

Contamination history of suspended river sediments accumulated in oxbow lakes over the last 25 years

Morava River (Danube catchment area), Czech Republic

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Abstract

Background, aims, and scope Embankment of meandering river systems in many industrial areas results in the formation of artificial oxbow lakes that may act as perennial or intermittent traps for river sediments. Their deposits can be dated using a combination of historical and stratigraphic data, providing a good means to study historical records of contamination transported by rivers. Contamination history over the last few decades is of special significance for Central and Eastern Europe as it can reflect high pollutant levels in the second half of the twentieth century and the subsequent improvement after the fall of the Iron Curtain. The purpose of this study was to investigate recent sediments of an oxbow lake of the

Morava River, Czech Republic, their stratigraphic records, sediment architecture, and history of contamination.

Materials and methods Seven ground-penetrating radar (GPR) profiles and three sediment cores up to 4 m deep were studied. The stratigraphy of the cores was inferred from visible-light spectrophotometry, X-ray radiography, grain size analysis, and semiquantitative modal analysis of sandy fractions. The sediments were dated using the ^{137}Cs mass activity and combinations of stratigraphic and historical data. The cores were sampled for concentrations of heavy metals and persistent organic pollutants. Wet sampled, lyophilized, and sieved sediments were extracted and analyzed for heavy metals by inductively coupled plasma mass spectrometry (ICP-MS) of aqua regia leachate and for persistent organic pollutants by gas chromatography (GC-ECD and GC-MS).

Results Three distinct sedimentary sequences (S1, S2, and S3) were identified. The basal sequence S1 represents river channel sediments deposited before the formation of the oxbow lake, most likely before the 1930s. The boundary between the S1 and S2 sequence correlates with the level of sediment dredging from 1981 evidenced from historical data. The overlying sequences S2 and S3 represent a post-dredging sediment wedge, which progrades into the lake. ^{137}Cs dating revealed a distinct Chernobyl 1986 peak at ~150 cm depth inferring sedimentation rates up to 7.7 cm/year. Sediment contamination abruptly increased from the pre-1930s deposits to the post-1981 deposits. The concentration levels increased two to five times for Pb, As, Zn, and Cu, about 10 to 15 times for Cr, Sb, and Hg, up to 34 times for Cd, and 25 to 67 times for DDTs, PCBs, and PAHs. The concentrations of most contaminants remained approximately constant until the late 1980s when they started to decrease slowly. The decreasing trends

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were most prominent for heavy metals and anthracene, less prominent for DDTs, and almost absent for PCBs and most PAHs.

Discussion Different temporal and spatial patterns for various contaminants make it possible to distinguish between anthropogenic point sources from local industry (anthracene, Cr, Cd), possible diffuse sources (most PAHs), and geological background (V, Co, Ni, and Mo). The observed recent trends in heavy metal and persistent organic pollutant contamination are generally consistent with data from other Central European rivers. The roughly balanced contamination levels in sediments from the lake and the adjacent river channel suggest that the oxbow lake deposits reflect immediate levels of the contamination bound to suspended particulate matter passing through the river.

Conclusions The investigated oxbow lake accumulated suspended sediment from Morava River, developing a thick sedimentary body. The sediments offer a good time framework to study historical contamination of the river on a decade time scale. Continuous contamination trends can be traced back to the early 1980s. The results show that stratigraphic analysis of cores has a good potential for identification of uninterrupted historical trends and unconformities, e.g., due to dredging.

Recommendations and perspectives Oxbow lakes may provide an alternative to floodplains and reservoir deposits when studying river contamination history. High sedimentation rates of up to 7.7 cm/year offer a very good stratigraphic resolution, making it possible to study contamination patterns on annual or even seasonal time scales. On the other hand, oxbow lakes may represent long-term contamination stores, which are unlikely to be redistributed by river erosion and, hence, may possess significant environmental risks for the farther future.

Keywords Alluvial sediments · Czech Republic · Danube catchment area · Heavy metals · Morava River · Oxbow lakes · Persistent organic pollutants · POPs · Reservoir deposits · River sediments · Sediment dating · Stratigraphic architecture · Temporal patterns

1 Background, aims, and scope

Most of the heavy metals and organic contaminants in fluvial environment are bound to fine-grained solid particles, which are transported as a suspended load and deposited as contaminated sediments along watercourses (Förstner 2004). Many hydraulic, chemical, and biological mobilization processes may release older contaminants from the sediment into water column or groundwater, constituting potentially serious environmental hazards (Förstner 2004; Wildi et al. 2004; Westrich and Förstner

2005; Gerbersdorf et al. 2007). It has been demonstrated that contaminated sediments can be eroded during floods, dam failures, or other short-lived events (Haag et al. 2001) and/or release toxic compounds in elevated concentrations on a long-term scale (Miller et al. 1996; Hudson-Edwards et al. 1997). The history of fluvial contamination thus provides an important source of information in the environmental risk assessment with several contamination history studies being conducted in river basins worldwide (Kern and Westrich 1995; Wildi et al. 2003, 2004; Heim et al. 2004; Forsythe et al. 2004; Förstner et al. 2004; Westrich and Förstner 2005).

Long-term deposition of fine-grained sediments is limited in active river channels. In both ancient and modern rivers, channel deposits are characterized by lateral and longitudinal accretion units (bars) composed typically of very fine to coarse sand and gravel transported by bed load (Collinson 1996; Miall 1996; Hesselink et al. 2003; Robert 2003). Although coarse-grained sediments may locally contain considerable levels of contamination (Bervoets et al. 1999), their transport pathways and residence times in the highly dynamic channel settings are difficult to predict. There is also a strong spatial variability of sediment contamination in many rivers due to the decrease of contaminant concentrations with increasing distance from point sources (Wardas et al. 1996; Hudson-Edwards et al. 1997; Richman and Dreier 2001) due to hydrological factors and short-term discharge variation (Herr and Gray 1996). Potential long-term studies of contamination history from the channel deposits are thus subject to considerable error.

On the other hand, clay, silt, and organic particles that carry most of the contaminants are usually transported as suspended load and deposited in low-energy settings such as natural levees, floodplains, and abandoned channels. In regulated river systems, such deposits accumulate preferentially in lock reservoirs, embanked floodplains, residual channels, and other artificial sediment traps (Hesselink et al. 2003). Stratigraphic record of these sediments is usually much more complete than in river channels, but omissions are still frequent. While incompleteness of the stratigraphical record is self-evident due to the intermittent nature of floods in floodplains, major floods may erode the bottom and generate unconformities in some reservoirs (Kern and Westrich 1995; Haag et al. 2001). In this paper, we studied the history of river contamination recorded in sediments of an abandoned channel (oxbow lake) of Morava River, Czech Republic. The lake was separated from the active channel during river embankment in the 1930s, but permanent water communication with the active channel has been provided via underground pipe ever since enabling the lake to act as a permanent trap for suspended sediment from the river. This unique sedimentary system

generated a relatively uninterrupted sedimentary record. In 1981, sediments of the proximal part of the lake near the pipe were dredged in a zone about 200 m long and 50 m wide to a level about 2.2 m below the mean water level in the lake. Since the dredging, the lake has received new sediment, which now stands more than 0.5 m above the mean water level in the most proximal part of the lake, forming a thick sediment wedge.

