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Contamination of bank sediments near historic glass works in the Bohemian Forest, Czech Republic

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Abstract
Basic characteristics (texture, dry bulk density, pH(H_2O) and pH($CaCl_2$), total C and N contents) and the vertical distribution 46 element contents were determined at 5 cm intervals in vertical bank sediment profiles from 9 pits dug along the Teplá Vltava and Řasnice Rivers, in order to uncover potentially archived contamination from the operation of a former (1834–1995) glass works in Lenora. Ample amounts of charcoal fragments buried in the sediments of two pits had ^{14}C ages between 1250 and 1445 BP. Charcoal affected the bulk density and content of elements in fine earth. The contents of the anthropophile elements As, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Sb, Se, Sn, V and Zn, the thickness of the contaminated topsoil layers and the element content gradients in sediment profiles decreased with the distance of pits from the former glass works. The sediment topsoil was most heavily contaminated by Cd, Hg, Pb, Sb and Sn, especially near the former glass works. Most of the As in sediments from the pit near Borová Lada was of geogenic origin. Surprisingly, sediment pollution by Pb near the glass works was lower than expected. However, the $^{206}Pb/^{207}Pb$ ratio increased with the depth of sediments, indicating an anthropogenic origin of Pb in the topsoil. The geoaccumulation indices (I_{geo}) of elements mainly in the topsoil were highest for As, Cd, Hg, Pb, S, Sb and Sr, while enrichment factors (EF) were highest for As, Be, Bi, Cd, Hg, Mo, Pb, S, Sb, Sn, Ti, W and Zn. Increased contents of especially lithophile elements in the flood sediment layers exceeding local background element levels were caused by the accumulation of weathering products of local granites and other bedrocks rich in these elements. Contents of 8 potentially toxic elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the topsoil and in the whole sediment profiles near the glass works represent moderate to severe potential ecological risks. Cd, Hg and As, with the highest toxicological effects, contributed most to the total potential ecological risk. However, contributions to the total ecological risk from other elements with biological impacts (e.g., Be, Sb, Sn, Th, Tl, etc.) could not be estimated due to the unknown toxic response levels of biota.

Key words: Lenora glass works, bank sediments, potentially toxic elements, contamination loads, potential ecological risk

Introduction

The beginnings of manufactured glassmaking in Central Europe has been documented by archaeological findings from as early as the second half of the 13th century, with glass production significantly expanding in the 17th century due to increased demand for new colour forms and ornamental glassware products (WHITEHOUSE 2012). Glass works were founded mainly in mountain areas rich in forests and streams, because considerable amounts of wood

were needed to obtain potash for melting silicates and fuel for glass furnaces. Various elements and compounds that are potentially toxic have been used to obtain desired glass properties or colour. For example, to produce brilliant lead glass (crystal glass), 18–40% (by weight) of PbO must be admixed in the melt (GRAZIANO et al. 1991, FRANCIS 2000). Besides the basic element contents of glass (Si, B, K, Na, Ca), numerous other elements such as As, Au, Cd, Ce, Co, Cr, Cu, Fe, Mn, S, Sb, Sn, Ti and U compounds and their blends have been used to obtain opal or coloured glass (BAMFORD 1977, WEYL 1999, BRATCHLOW 2019, ZLÁMALOVÁ CÍLOVÁ et al. 2021). For the production of glasses with specific properties, other additives (e.g., Be, Nb, La, Te, Ti and Zr base compounds) have recently been used (e.g., LOCARDI & GUADAGNINO 1992, WANG et al. 1994, CHEN et al. 2012, MIAO et al. 2020). In order to eliminate the effects of highly toxic lead, it is being substituted by BaO, MgO, Sb_2O_3, SrO, ZnO and other compounds in the manufacture of crystal, protective and optical glasses (e.g., HONG et al. 2010, BERKIN 2013). As, Sn and their oxides are generally used for refining molten glass (STÅLHANDSKE 1999).

The combustion of fossil fuels in glass furnaces releases acid and greenhouse gasses, persistent organic pollutants (e.g., CO_2, NO_x, SO_2, PAHs), soot and ash particles. During glass making, vapours of volatile metals (e.g., Hg, As, Sb, Sn) and fluorine are emitted from the glass melt and hydrofluoric acid and dissolved metals are released during the final working of the glass surface. The harmful health effects of toxic and high-risk emissions from glass works, primarily As, Cd, Pb and Sb, on nearby residents have been investigated in numerous studies (e.g., SEMRAU 1957, ŠRÁM et al. 1985, ANDRÉN et al. 1988, ANDERSSON et al. 1990, IARC 1993, WINGREN & AXELSON 1993, KIRCHER 1997, BARTOLI et al. 1998, SCALET et al. 2006, RAMPAZZO et al. 2008, ROSSINI et al. 2009, OZCAN et al. 2012, NYQVIST et al. 2017, MATTISSON et al. 2020). In addition, toxic mercury and other elements represent health and environmental risks during the recycling of fluorescent lamps, cathode ray tubes and other PC and TV waste glasses, as well as from the use of recycled glass as an additive into pavement bases, cement concrete, cement mortars, etc. in road and building engineering or glass fertilizers (DISFANI et al. 2012, LECLER et al. 2015, MOHAJERANI et al. 2017, WILSON et al. 2018, QI et al. 2019).

The surroundings of glass works are affected by the atmospheric deposition of pollutants and other ground point pollution sources such as a wastewater sewage, ash and glass waste dumps, pools for the neutralization of splashes with dissolved metals and hydrofluoric acid from glass etching etc. LARSSON et al. (1999) retrospectively reconstructed Pb emissions in Sweden from historical crystal glass production. Toxic and high-risk elements, as well as other macro- and microelements can be released from glass dumps and spread due to wind erosion or can be extracted by rain water and enter the soil, water, vegetation and food chains in considerable amounts (AHMED & YOUSSOF 1997, BUNKER 1998, GIUSTI & ZHANG 2002, HYNES et al. 2004, AUGUSTSSON et al. 2016a, JANI & HOGLAND 2017, 2018, HAGNER et al. 2018, JANI et al. 2019, FORMENTON et al. 2021). Some studies have not confirmed a high risk of atmospheric deposition and glass waste dumps except for deposits of some raw materials and glass pigments (e.g., AUGUSTSSON et al. 2016b, HELMFRID et al. 2019). Overall, however, there is extremely little information about contamination of the environment around glass works and their ecological risks. For example, HAGNER et al. (2018) tested toxic effect of glasswork soils with increased contents of Pb, As, Ba, Cd and Zn on organisms of biotest sets. Toxic effects were observed on enchytraeid abundance but not on *Lepidium sativum* trial plant.

