsequently, in the period since 1955, emissions decreased as a result of improved waste water treatment as well as reductions related to the economic situation.

The TCBTs are very specific marker compounds for mining activities. However, their usage as indicator substances is restricted to their application time since approx. 1970. In contrast, PCBs which were formerly used in the same field of technical application are not specific mining marker compounds due to multiple emission sources.

Besides the mining industry, two further important industrial fields were characterized. Halogenated aromatic and aliphatic compounds indicated a huge discharge derived from the chlororganic chemical industry. Maximum emissions were attributed to the time period between 1947 and 1955. These emissions are paralleled by decreasing emissions related to mining activities after 1955. In accordance with other publications, we suggest that both types of contaminations were reduced mainly by improved waste water treatment techniques. In addition, the concentration profiles of organotin compounds as another group of industrial pollutants indicate a pollution history corresponding to their individual usage time period since 1970.

In addition to the main classification system which relates the described contaminants to mining and industrial activities, municipal sewage and agricultural effluents, we suggest, as a second set of criteria regarding pollution history, classifying contaminants as either common or modern. Common contaminants occurred in the sedimentary record over a long period of time, whereas more modern contaminants occurred only in sediment layers representing a time period since 1970. However, for most of the contaminants described, a significant decrease in concentration and, consequently, of corresponding emissions into the Lippe River, was observed in the top layers. These observations indicate the beginning of an efficient cleaning process covering a broad spectrum of contaminants, probably as the result of modern sewage treatment techniques.

Interestingly, indications for a significant contribution of agricultural contaminants were not observed. However, several obviously anthropogenic compounds (e.g., 3,6-dichlorocarbazole) remain uncorrelated with distinct emission sources due to limited information concerning their technical application and usage or their emission pathway. In consequence, they could not be considered for the comprehensive reconstruction of the pollution history of the Lippe River for the time period between 1935 and 1986.

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