2 Geographic setting

The study area is located in the lowlands of the Lower Morava Valley, in the eastern part of the Czech Republic. Geologically, it forms the northern tip of the Vienna Basin filled with Upper Miocene marine and lacustrine sediments almost 5,500 m thick. Fluvial sedimentation of Morava River, a left-hand tributary to the Danube River, started with deposition of aggrading braided-channel gravels and sands in the late Pleistocene. During the late Pleistocene to Holocene, the river turned to meandering mode giving rise to alluvial terraces and extensive floodplains composed mainly of silty clays, sandy silts, and soils (Havlíček 1994). The river lowlands have been permanently settled since the sixth century AD. The river was embanked in the first half

of the twentieth century when the main channel was straightened and shortened by about 40% giving rise to more than 180 artificial oxbow lakes. The oxbow lake Certak is located on the right bank of the river, in the SE outskirts of Uherské Hradiště, eastern Czech Republic (Fig. 1). The lake, about 1.2 km long and 50 m wide, is connected to the active channel of the Morava River by underground pipe with 0.8 m diameter located at its south-eastern end (WGS-84: 49°04'05.47" N; 17°26'09.69" E, mean water level altitude is 175 m). Data from the hydrological station Spytihnev located in the river 8 km upstream to the oxbow lake indicate the total catchment area to reach 7,891.12 km², the mean annual river discharge being 55.4 m³·s⁻¹, and the maximum measured discharge 791 m³·s⁻¹ (11 June 1997).

3 Materials and methods

3.1 Sediment sampling and stratigraphy

Stratigraphy of the lake sediments was studied from two 4-m-deep cores on dry land (CRT1, CRT2) and one 2-m-deep core (CRT3) under water (see Fig. 1). On dry land, the cores were taken into four 1-m-long translucent foil liners with

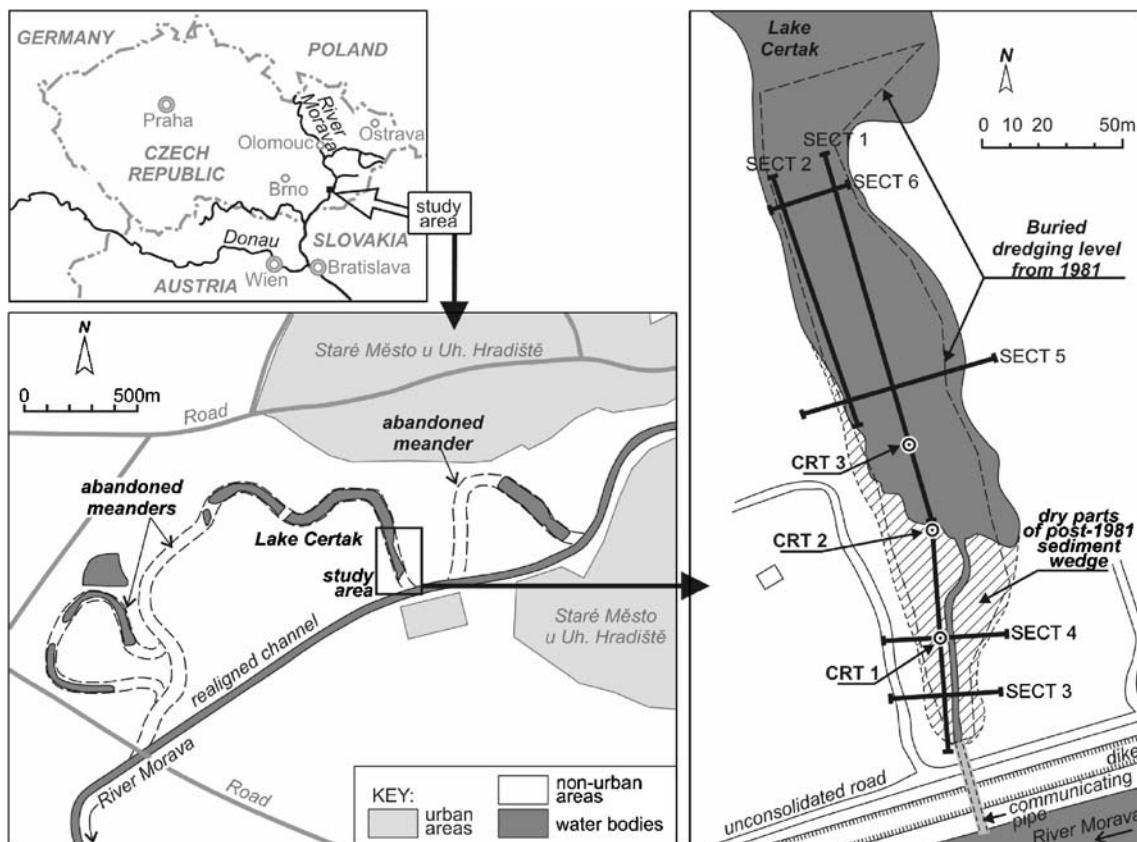


Fig. 1 Map of study area with localization of sampling sites and GPR profiles

46 mm diameter using a percussion drilling set (Eijkelkamp, The Netherlands). Under water, the cores were taken into two 1-m-long translucent sampling tubes with 40 mm inner diameter using a rod-operated Multisampler piston core sampler (Eijkelkamp, The Netherlands) to eliminate sediment compaction. Several cores were taken from one sampling site to increase sediment yield. Some of the cores were cut, described, and sampled for the pollutant concentration study directly in the field. Other cores were sent to the laboratory, X-ray radiographed, then cut lengthwise, described, photographed, and sampled for petrographic description, grain size analysis, ^{137}Cs dating, and chemical analysis of major pollutants. Sediment grain size was studied from samples weighing 6.7 to 25.7 g (dry weight), taken at 0.2 to 0.7 m intervals. The grain size distribution was analyzed by wet sieving ($>63\ \mu\text{m}$ fraction) and CILAS 1180 laser particle sizer ($<63\ \mu\text{m}$ fraction). To characterize sediment color and organic carbon content (Viscara-Rossel et al. 2006a, b), two cores were measured by SP62 spectrophotometer (X-Rite, USA) with an 8-mm aperture, operating in CIE $L^*a^*b^*$ color space and D65/10° illuminant/observer mode. The measurement was carried out in a wet condition with 1 to 3 cm vertical interval. Two cores were dated using ^{137}Cs method. Samples weighing 30 to 218 g (dry weight) were taken at 4 cm vertical intervals and then stored in sealed plastic containers for 2 weeks to establish radioactive equilibrium. Afterwards, the samples were analyzed for concentrations of K (%), Th (ppm), U (ppm), U(Ra) (ppm), and mass activity of ^{137}Cs ($\text{Bq}\cdot\text{kg}^{-1}$) using a PCAP (Nucleus, USA) laboratory gamma-ray spectrometer with NaI(Tl) $\varnothing 100\times 100$ mm scintillation detector with 7.9% resolution. The obtained spectra were compared to a set of IAEA laboratory standards and Exploranium, Canada reference samples. The detection limit for the ^{137}Cs mass activity of the equipment was $4\ \text{Bq}\cdot\text{kg}^{-1}$. Core data were supported by ground penetration radar (GPR) profiles. Three longitudinal and four transversal profiles in total length of 436 m were measured by Sensors & Software PULSE EKKO 100 A equipment at 200 MHz frequency with 2 m antenna spacing and a 0.25-m step of measurement. Three profiles were measured on dry land and four under water from a boat.