The goal of our investigations was to determine multi-element contents of bank sediments in the vicinity of the former Lenora glass works, assess the extent of contamination caused by the operation of the glass works, and estimate the ecological risk of detected pollution loads in the surrounding natural protected area.

Material and methods

The study area

Bank sediment contamination was investigated along the Teplá Vltava River and the Řasnice River in the protected landscape area of the Bohemian Forest stretching along the state borders with Germany and Austria. The bedrock of the area comprises a featureless complex of metamorphic rocks (migmatites, paragneiss, quartzite bands, erlans and similar rocks) occurring over a larger territory and locally granite massifs (René & Hájek 2011). Flatter areas are locally covered by deluvial sediments and peats (ČGS 2022). Fluvial sediments along the Teplá Vltava River and the Řasnice River, an important tributary of the Teplá Vltava, were investigated in the wider surroundings of the former Lenora glass works founded near the confluence of these rivers. The catchment areas of the Teplá Vltava and Řasnice are 747 km^2 and 89.4 km^2, respectively. The base flow of the Řasnice at the confluence with the Teplá Vltava is 1.62 $m^3.s^{-1}$, and the base flow of the Teplá Vltava at the confluence with the Studená Vltava is 5.90 $m^3.s^{-1}$. The upper reaches of the Teplá Vltava River run in an area of paragneis and migmatite (Schulmannová & Verner 2004) while the lower reaches run in granites. In contrast, the upper reaches of the Řasnice River run in a granite area (René & Hájek 2010, 2011, Pour 2012, René 2020), while the lower reaches flow in an area comprised of monotonous migmatites and paragneis.

The Bohemian Forest was not significantly industrialized except for individual glass works utilizing wood from the large virgin forests. This is why the area was one of the cleanest parts of the country even in the period from the 1960s–1980s (Strnad et al. 1989) when atmospheric pollution and deposition rates culminated in Central Europe. For all that, territorial acid rains affected surface water chemistry (e.g., Vrba et al. 2016) and increased concentrations of heavy metals have been archived in peat and lake sediments in the Bohemian Forest (Veselý 2000a, Zuna et al. 2011). The first small glass melting furnaces in the Bohemian Forest are known from the mid of 14th century, but about 41 more developed glass works were gradually founded in the 17th and 18th centuries. In addition, several small historical glass works operated along tributaries of the Teplá Vltava River between the 15th and 19th centuries (e.g., near Kvilda, Nové Hutě, Tobyášova Huť, Lipka, Horní Vltavice, Kubova Huť, Strážný and others), producing mainly flat glass, containers, beads and watch glasses (Lněničková 2002). Glass fragments can be found in streams near these former glass works in the Teplá Vltava catchment, but data on the contamination of soil, sediments and water around these historical glass works is sparse. In the 19th century about 15 glass works operated in the Bohemian Forest. They all were gradually shut down, with the last glass work in Lenora closed in the mid 1990s (Lněničková 2002, Kirsch 2003a, 2003b, Drahotová 2005).

Our investigations of bank sediment contamination were conducted around the former glassworks situated in the Lenora municipality (currently ca 715 inhabitants) near the northern bank of the Teplá Vltava River (48.9209N, 13.7981E). The glass works (equipped with

1–4 glass furnaces) operated between 1834 and 1995. Glass products included crystal, green and ruby glasses, flat, cut, hollow, shear, jar and painted glasses in the 19th/20th centuries. An extra glass furnace was temporarily established just next to the Vltava bank below the Lenora glass works in 1841 and it was pulled down in the mid of the 1950s. No detectable remains of this furnace have persisted to the present time. After 1945 until the glass works was shut down mainly blown, leaded crystal, watch glasses, cut and decorative and art glass wares were produced in Lenora (SKOČNÝ 2016, PECKA 2019). As depicted in a wind rose for Lenora, winds from the SE are the most frequent and from the SW the least frequent (METEOBLUE 2022).

Potentially dangerous remains of oils, petroleum products, glass wastes and toxic chemicals were stored in rusted barrels at the glass works for about 10 years before being removed in 2006 (POKORNÝ 2006).

No important industrial sources of atmospheric contamination are present in the Teplá Vltava catchment. However, six sewage treatment plants are located along the river, with one plant operating at the Kubohuťský stream tributary and one located along the Řasnice River in Strážný.

Few records about flood episodes in the study area before 1947 are available. The highest recent floods were measured in December 1993 (a one-hundred-year flood), June 2002 (a twenty-year flood) and June 2013 (a ten-year flood). A significant flood episode in 1587 is evidenced by historical records about a dam crack on the Řasnice River near Strážný.

MAŘÍKOVÁ (2008) found twice and three-times higher total contents of Pb and Hg against "background contents" in bed sediments of the Teplá Vltava River in the vicinity of the Lenora glassworks but no substantial contamination of the river sediments was reported up or down the river. NOVOTNA et al. (2016) found relative small contents of extractable Pb from forest soils up to 3 km around the Lenora glass works.

Collection of samples

Nine pits were dug in banks along the Teplá Vltava River (7 pits) and the Řasnice River (2 pits) in 2018 (pits 2–6 and 9) and 2020 (pits 1, 7, and 8). The positions of the pits are depicted in Fig. 1 and selected characteristics of the pits are given in Table 1.

The pits measured 40×40 cm at the base and were dug out to the current ground water levels. Samples of vertical sediment layers were collected from the pit walls in 5 cm intervals. In pits 1, 7 and 8 that were farthest from the glass works, a 10 cm sample collection interval was used for depths below 30 cm. In parallel, 3 specimens were cut out from intact sediment layers using steel cylinders with a volume of 100 cm^3 in 20 cm intervals in pits 2, 5, 6 and 9. The colour of fresh sediment was estimated using a soil colour chart (MCC 1994). Sediment samples were air dried, weighed and sieved through a plastic sieve for particle size <2.00 mm. The proportion of soil skeleton (fraction ≥2.00 mm) was estimated by weighing particles remaining on the sieve mesh. A part of the sieved fine earth was used for determinations of soil texture, radionuclide activities and sediment reaction (pH-H_2O and pH-$CaCl_2$). The remaining fine earth was further sieved through 0.25 mm netting for a finer fraction intended for element content determination. In sediments of three pits wood remnants or carbonized woody pieces were found, and were collected for dating.

The grain size distribution was detected using a simplified pipette method (KETTLER et al. 2001) and checked by laser grain-size determination. Activities of radionuclides in selected samples were determined gammascopically in an accredited laboratory of the National Radiation Protection Institute in Prague. Dating of the woody and charcoal materials was done in the Poznan Radiocarbon Laboratory.

Sediment reactions of pH(H_2O) and pH($CaCl_2$) were determined in suspensions with deionised water or 0.01M $CaCl_2$ solution 10 g : 50 mL using a pH meter with a combined pH electrode system calibrated by commercial buffers at 4.01 and 7.00.

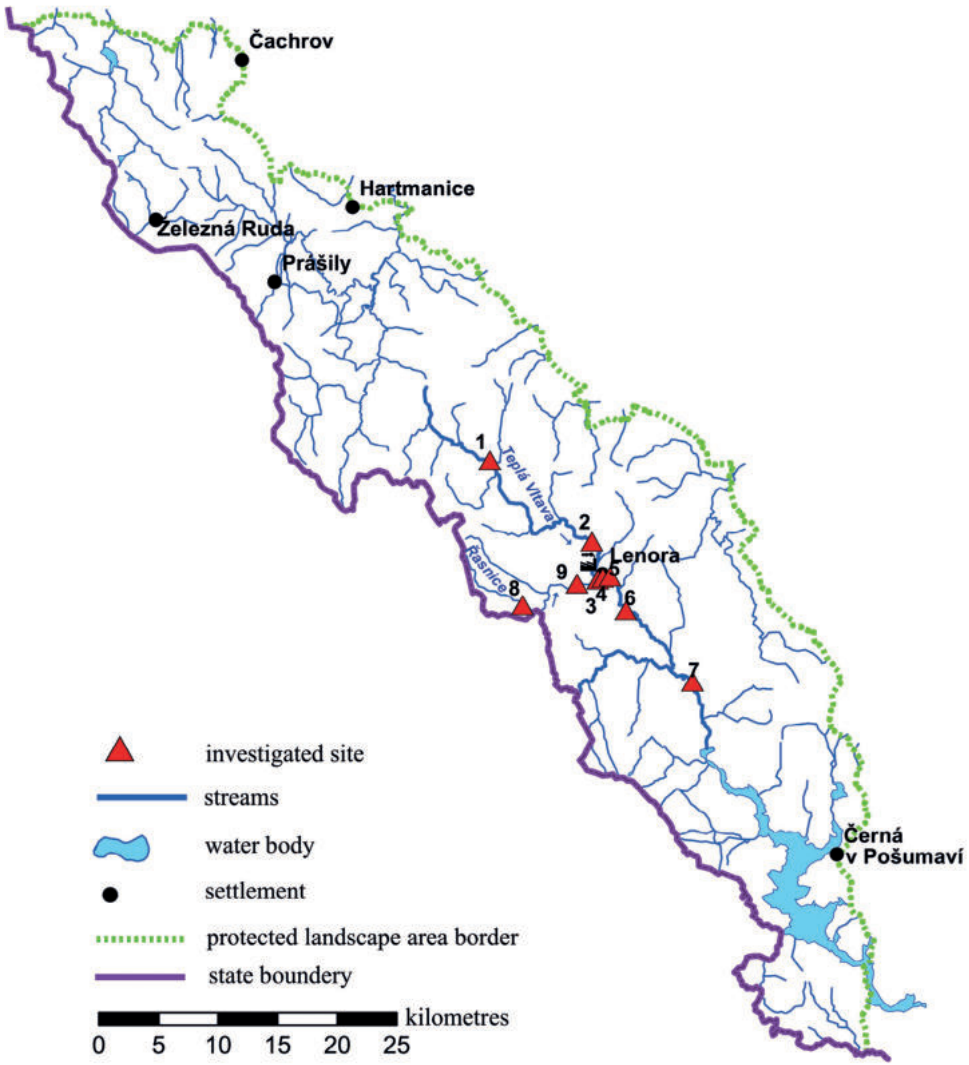

Fig. 1. The location of probe pits along the Teplá Vltava and Řasnice Rivers.

Table 1. Selected location characteristics of probe pits along the Teplá Vltava and Řasnice Rivers.

Pit no.	River	Close settlement	Location of the pits		Depth of the pits (cm)	From the glasswork chimney		Elevation (m. a.s.l.)	River kilometre (km)
			Latitude (°)	Longitude (°)		Direction (°)	Distance (km)		
1	Teplá Vltava	Borová Lada	48.995161	13.653477	50	275	13.3	905	418.2
2	Teplá Vltava	Nová H. Vltavice	48.945836	13.783187	60	340	3.0	775	399.3
3	Teplá Vltava	Lenora glasswork	48.920200	13.800133	80	90	0.2	755	393.8
4	Teplá Vltava	Lenora west	48.919933	13.801117	80	115	0.3	115	393.9
5	Teplá Vltava	Lenora east	48.921917	13.804433	90	75	0.5	755	393.7
6	Teplá Vltava	Dobrá	48.898286	13.833036	80	135	3.6	745	387.8
7	Teplá Vltava	Pěkná	48.852128	13.919898	90	130	11.7	740	373.5
8	Řasnice	Strážný	48.890945	13.715084	50	240	6.9	815	8.1
9	Řasnice	Vlčí Jámy	48.912900	13.773049	90	245	2.0	760	15.8

Total contents of Si were detected in all sediment samples first and then the sediment samples were totally digested using Si content specific blends of HNO_3+H_2O_2+HF+H_3BO_3 in a high pressure digestion appliance (CEM) (SUCHAROVA & SUCHARA 2006). Total contents of macroelements (Al, Ba, Ca, Fe, K, Mg, Mn, P, S and Si) were determined by an Avio® 500 ICP-OES–PE spectrometer, microelement contents (Ag, As, B, Be, Bi, Cd, Ce, Co, Cs, Cs, Ga, Ge, La, Li, Mo, Nd, Ni, Pb, Pr, Pt, Rb, Sb, Se, Sn, Sr, Th, Tl, U, V, W, Y and Zn) and stable lead isotope ratios were measured using a NexION® 2000 ICP-MS–PE spectrometer. Total contents of Hg, C and N were determined directly in powdered sediment samples using an AMA 254 Hg atomic absorption spectrometer and a C/N LECO appliance, respectively calibrated with commercial analytical reference materials (SRM NIST 2709a San Joaquin Soil, IAEA Soil 7, and LECO CRM 502-697 Soil and 502-694 Soil). Determination of sediment characteristics included three independent measurements (specimen weights), and contents of Pb isotopes were measured ten times.