3.2 Heavy metals and persistent organic pollutants

Heavy metal contents in sediment samples were evaluated based on the aqua regia leaching process and after total decomposition of silicate matrix. For aqua regia leaching, the ISO 11466 protocol was used and modified with respect to analytical instrumentation used (3 g of dry sediment sample was leached by 7 ml HNO_3 and 21 ml HCl overnight followed by heating under reflux for 2 h; after cooling, the mixture was filled up in the volumetric flask

and diluted before inductively coupled plasma mass spectrometry [ICP-MS] measurement). For total dissolution of sample, the ISO 14869-1 procedure was used employing silicate matrix decomposition in an open vessel system by mixture of hydrofluoric and perchloric acid. One gram of ground sample was used for digestion and sample solution was diluted adequately before analysis.

ICP-MS (Agilent 7500ce, Agilent Technologies, Japan) was used for the determination of heavy metals in aqua regia leachate and total decomposed sediment samples. Elements (isotopes) suffering from polyatomic interferences were measured in He collision mode using an Octopole Reaction System. Internal standards (Ge, In, Bi) were applied for diminution of matrix effects and drift. The accuracy of the methodology was verified by analysis of soil certified reference materials (ANA 7001–7004).

For instrumental analyses of persistent organic pollutants, wet sediments were lyophilized and sieved at 2 mm sieve and 10 g of dry sediment was extracted on a Soxhth extractor simultaneously with laboratory blank and reference material. Surrogate recovery standards for the analysis of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (D10-phenanthrene, D12-perylene, PCB 30, and PCB 185; 10 ng per sample) were spiked on each sample before extraction. Terphenyl and PCB 121 were used as internal standards for PAH and PCB analyses, respectively. After extraction, volume was reduced on a rotary evaporator under a gentle nitrogen stream at ambient temperature. Activated copper was used for sulfur removal. Fractionation was achieved on silica gel columns; a sulfuric acid-modified silica gel column was used for PCB/organochlorine pesticides (OCP) samples. Samples were analyzed using GC-ECD (HP 5890) supplied with a Quadrex fused silica column, 5% Ph for PCBs (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180), and OCPs (α -HCH, β -HCH, χ -HCH, δ -HCH, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT). Sixteen US EPA PAHs were determined in all samples using a GC-MS instrument (HP 6890–HP 5973) supplied with a J&W Scientific fused silica column DB-5MS. Samples were quantified using Pesticide Mix 13 (Dr. Ehrenstorfer) and PAH Mix 27 (Promochem) standard mixtures. Laboratory blanks always contained less than 1% of the amount determined in the samples.

4 Results and discussion

4.1 Lithology and stratigraphy

Three distinct sedimentary sequences were revealed in the cores (Fig. 2). The basal sequence (S1, depths 260 to >400 cm) is composed of light gray to greenish and bluish

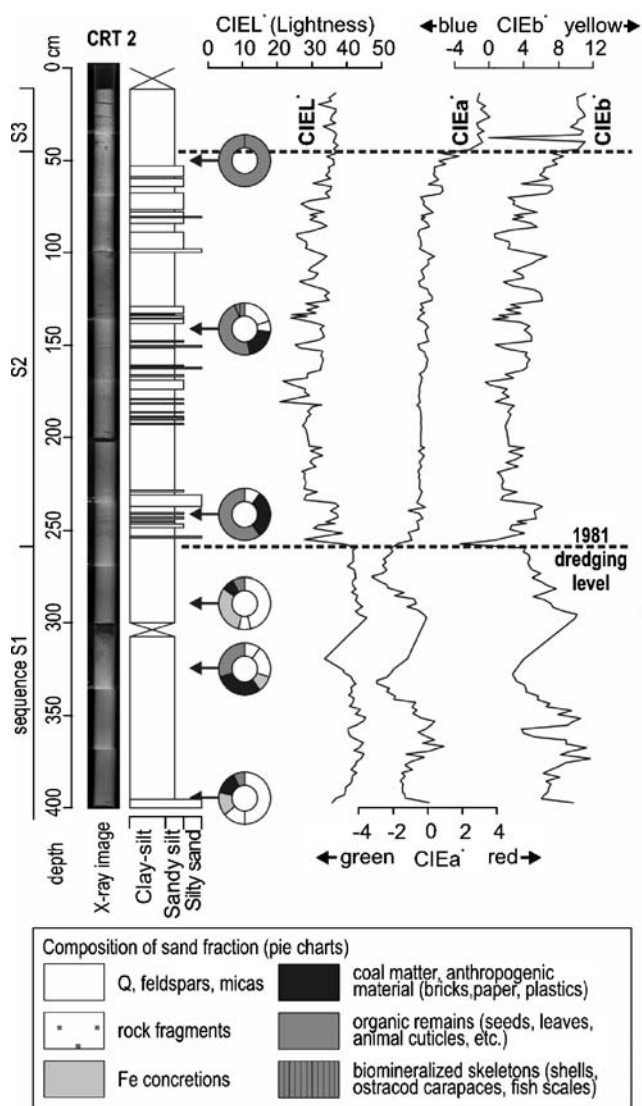


Fig. 2 Lithology, structure, color data, and composition of sand fraction of cores CRT1 to CRT3

gray (mean CIE $L^*a^*b^*$ values: L^* , 41.83; a^* , -1.33; b^* , 6.59), massive sandy silts with rare silty sand layers. Grain size study (five analyses) indicates a predominance of the silt fraction (silt: mean $76.5 \pm 6.74\%$; sand: mean $17.9 \pm 7.50\%$; clay: mean $5.6 \pm 0.85\%$). The sand fraction is relatively well-sorted and composed of abundant angular to rounded quartz grains, concretions of iron oxides, less abundant feldspars, clasts of metamorphic and sedimentary rocks, coal matter (including charcoal), and rare organic remains (insects). The overlying sequence S2 (depths from 45 to 260 cm in core CRT2, 60 to 275 cm in CRT1) consists of ~2 to ~25 cm thick layers of silts and sandy silts, which alternate with <5 cm thick, rarely cross and/or ripple cross-laminated layers of silty sands. This sequence is more dark-colored than S1 (mean CIE $L^*a^*b^*$ values: L^* , 30.53; a^* , -0.36; b^* , 2.99). It is characterized by distinct color banding with light gray to brown-gray bands