We computed the geoaccumulation index (I_{geo}) established by MÜLLER (1979), which has frequently been used to assess heavy metal pollution loads of sediments (e.g., GHREFAT et al. 2011) using the following formula

$$I_{geo} = ln \frac{Cn}{1.5 \times Bn}$$

where C_n represents a given element content in a sediment sample, B_n stands for the local

background content of this element, and the coefficient 1.5 is used with respect to the potential variability of element contents in the background sediments. The following pollution categories were defined (MÜLLER 1979): unpolluted $I_{geo} \leq 0$, unpolluted to moderately polluted $0 < I_{geo} \leq 1$, moderately polluted $1 < I_{geo} \leq 2$, moderately to strongly polluted $2 < I_{geo} \leq 3$.

We used enrichment factors (EFs) as an another indicator of element accumulation levels in sediments in comparison to local background element contents in unaffected "preindustrial" sediments, originally compared to average element contents in the upper continental crust (BUAT-MENARD & CHESSELET 1979). In order to account for the effect of the variable contents of the finest grain size particles, which are rich in adsorbed elements, the chemical normalization of sediment element contents detected in bulk sediment samples have frequently been done using Al (HO et al. 2012, POH & TAHIR 2017). Here, EFs were calculated using the following equation

$$EF = \frac{\left(\frac{M}{Al}\right)_{sample}}{\left(\frac{M}{Al}\right)_{background}}$$

where $(M/Al)_{sample}$ and $(M/Al)_{background}$ denote the normalized Al content of element M in the sample and the normalized M element content in the background matrix, respectively. "Background" composition of the subsoil at a depth of 60–65 cm in pits 4 and 9 were used for calculation of EFs in all sediment samples of the Teplá Vltava and Řasnice, respectively. The following EF classes were used (e.g., SUTHERLAND 200): minimal enrichment (EF<2), moderate enrichment EF = 2.1–5.0), significant enrichment (EF = 5.1–20), very high enrichment (EF = 20.1–40).

A potential ecological risk index (PERI) procedure introduced by HAKANSON (1980) was applied to assess the ecological risk of sediments contaminated by potentially toxic elements, using the following formula:

$$PTRI = \sum_{(i=1)}^{n} E_r^i$$

where E_r^i stands for a potential ecological risk index of the toxic element "i". E_r^i is the product of the toxic response factor T_r^i and the pollution factor for the given risk element "i" ($E_r^i = T_r^i \times C_f^i$). However, the respective T_r^i values of 10, 30, 2, 5, 40, 5, 5, and 1 have only been defined for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn (ZHANG & LIU 2014), so the contribution of contamination by other toxic elements are not included in the PTRI. The C_f^i pollution factor is defined as a quotient of the risk element content in a sediment sample (C_s^i) and the element content in background ("preindustrial") sediments (C_b^i):

$$C_f^i = \frac{C_s^i}{C_b^i}$$

Computed PTRI values were interpreted using the following classes of potential ecological risks: PTRI<150 low-grade, 150≤PTRI<300 moderate, 300≤PTRI<600 severe and 600≤PTRI serious ecological risk.

Medians and median absolute deviations were preferentially used for the presentation and evaluation of analytical results. Basic statistics and correlation analysis were done in the StatSoft STATISTICA programme. Log+2 transformation of data was used for the correlation analysis.

Results and discussion

Buried organic matter and ^{14}C dating

Pits 1, 4 and 8 were located close to former but still recognizable slip-off-slopes, where a dominant lateral aggradation of sediments in the past was expected. In the remaining pits, a mainly horizontal aggradation of sediments was expected. Woody pieces of fluvial deposits were found at a depth of 50–52 cm (a former river bed) and at a depth of 32–34 cm, with respective ^{14}C ages of 135±30 BP and 90±30 BP in pit 1. If the age of sediments corresponds with the age of smothered organic remains, then mean annual sediment deposition rates would be about 0.24 and 0.20 cm.year^{-1}, respectively. In pit 5, layers of alder leaves and twigs at the top of a thick sediment layer rich in enormous amounts of charcoal pieces and charcoal dust were found at depths between about 35 and 65 cm. Charcoal material of most likely the same origin appeared at a depth of 30–60 cm in pit 6 lower down the Teplá Vltava River, as documented by the C content in sediment profiles (Fig. 2). However, this charcoal layer was not found in the remaining pits 3 and 4 near the glass works. Charcoal and woody pieces collected at a depth of 45–55 cm in pit 5 had ^{14}C ages of 1250±30 BP and 1290±30 BP, respectively. Charcoal from the depth of about 40–45 cm in pit 6 was older, dated at 1445±30 BP. Despite this, it is difficult to determine if buried organic sediments from the catchment were aggraded during one catastrophic flood and forest wildfire or rather if the charcoal material was accumulated gradually over a longer period. Reports about large-scale forest burnings in the past are not available. The ancient individual glass works scattered in the catchment burnt a huge amount of wood in furnaces and for potash production much later, in the 14th century. A large-scale cutting of a dense virgin forest for the construction of a new glass works and workers' houses in Lenora in 1834–1835 was reported. A temporary extra "Lower" glass furnace was constructed next to the river bank of the Teplá Vltava in 1841 near the position of pit 3 (Šmrha 2008). The building and demolition (in the late 1950s) of this temporary furnace and the manipulation and storage of floated logs at the bank of the Teplá Vltava in Lenora likely increased the turbation of sediment topsoils. In any event, if the age of tree death and the sediment aggradation are same then the theoretic mean speed of sediment accumulation is estimated to be 0.037–0.038 and 0.026 cm.year^{-1} in pits 5 and 6, respectively.

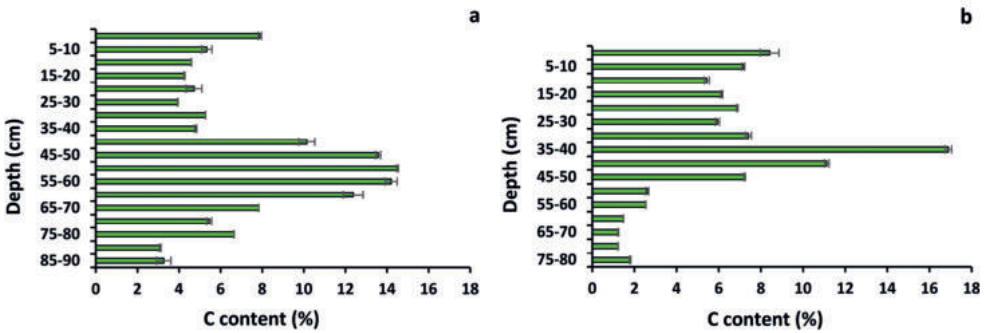

Fig. 2. Medians of organic carbon contents (%) in sediment profiles in pits 5 (a) and 6 (b). Error bars show ± median absolute deviations.

Activities of remaining radionuclides

Specific activities of ^{137}Cs, ^{210}Pb and ^{40}K radionuclides in sediments were measured along sediment profiles in pits 5 and 6 (Fig. 3). Activities of the artificial ^{137}Cs radionuclide exponentially decreased from 49.9 to 1.6 Bq.kg^{-1} in the surface layers 0–30 cm of pit 5 and from 63.2 to 3.0 in 0–35 cm in pit 6. The ^{137}Cs signal comes from the fallout following the Chernobyl accident in spring 1986 because activity peaks related to fallouts from nuclear weapons tests in the 1960s and the Fukushima Daiichi Nuclear Power Plant accident in spring 2011 are not generally detectable in soils in the Czech Republic (SUCHARA et al. 2016). In contrast to topsoil turbation, the natural vertical migration of ^{137}Cs in soil is very low (SUCHARA et al. 2016). An approximately 30 cm thick surface layer with ^{137}Cs was deposited during last 35 years. Due to absence of ^{137}Cs inventory data from a reference plot, it was not possible to estimate aggradation or denudation sediment rates in the bank topsoil.

Total ^{210}Pb activities showed a decrease in the 0–30 cm topsoil, and in deeper sediment depths fluctuated between 40 and 65 Bq.kg^{-1} due to varying contents of inorganic and organic sorbents in different sediment layers. Attempts to determine ^{214}Pb/^{214}Bi activities resulted in high uncertainties due to vertical changes in activities within the 5 cm sediment segments and the small volume of samples available for measuring ^{214}Pb. Hence dating of the topsoil sediment by ^{210}Pb and ^{214}Pb activities and an assessment of erosion of the topsoil bank sediments (PITTAUEROVÁ et al. 2011, MABIT et al. 2014) could not be done.

^{40}K activities ranged between 350 and 701 Bq.kg^{-1} in pit 5, and 450 and 736 Bq.kg^{-1} in pit 6. Changes in ^{40}K activities along sediment profiles reflect changes in sediment bulk densities and the content of fine size mineral particles derived mainly from the weathering of granites (FUJIYOSHI & SAWAMURA 2004). Decreases in ^{40}K activities are obvious in sediment layers rich in organic material (Fig. 3).

Colour of sediments

According to the characteristics of the sediment layers, the soil cover can be classified as modal Fluvisol even if the ages of sediments in pits 1 and 8 are relative young, probably less than 200 years.

The fresh uppermost layers 0–25 cm in the grass root zone were dusky red to weaker red (10YR 3/2–10YR 5/3), while deeper mineral sediments showed weak red to light red colours (10YR 5/3–10YR 6/6). Rather little colour changes were observed in the sediment profiles, except for a weak red zone with charcoals (10YR 4/3) red and deeper pale red layers (10YR 6/3). No sharp colour interfaces marking sediment layers were observed along the sediment profiles. Colour features of gleization associated with redox changes in the subsoil zone of ground water fluctuation were not distinctly developed due to the low content of Fe bearing clay minerals in deeper sediment layers.

Sediment textures

The sediment layers visibly contained relatively small amounts of skeleton (particles >2.00 mm) especially gravel, stones and pebbles. Pits 1, 3, 6, 8 and 9 had gravel and pebbles usually up to 5 cm in diameter exceeding about 10% of the sediment volume, mainly in the deeper subsoil. Median skeleton contents in sediments of upper flows in pits 1 and 8 were 60 and 45%,

respectively, while typical skeleton contents of 35–40% were found in sediments in the remaining pits. An increasing content of coarse sand was observed elsewhere, more frequently above pit bottoms at sites 1, 3, 4, 5, 6, 8 and 9.

Table 2 shows the contents of clay, silt and sand in fine earth sediments (≤2.00 mm) of selected pits and depths. The texture of the upper layers of investigated sediments could be categorized (USDA 1987) as silt loam, loam or sandy loam, while deeper sediment layers mostly fit the categories loamy sand or sand.

Bulk density

The bulk density is proxy of soil compaction. The values of bulk densities along sediment profiles in four pits are shown in Table 3. No measured values approached the critical levels of 175–185 g.100 cm^{-3}, which indicate extreme soil compaction causing poor soil permeability for water and air, and an inhibition of root growth (e.g., HOULBROOKE et al. 1997) as well as causing reduction conditions controlling sediment geochemistry (LAL & KIMBLE 2001).

Contents of sand in sediments significantly and positively correlated with sediment bulk densities (r = 0.92***), while contents of clay and silt correlated negatively with bulk densities (r = –0.68*** and r = –0.84***, respectively).

Sediment pH values

Median pH(H_2O) and pH($CaCl_2$) values of sediments in the pits reached 4.02–5.55 and 3.72–4.57, respectively. Sediment reaction pHs in pits increased in the order 7<6<8<9<5<2<1<3<4. These pHs corresponded with categories of extreme acid or strongly acid, and in pits 3 and 4 as acid (SÁŇKA & MATERNA 2004). In some pits the acidity of sediments increased with depth in the topsoil 0–25(30) cm and then decreased with the depth (pits 1, 2, 4 and 6), while

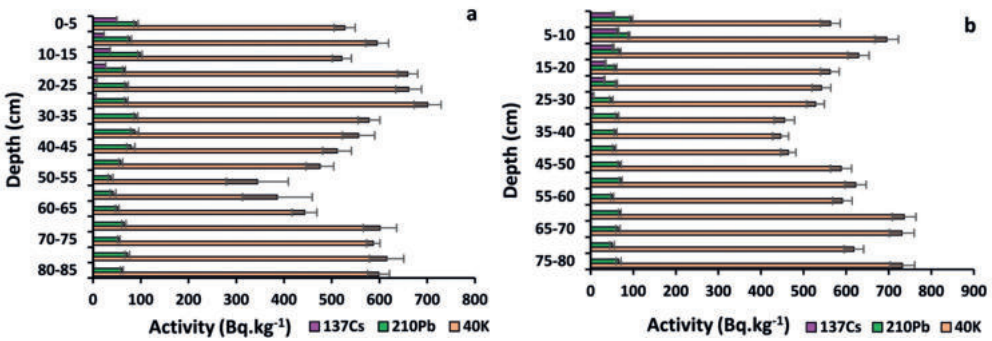

Fig. 3. Mean specific activities of ^{137}Cs, ^{210}Pb and ^{40}K in sediment profiles in the pits 5 (a) and 6 (b). The error bars show ± 1σ.