alternating with bands of dark-gray to black sediment rich in organic matter, which is nicely visible in the cyclic patterns of the CIE $L^*a^*b^*$ color data (see Fig. 2). Compared to S1, the S2 sequence contains more silt (mean $84.2 \pm 4.80\%$; six analyses) and less sand (mean $11.0 \pm 5.26\%$) and clay (mean $4.8 \pm 1.23\%$). The sand fraction is composed of abundant plant remains (seeds, leaves, and wood), invertebrate organic remains, ostracod carapaces, snail shells and coal matter, and rare angular to subangular grains of quartz, feldspars, and white mica. The uppermost sequence S3 (depths from 0 to 45 and 60 cm in CRT2 and CRT1 cores, respectively) is composed of light brown to brown-gray (mean CIE $L^*a^*b^*$ values: L^* , 35.43; a^* , 1.99; b^* , 8.82) silty loam with thin laminae of sandy silts enriched in plant remains. Grain size distribution (three analyzes) is similar to the sequence S2 (silts: mean $84.0 \pm 1.80\%$; sands: mean $10.81 \pm 1.04\%$; clays: mean $5.18 \pm 0.84\%$). The sand fraction is composed of abundant plant remains (seeds, leaves, grass, rootlets, and wood), invertebrate organic remains (insect cuticles), quartz grains, concretions of iron oxides, and rare anthropogenic material (plastics and brick fragments).

4.2 Ground penetration radar profiles

Four reflector units have been revealed from the GPR sections (Fig. 3). The basal reflector unit RU1, which is more than 6 m thick, consists of relatively well-defined, inclined reflectors, which are sometimes stacked with downlap geometry. In longitudinal sections, they form several overlapping convex-upward bodies 10 to 35 m long and up to 2 m thick. Under water, the reflectors are less visible. The arrangement of the reflectors in the transversal sections indicates lateral sediment accretion. The upper parts of the RU1 correspond to the basal parts of the sequence S1 in the cores CRT1 and CRT2. The overlying unit RU2 has a thickness from 0 m in the proximal part of the lake to ~2.5 m in its distal part. The unit has irregular bottom surface as it overlaps the convex-upward units of the RU1, and more-or-less flat upper surface, which corresponds to the level of 1981 dredging. The unit RU2 does not have very distinct reflector patterns consisting of weak, horizontal to subhorizontal reflectors, which are discontinuous to almost absent in the water part of the section. The unit RU2 corresponds largely to the sequence S1 in the cores CRT1 and CRT2. The overlying unit RU3 is only visible in the proximal part of the lake and wedges out toward the lake center. The unit has a maximum thickness of ~1.8 m, a more-or-less flat bottom surface and a slightly irregular top surface. It consists of relatively well-defined, subhorizontal to inclined, convex-upward reflectors. The unit RU3 corresponds to the sequence S2 in the core CRT1. The uppermost unit RU4 has sheet-like

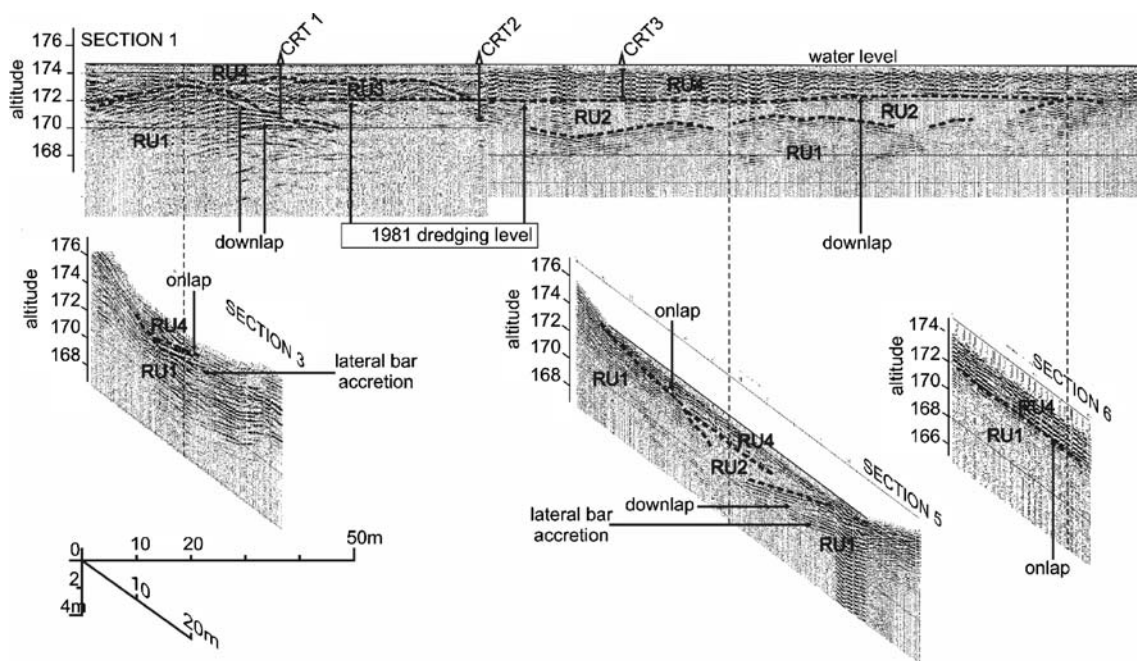


Fig. 3 Selected ground penetration radar profiles (see Fig. 1 for location)

geometry and a thickness from ~1.0 m in the proximal part to ~2.2 m in the distal part of the lake. It consists of strong, continuous horizontal to subhorizontal reflectors that indicate vertical sediment accretion. The reflectors are slightly discontinuous, slightly wavy, but still subhorizontal in the water part of the section. The reflectors show onlap or downlap terminations against the underlying RU1 unit. Several strong reflectors are slightly inclined in a proximal-to-distal direction, which indicates sediment progradation toward the center of the lake. The RU4 unit represents an active sediment wedge supplied from the point source located at the connection to the active river channel. This unit corresponds to the sequences S2 and S3 in the cores CRT1, CRT2, and CRT3.

4.3 Sedimentary environment and relative dating

The position of the 1981 dredging datum level can be interpreted from the stratigraphy and partly from the GPR sections. The most prominent stratigraphic boundary is located between sequences S1 and S2 in the cores CRT1 and CRT2. Due to their light color and, hence, low organic carbon content and the predominance of mineral grains and lack of organic matter in sand fraction, sediments of the sequence S1 are considered to represent oxygenated deposits that accumulated under permanent influence of slow currents. The GPR characteristics (RU1 and RU2) of this sequence, thus suggest the presence of bars and their lateral accretion in a river channel environment (Heinz and Aigner 2003; Robert 2003). The sequence S1, therefore, represents fluvial channel deposits. Because the river was

embanked during the 1930s, turning the depositional setting from fluvial to lacustrine, the age of this sequence is interpreted as pre-1930s.