Table 2. The proportions of clay, silt and sand contents in the sediment profiles of five pits.

Pit no. 1			
Depth (cm)	**Clay (%)**	**Silt (%)**	**Sand (%)**
0–5	7.5	59.5	33.0
10–20	8.1	46.9	45.0
20–30	6.4	16.6	77.0
30–40	5.0	10.0	85.0
40–50	3.9	9.1	87.0
Pit no. 3			
0–5	11.1	37.4	51.5
20–25	8.0	21.1	70.9
40–45	6.7	19.1	74.2
60–65	4.4	9.6	86.0
80–85	4.8	9.4	85.8
Pit no. 5			
0–5	11.2	52.6	36.2
20–25	9.5	45.1	45.4
40–45	7.1	46.7	46.2
60–65	6.2	12.5	81.3
80–85	4.6	8.1	87.3
Pit no. 6			
0–5	9.9	52.2	37.9
20–25	8.2	40.4	51.4
40–45	12.1	55.7	32.2
60–65	13.4	40.6	46.0
80–85	4.0	44.8	51.2
Pit no. 9			
0–5	7.2	23.3	69.5
20–25	7.8	25.2	67.0
40–45	6.1	16.1	77.8
60–65	7.2	20.0	72.8
80–85	5.3	10.7	84.0

in pits 5 and 8 pH values increased through the whole profile (Fig. 4). However, with increased ground water levels the redox potential (Eh) decreases, and the pH of acid sediments further increases (KOZLOWSKI 1984). The highest differences between pH(H_2O) and pH($CaCl_2$) of about 0.75–1.16 pH units of sediments in pits 3, 4 and 9 indicate a large exchanging acidity (abundant adsorption of H+) of these sediments. The high acidity of the topsoils in bank sediments is caused by the sandy texture of these sediments, which have a low buffering capacity with an increased admixture of organic matter with acidic properties. However, element extractability and mobility in sediments were not investigated.

Measured pH(H_2O) and pH($CaCl_2$) values strongly correlated (r = 0.89***). For example, pH(H_2O) significantly correlated with bulk density (r = 0.59***) and with sand content (r = 0.75***). Significant negative correlations were found for pH(H_2O) and both clay content (r = –0.57***) and silt content (r = –0.89***).

Total carbon and nitrogen contents

Medians of total C content in the topsoil reached 3–10%, and contents of C usually exponentially decreased with sediment depth. However, due to buried plant organic matter mainly in pits 5 and 6, the C contents peaked in deeper soil layers (Fig. 2). Total C content significantly and negatively correlated with the bulk density (r = –0.64***) and sand content (r = –0.57***). Contrarily, a negative but not significant relation was found between the C content and pH(H_2O). There were positive significant correlations for C and clay content (r = 0.49**), silt content (r = 0.50**) and total N content (r = 0.51**).

The vertical course of median total N contents in sediments showed a similar pattern as total C. In addition, the medians of C and N contents significantly correlated (r = 0.51**), which implies that a considerable proportion of N in sediments is present in organic matter.

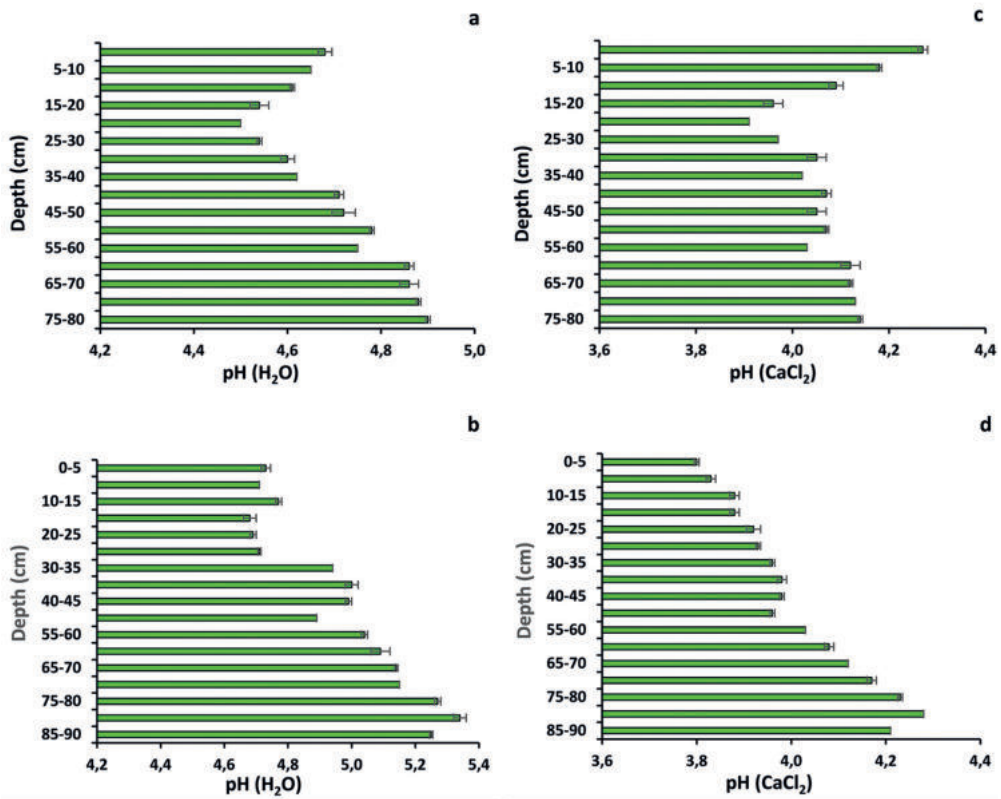

Fig. 4. Medians of sediment pH(H_2O) in the pit 6 (a) and 9 (b) and medians of pH($CaCl_2$) in pits 6 (c) and 9 (d). Bar errors show median absolute deviations.