The more fine-grained lithology, presence of numerous dark-gray to black bands rich in organic carbon, and presence of poorly decomposed organic matter (plant remains) in the sand fraction of sequences S2 and S3 suggest dysoxic conditions and slow to zero current speed for their depositional setting. The GPR characteristics of the RU4 unit suggest that the sediments accumulated by vertical accretion from water suspension, at least in the distal parts of sequences S2 and S3. In its proximal part, the inclined reflectors of the RU3 suggest a lateral accretion of minor sediment bars along the feeder channel connecting the present-day lake to the feeder pipe. In any case, sequences S2 and S3 and their corresponding reflector units RU3 and RU4 represent oxbow lake deposits. Historical technical documentation (Beníček 1981) suggests that the ground level of dredging was located ~2.2 m below water level in 1981. This level matches the position of the sequence S1/S2 boundary in the CRT1 and CRT2 core, although there are decimeter-scale differences due to the relative height of the drilling sites above water level (Fig. 4), and possibly due to water level fluctuations in the lake. The whole sequences of S2 and S3 have, therefore, accumulated in the proximal part of the lake since 1981.

4.4 ^{137}Cs dating

A distinct peak in ^{137}Cs mass activity (maximum $254 \text{ Bq}\cdot\text{kg}^{-1}$) was found in sequence S2 at 148 to 124 cm depth in the

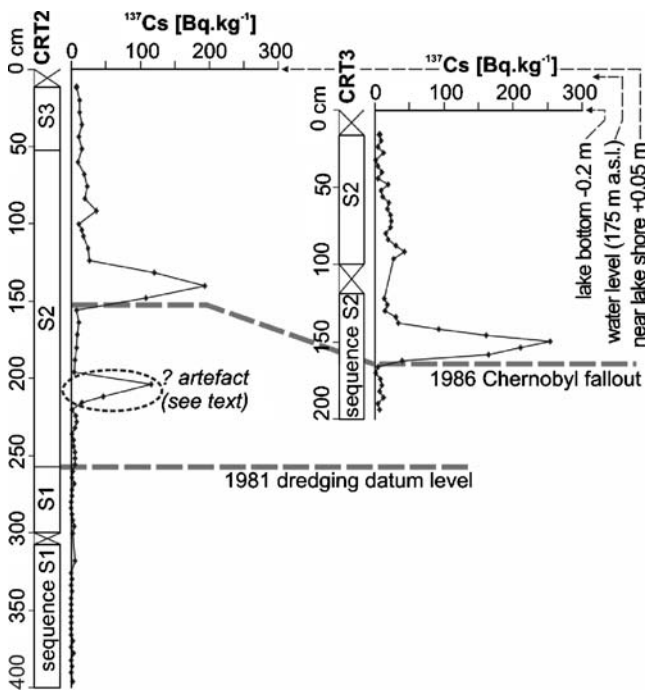


Fig. 4 Mass activity of ^{137}Cs from the CRT2 and CRT3 cores and interpretation of datum levels

CRT2 core and 162 to 138 cm depth in the CRT3 core (see Fig. 4). The peak is considered to indicate the Chernobyl nuclear power plant accident in 1986. Similar peaks associated with threefold to ninefold increases in the mass activity were reported to indicate the Chernobyl fallout in marsh and river deposits in the UK, the Netherlands, and Poland, although the background values may vary by one to two orders of magnitude depending on the geographic location (Callaway et al. 1996). The peak is located above the 1981 dredging datum level and, therefore, does not likely represent older nuclear weapon tests from the 1960s (cf. Roussel-Debel et al. 2006). The ^{137}Cs mass activity values are very low (0 to $12 \text{ Bq}\cdot\text{kg}^{-1}$) in sequence S1 and in the lower parts of sequence S2 below the peak. The only exception is represented by a second distinct peak at 204 to 216 cm depth in core CRT2, which is considered an artifact caused by sediment washed down from the Chernobyl peak level to the bottom of the borehole during sequential drilling. Above the peak, the ^{137}Cs mass activity values gradually decrease to $\sim 10 \text{ Bq}\cdot\text{kg}^{-1}$ just below the sediment surface.

The position of the ^{137}Cs peak indicates that total accumulation rates reached 7.0 to 7.7 cm/year between 1986 and 2007. The peak in the CRT2 core is located $\sim 0.35 \text{ m}$ higher than in CRT3, if we consider the 0.25-m difference in altitude between the two drilling sites. This implies that the 1986 datum surface is inclined at an angle of about $0^\circ 45'$, which, consistently with the reflector geometry in the GPR profiles, indicates sediment progradation into the lake.

4.5 Temporal distribution of major pollutants

4.5.1 Heavy metals

The distribution of heavy metal contamination shows a distinct stratigraphic pattern. Concentrations and recalculated ages of most heavy metal samples are summarized in Table 1. The lowest concentrations were found in the pre-1930s sediments of sequence S1 (Fig. 5). The concentrations of most heavy metals increased rapidly at the S1/S2 sequence boundary between 280 and 255 cm depth in core CRT1 and between 285 and 230 cm depth in CRT2, which corresponds to the 1981 datum level. Concentrations of Pb, As, Zn, and Cu in the post-1981 deposits of core CRT2 increased with respect to pre-1930s sediments by a factor of 2 to 3.5; for example, concentrations of Pb increased from 17.4 to $47.7 \mu\text{g}\cdot\text{g}^{-1}$ and As from 6.5 to $14.9 \mu\text{g}\cdot\text{g}^{-1}$. The concentrations of Cr, Sb, and Hg increased from five to nine times (Cr, from 66.2 to $348.4 \mu\text{g}\cdot\text{g}^{-1}$; Sb, from 0.16 to $1.49 \mu\text{g}\cdot\text{g}^{-1}$; Hg, from 0.06 to $0.55 \mu\text{g}\cdot\text{g}^{-1}$). Maximum increase, by a factor of ~ 34 , was found in concentrations of Cd (from 0.11 to $3.73 \mu\text{g}\cdot\text{g}^{-1}$). Similar values have been found in the CRT1 core. On the other hand, the contamination levels of V, Co, Mo, and Ni remained approximately constant from the pre-1930s to post-1981s. Peak concentrations of Cr, Cu, Zn, As, Cd, Sb, Pb, and Hg were found in sediments of the sequence S2 in the depth range from 255 to 135 cm in the CRT1 core and 230 to 150 cm in the CRT2 core. As recalculated from the average sedimentation rate, these sediments were deposited during the early to mid-1980s. The contamination levels slowly decrease in the upper parts of sequence S2 and in sequence S3 (135 to 47 cm depth in CRT1, 150 to 40 cm depth in the CRT2 core), which corresponds approximately to the late 1980s to late 1990s. The decrease is even more pronounced in the sediments of the CRT3 core, which were deposited approximately between 1995 and 2005. Contamination levels of most heavy metals in the most recent sediments improved with respect to those from the mid-1980s: Cr (19% of the maximum level from mid-1980s), Cd (24%), Sb (30%), Zn (42%), Hg (46%), As (47%), Pb (55%), and Cu (60%).