Table 3. Median ± MAD of bulk sediment density ($g_{d.w.}$ 100 cm^{-3}) along sediment profiles in five pits (n. a. – not available data, MAD – Median Absolute Deviation).

Depth (cm)	0–10	20–30	30–40	60–70	80–90
Pit 2	67.9±1.9	125.7±1.6	122.2±1.8	122.5±6.2	131.7±2.4
Pit 4	90.2±2.6	94.4±1.5	101.9±2.2	115.4±2.9	n.a.
Pit 5	61.3±1.3	79.9±1.0	41.2±1.8	100.7±4.1	118.3±3.1
Pit 6	54.8±5.0	69.3±1.9	45.1±2.2	60.9±6.8	86.6±2.9
Pit 9	87.6±5.1	117.0±1.9	128.3±2.3	111.4±2.7	126.5±2.5

Generally, C : N ratios decreased with sediment depth, in the topsoil from about 17 : 1 to 4 : 1 and in the subsoil to about 1 : <1. The median C : N ratio for all sediment samples approached 1 : 7, which is considered the typical soil microbial ratio. However, in sediment layers rich in woody and charcoal materials the C : N ratio reached 16 : 1, indicating a decreased microbial decay of the organic matter.

Total N content negatively correlated with bulk density (r = –0.69***), sand content (r = –0.68***) and pH(H_2O) values (r = –0.62***), and positively correlated with clay content (r = 0.56**) and silt content (r = 0.67***).

Contents of all elements

Basic statistics for the total contents of 46 elements in the topsoil (0–30 cm) and the subsoil (>30 cm) of sediments in 9 pits are shown in Table 4. The distribution of element contents along sediment profiles showed three basic patterns.

Anthropophile elements

The first group of elements consists of typical anthropophile elements (CHEN et al. 2014), including As, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Sb, Se, Sn, V and Zn, and had exponential, power or possibly linear decreases in concentrations with sediment depth (Fig. 5a, b). The highest contents in the topsoil 0–30 (0–35) cm of sediments close to the former glass works, such as pits 3, 4, 5, and 6 in the case of Cd, Pb, S and Sb, indicate the contamination of sediments due to operation of the glass works. For example, many of elements in this first group have been frequently used in glass production, for example, crystal glass (Pb), glass and glass enamel colouring (e.g., Cd, Co, Cr, Cu, Mn, Ni, Se, Sb, Sn, V and Zn), molten glass refinement (As, Sb), and Sn in tables used to make sheet glass (KIRSCH 2003a,b, DRAHOTOVA 2005). The preponderance of S in the sediments was mainly associated with organic matter, as shown by the similar vertical course of S as C and the very strong and positive correlations of S and C contents (r = 0.87***). The rate of element content decreases with sediment depth declined from exponential to linear with distance from the glass works, as illustrated for Cd in Fig. 6. However, the very high As contents, approaching 50 $mg.kg^{-1}$ in the topsoil with a peak content between 20 and 30 cm in pit 1, were most likely not only due to the Lenora glass works. Increased contents of As from mining of gold deposits in agricultural soils and waters in the area have been found, for example, by ŠREIN et al. (2008) and SKÁLA et al. (2011). Some part of As may come from atmospheric deposition, which peaked in the area between 1956 and 1980, and low deposition rates of As go on mainly in the occult and bulk precipitation (TESAŘ et al. 2000, VESELÝ 2000b).