Three heavy metal groups can be identified based on their temporal contamination patterns, which likely reflect different sources. The group including V, Co, Ni, and Mo does not show any temporal changes in concentration in sediments since the 1930s. Therefore, they are assumed to reflect the geological background. Contamination by Cu and Pb shows a rapid increase in concentrations between the 1930s and 1981, but only very moderate improvement in contamination levels since then. This group is clearly anthropogenic in origin and may be derived from diffuse sources, e.g., traffic emissions. The third group includes Cr,

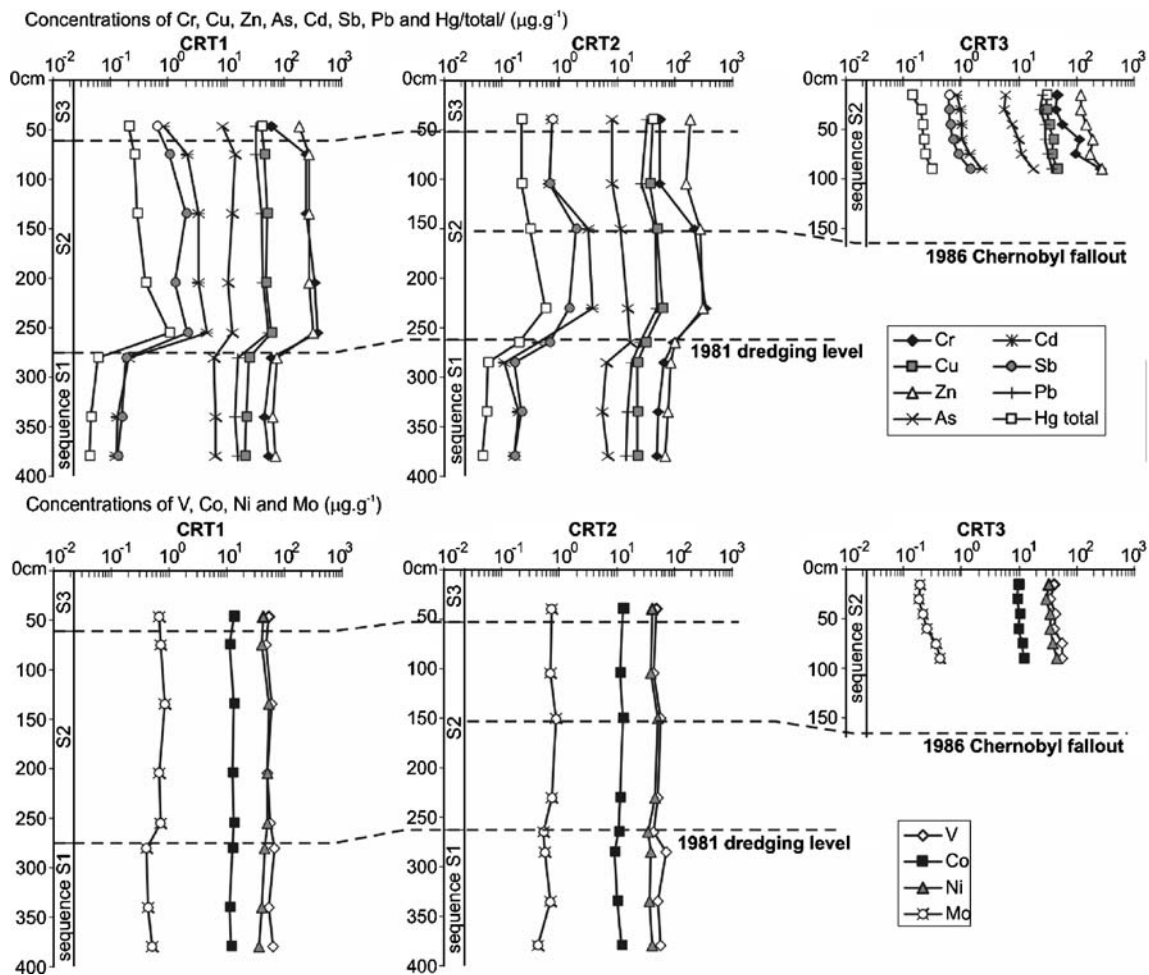


Fig. 5 Concentrations of heavy metals in cores CRT1, CRT2, and CRT3

Cd, Sb, As, Zn, Hg, and As, which show a rapid increase in concentrations between the 1930s and 1981 and a gradual improvement in the 1990s to 2000s. This group is also most likely derived from industry sources. Decreasing trends in heavy metal concentrations over the last ~10 to ~15 years have been noted by several long-term sediment quality studies of river bed and cores from European river basins including: the Elbe River, Germany (Heininger and Pelzer 1998; Netzband et al. 2002; Heininger et al. 2004), Limmat River, Switzerland (Wildi et al. 2003), and the Wisla River catchment, Poland (Wardas et al. 1996). In the Central and Eastern European countries, this trend was attributed to the closure of substantial parts of industry and by sanitation efforts after the fall of the Iron Curtain (Heininger and Pelzer 1998), which is also suggested as the main reason for the improvement in our study area.

4.5.2 Persistent organic pollutants

Stratigraphical distribution of persistent organic pollutants shows similar patterns for heavy metals. Their concentrations in sediment samples are summarized in Table 1.

The lowest levels of contamination were found in the pre-1930s sediments of the basal sequence S1 (PAHs, 36.1 to 228.4 ng·g⁻¹; PCBs, 0.65 to 2.26 ng·g⁻¹; DDTs, 0.05 to 0.86 ng·g⁻¹; HCHs, 0.73 to 1.28 ng·g⁻¹). The only exception is provided by anomalously high concentrations of DDTs (21.98 to 36.45 ng·g⁻¹) and HCHs (5.78 to 7.47 ng·g⁻¹) at 380 and 285 cm depth in the CRT2 core. Concentrations of all organic pollutants increase rapidly at the S1/S2 sequence boundary between 280 and 255 cm depth in the CRT1 core and between 285 and 230 cm depth in the CRT2 core (Fig. 6), which corresponds to the 1981 datum level. In the CRT1 core, for example, the contamination levels in the post-1981 sediments increased with respect to the pre-1930 sediments about 145-fold for PAHs (Σ PAH15, excluding anthracene), about 72-fold for DDTs, about 17 times for PCBs, and about fourfold to fivefold for HCHs. The highest concentrations were found in the basal sediments of sequence S2, which were deposited in the first half of the 1980s (maximum measured concentrations of PAHs, 18,479.5 ng·g⁻¹; PCBs, 24.84 ng·g⁻¹; HCHs, 8.3 ng·g⁻¹; DDTs, 45.35 ng·g⁻¹). Since then, the contamination levels

Table 1 Concentrations of major pollutants in core samples and recalculated ages of samples

Age	Depth	Cr	Cu	Zn	As	Cd	Sb	Pb	Hg(total)	ΣPAHs	ΣPCBs	ΣHCHs	ΣDDTs	Anthracene
		μg·g ⁻¹									ng·g ⁻¹			
CRT1														
~2001 ^a	47	60.9	41.0	189	8.8	0.83	0.62	33.1	0.21	10860	14.17	1.72	7.28	154.5
~1998 ^a	75	247.7	45.2	276	14.0	2.10	1.02	33.4	0.25	6341.3	19.10	1.66	11.24	323.5
~1993 ^a	135	249.7	52.6	273	12.9	3.35	2.04	41.7	0.29	7749.6	24.84	8.30	10.37	17 388.4
~1986 ^a	205	351.6	49.8	282	10.6	3.39	1.26	43.0	0.40	8598.9	19.23	2.86	15.80	10 555.9
1981	255	387.4	62.5	321	13.2	4.77	2.16	54.5	1.02	18479.5	11.11	5.89	45.35	650.1
pre-1930s	280	60.7	24.9	78	6.1	0.21	0.18	16.0	0.06	127.8	0.65	1.28	0.63	56.1
	340	47.2	22.2	66	6.4	0.13	0.16	14.0	0.04	36.1	1.02	0.73	0.05	32
	380	54.6	21.5	70	6.5	0.13	0.13	15.6	0.04	47.7	1.33	1.06	0.19	210
CRT2														
~2001 ^b	40	53.6	40.7	190	8.2	0.74	0.73	33.1	0.21	10757.5	14.45	2.21	11.09	213
~1992 ^b	105	55.1	36.5	161	8.0	0.64	0.65	27.1	0.22	8245.4	12.74	2.98	21.83	398.5
1986	150	220.1	49.7	281	11.6	3.23	1.96	46.9	0.30	9968.7	24.61	4.02	17.99	18985
~1982 ^b	230	348.4	60.1	302	14.9	3.73	1.49	47.7	0.55	10275.5	21.26	7.05	25.96	5826.6
(?)	265	93.9	31.8	102	17.3	0.43	0.66	25.5	0.19	1724.9	2.57	1.30	0.41	81.7
pre-1930s	285	66.2	23.0	85	6.5	0.11	0.16	17.4	0.06	214.8	2.26	7.47	36.45	89.6
	335	51.3	21.9	75	5.6	0.19	0.22	14.9	0.05	228.4	1.30	1.07	0.86	196.7
	380	49.4	22.8	69	7.1	0.16	0.16	14.4	0.05	130.9	1.40	5.78	21.98	35.4
CRT3														
~2005 ^b	15	46.9	31.4	118	6.03	0.82	0.61	26.0	0.14	7009.5	11.17	1.9	7.40	296.3
~2003 ^b	30	43.6	31.0	124	5.57	0.99	0.62	24.1	0.20	7127.2	10.78	1.9	8.61	307.4
~2001 ^b	45	57.3	34.3	151	7.61	1.03	0.66	28.4	0.22	8097.8	19.10	0.5	5.68	482.7
~1999 ^b	60	112	39.4	194	10.2	1.04	0.72	29.5	0.23	8115.0	15.72	2.2	9.53	648.5
~1997 ^b	75	98.9	37.5	175	11.3	1.41	0.88	32.2	0.24	6542.6	13.38	2.7	14.81	742.1
~1995 ^b	90	270	47.9	283	18.5	2.35	1.40	37.7	0.31	10946.9	22.03	6.2	9.61	2981.7

^a Recalculated from the position of the 1981 dredging level and average sedimentation rate.

^b Recalculated from the 1986 Chernobyl fallout event and average sedimentation rate.

of PAHs and PCBs have remained approximately constant until about 2005. On the other hand, the contamination levels of HCHs and DDTs in sediments have slightly decreased. The decreasing trend accelerated in the period from the early 1990s to the first half of the 2000s (CRT3 core). The most recent contamination levels

(15 cm depth in the CRT3 core) reach about 27% of the maximum values from the early 1980s for HCHs and 16% for DDTs. Anomalous patterns were found for anthracene. Anthracene concentrations in the pre-1930 sediments of sequence S1 are low, from 32 to 210 ng·g⁻¹. Similar to other persistent organic pollutants, the concen-

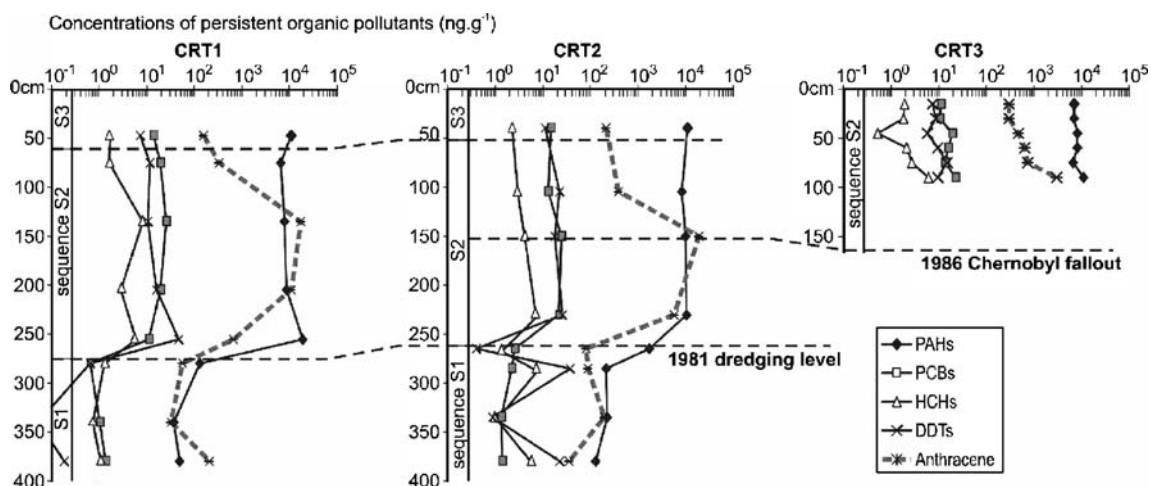


Fig. 6 Concentrations of persistent organic pollutants in cores CRT1, CRT2, and CRT3

trations of anthracene increased above the 1981 datum level by a factor of 211 to 309, to reach peak values of $18,985.0 \text{ ng}\cdot\text{g}^{-1}$ at 150 cm depth in the CRT2 core, corresponding to the 1986 datum level. The anthracene peak is located higher and is, therefore, slightly younger than the other PAH peak. Anthracene concentrations rapidly decrease between 135 and 75 cm depth in CRT1 core and between 150 and 105 cm depth in the CRT2 core, which corresponds approximately to the early to mid-1990s.

Former studies indicate that the contamination by persistent organic pollutants in the study area was derived from both industrial centers and regional background, including agriculture, chemical, food and other industry, sewage waters, combustion of solid fuels, traffic emissions, and old ecological onuses (Hilscherová et al. 2007). The difference in their stratigraphic patterns suggests that anthracene, which shows significant improvement for the last ~15 years, might be derived from different sources other than the PAHs, which do not indicate any improvement. While most PAHs seem to be derived from diffuse sources, anthracene may be derived from a local point source, the anthraquinone producer DEZA, in Otokovice located approximately 19 km upstream of the Lake Certak. This assumption is strongly supported by regional distribution of recent contamination in the Morava River, which shows a distinct anthracene peak just downstream of Otokovice (Fig. 7). Release of contamination from point sources can be also assumed for HCHs, DDTs, and several

heavy metals (Cr, Cd), which show similar temporal and spatial distribution patterns to anthracene (see Figs. 6 and 7). On the other hand, PAHs share similar distribution patterns with PCBs and the two are probably derived from similar sources, most likely diffuse ones. In general, the contamination levels of most persistent organic pollutants in the Lake Certak show only moderate improvement or no improvement at all over the last ~10 to ~15 years. This finding is consistent with the observations made from sediments of the Elbe River in Germany (Heininger and Pelzer 1998; Heininger et al. 2004) in which significant proportions of contaminants are likely derived from the territory of the Czech Republic.

4.6 Comparison between riverbed and oxbow lake contamination

A parallel study has been currently launched to investigate the contamination of recent deposits in the Morava River (cf. Hilscherová et al. 2007). The uppermost layers (<10 cm) of river channel deposits have been sampled underwater from lateral accretion bars in five sampling sites along the 31-km-long river profile from Kvasice to Kostelany (sampling sites S10, S11, S13, S14, and Sed14 of Hilscherová et al. 2007, p. 169) (see Fig. 7). Contamination was analyzed from samples taken in April and October 2005 and 2006. In all five localities, the concentrations of all analyzed heavy metals from October 2005 were up to four times higher than those from April

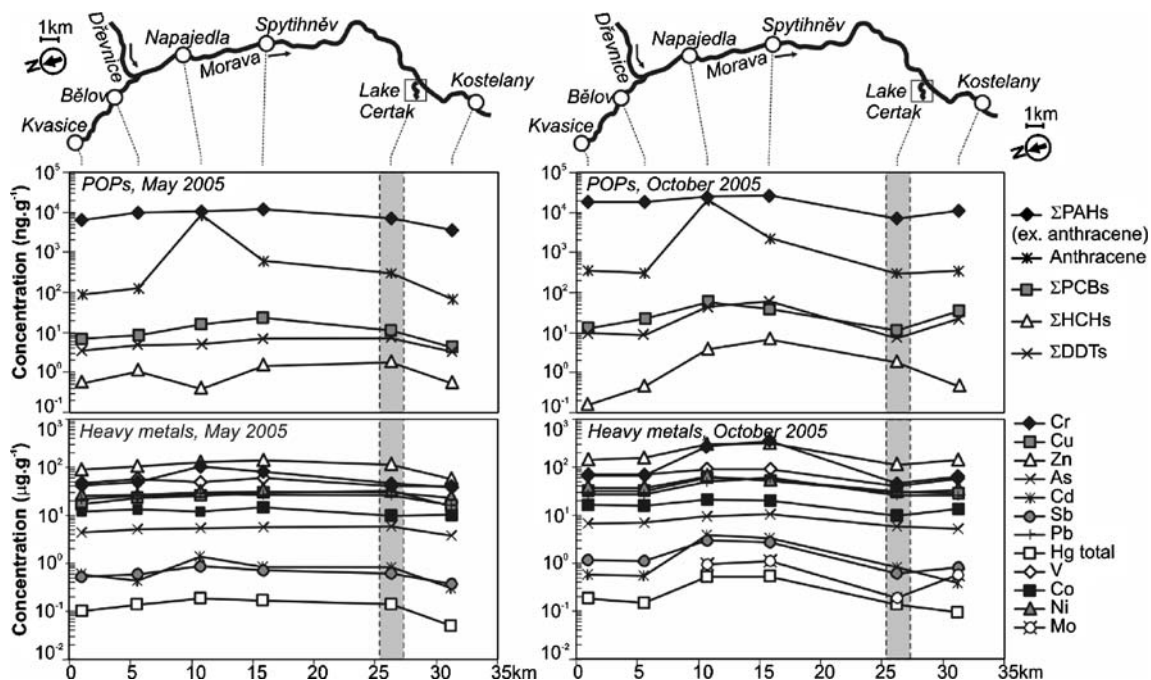


Fig. 7 Recent concentrations of persistent organic pollutants and heavy metals in channel deposits of the River Morava and comparison with recent concentrations from Lake Certak

2005. The concentrations of persistent organic pollutants from October 2005 were even higher: 3 times higher for PAHs, 5.3 times higher for anthracene, 6.8 times higher for DDTs, and 8.2 times higher for PCBs.

The concentrations of heavy metals from Lake Certak were compared to those from the nearest sampling site Kostelany located 3.8 km downstream of the Morava River. The most recent sediments from the CRT3 core show comparable concentrations of V, Cr, Co, Cu, Ni, Zn, Sb, Pb, PAHs, anthracene, PCBs, and DDTs to the river sediments, as they vary within the range between the April and October concentrations. Concentrations of As, Cd, Hg(total), and HCHs in the CRT3 core are 1.2 to 2.1 times higher than the October peak values from Kostelany. Although there is a distinct regional variance in heavy metal and persistent organic pollutant contamination levels along the Morava River water course, the pollutant concentrations in the lake sediments and the adjacent river bed sediments are well-balanced. Sediments of the Certak Lake are, therefore, assumed to reflect very well the immediate levels of pollutant concentration passing through the river. Since the lake is connected to the river via underground pipe, one can assume that the contaminants entering the lake are bound to suspended particulate matter, which is well-supported by the grain size data from most of the lake sediments with predominance of the silt-size fraction.

5 Conclusions

Oxbow lake deposits from our study area proved a good target to study the history of contamination bound to suspended river sediments. The oxbow lake accumulates suspended sediment from the river and develops a rapidly growing sedimentary body that provides an alternative to floodplains and dam deposits, which are susceptible to erosion during big floods. Relative dating based on detailed core stratigraphy, GPR profiles, environmental interpretation, historical data, and ^{137}Cs dating allowed us to establish a time framework for the contamination data for the last ~25 years. High sedimentation rates of 7.0 to 7.7 cm/year with uninterrupted sedimentary record offer a good potential for the future to study various temporal patterns with high resolution at an annual or even seasonal scale. The seasonal fluctuations in contaminant levels between May and October, which were revealed in the adjacent riverbed deposits, should potentially leave adequate records in the lake deposits. The Lake Certak may serve as a model for future studies of sedimentary and pollution migration processes in similar artificial sediment traps.

The contamination history study demonstrated that sediment contamination increased considerably between the 1930s and early 1980s. The most significant increase

was observed for PAHs, PCBs, DDTs, HCHs, and many heavy metal species, excluding V, Co, Ni, and Mo. From the late 1980s/early 1990s to ~2005, the contamination levels gradually decreased for most heavy metals including Cr, Cd, Sb, As, Zn, Hg, and As. Only moderate improvement was observed for Pb, Cu, and most persistent organic pollutants. In particular, PAHs and PCBs showed almost no improvement over the last ~15 to ~20 years with the exception of anthracene. Different temporal and spatial patterns for various contaminants allowed us to distinguish between point sources, likely diffuse sources and geological background. The revealed temporal trends are comparable to historical contamination data from other Central and Eastern European rivers.

6 Recommendations and perspectives

Oxbow lakes may provide an alternative to floodplains and reservoir deposits when studying river contamination history. High sedimentation rates of up to 7.7 cm/year offer a very good stratigraphic resolution, making it possible to study contamination patterns on annual or even seasonal time scales. On the other hand, oxbow lakes may represent long-term contamination stores, which are unlikely to be redistributed by river erosion and, hence, may possess significant environmental risks for the farther future.

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