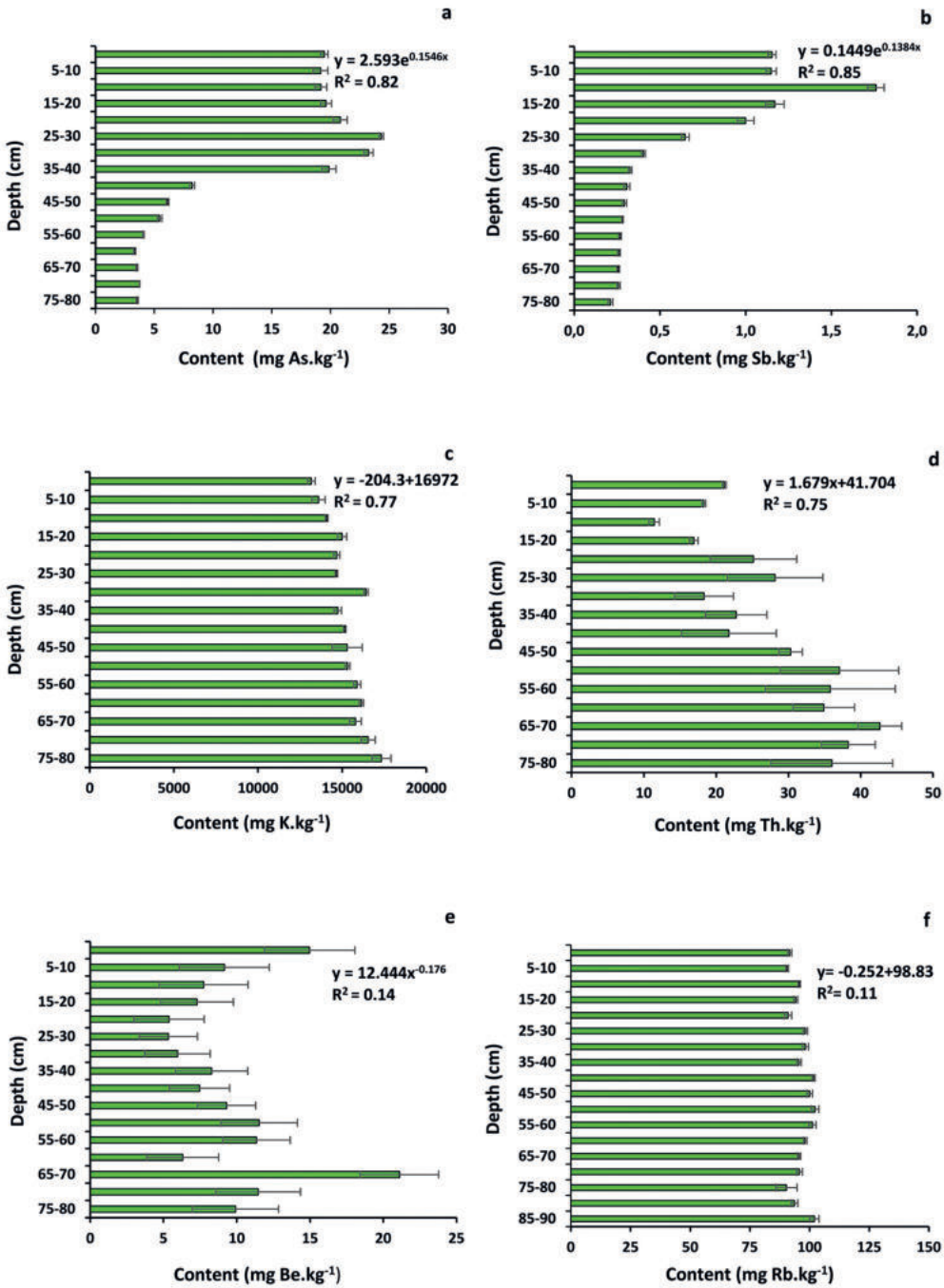

Fig. 5. Distributions of median contents of As (a), Sb (b), K (c), Th (d), Be (e) and Rb (f) along sediment profiles in pits 6, 4, 3, 3, 6 and 3, respectively. Error bars show ± median absolute deviations.

Table 4. Basic statistics for total contents of 46 elements in the topsoil (n = 54) and subsoil (n = 70) of bank sediments of the Teplá Vltava and Řasnice Rivers (SD – Standard Deviation, MAD. – Median Absolute Deviation).

	Topsoil 0–30 cm						Subsoil > 30 cm					
	Mean	**SD**	**Median**	**MAD**	**Min**	**Max**	**Mean**	**SD**	**Median**	**MAD**	**Min**	**Max**
Ag	0.295	0.083	0.274	0.064	0.173	0.492	0.274	0.066	0.274	0.042	0.077	0.442
Al	35744	10893	32795	6394	18461	62203	36696	12985	31106	7520	19762	63989
As	20.8	11.6	20.8	9.62	2.76	46.5	11.5	7.47	8.75	0.478	0.641	28.8
Ba	518	60.9	522	416	350	614	541	60.4	537	35.6	390	758
Be	2.95	0.894	2.89	0.581	1.08	5.40	2.61	0.526	2.54	0.398	1.71	4.05
Bi	0.266	0.084	0.277	0.064	0.120	0.428	0.199	0.072	0.176	0.033	0.048	0.413
C	42200	22330	38301	17607	6460	97390	32340	39830	16067	10802	290	168430
Ca	6156	1809	8505	857	3302	11030	5822	1644	5611	836	3072	10132
Cd	0.481	0.270	0.364	0,109	0.190	1.49	0.271	0.207	0.215	0.063	0.096	1.65
Ce	118	26.4	119	17.5	52.8	173	145	49.3	140	26.6	37.7	281
Co	8.40	2.89	7.81	2.27	3.49	14.1	6.78	2.75	6.43	1.07	2.38	14.0
Cr	55.7	19.0	52.7	19.0	17.3	86.3	54.9	15.1	55.1	11.8	5.95	77.3
Cs	6.12	1.07	6.01	0.910	4.46	8.76	5.85	1.04	5.80	0.552	3.17	9.23
Cu	15.1	6.03	14.9	4.93	5.71	25.1	12.4	4.09	12.9	2.51	2.34	23.7
Fe	25390	4916	24522	4202	15713	34380	22645	8339	21302	4309	7873	40718
Ga	17.6	2.21	17.9	1.30	13.0	22.1	18.1	2.30	18.1	1.51	12.7	24.6
Ge	5.80	0.981	5.63	0.667	3.98	7.82	5.45	1.48	5.25	0.862	2.05	8.50
Hg	0.091	0.037	0.084	0.028	0.32	0.167	0.052	0.031	0.043	0.011	0.017	0.193
K	16253	1676	16080	1085	13134	20589	17468	2901	17028	1730	11285	28709
La	59.2	13.0	60.8	7.39	26.9	90.6	72.7	24.1	69.3	13.4	20.9	138
Li	29.9	5.64	28.2	4.31	20.0	40.9	30.0	5.99	30.1	4.14	15.5	42.6
Mg	5636	1202	5880	942	3167	7545	5538	1595	5605	1109	1849	8606
Mn	549	185	539	172	277	888	403	148	363	108	115	693
Mo	0.571	0.207	0.514	0.172	0.193	0.931	0.442	0.179	0.422	0.134	0.114	0.820
N	6010	2250	5340	1476	2330	12300	4600	2140	4404	1210	1430	11000
Na	10337	4046	8645	924	6315	21926	9869	3264	8755	1701	5512	21289
Nd	51.8	10.8	53.5	6.47	23.7	74.9	62.7	19.5	61.2	12.8	18.4	114
Ni	17.7	6.06	18.8	5.17	6.45	25.7	17.3	4.69	17.5	4.14	3.22	25.0
P	893	212	924	177	487	1310	701	255	633	128	334	1567
Pb	50.1	23.8	38.8	8.86	23.6	105	26.0	7.08	23.9	2.67	19.0	61.5
Pr	13.7	2.93	14.1	1.78	6.13	20.0	16.7	5.44	16.2	3.35	4.88	31.0
Rb	92.9	13.9	90.6	7.21	72.3	135	93.7	15.9	91.2	7.41	63.9	151
S	640	198	623	136	271	1040	508	371	352	66.6	201	1797

Table 4. Continued.

	Topsoil 0–30 cm						Subsoil > 30 cm					
	Mean	**SD**	**Median**	**MAD**	**Min**	**Max**	**Mean**	**SD**	**Median**	**MAD**	**Min**	**Max**
Sb	1.01	1.09	0.512	0.216	0.219	5.93	0.322	0.202	0.291	0.070	0.098	1.16
Se	0.792	0.303	0.699	0.335	0.350	1.38	0.686	0.193	0.718	0.142	0.247	1.12
Si	249121	19652	247147	22757	214218	291980	261263	28569	270060	21152	174182	298789
Sn	8.59	6.99	5,34	1,57	2.44	29.5	3.66	1.10	3.46	0.353	1.85	9.30
Sr	103	11.7	103	5.48	77.7	129	103	12.9	103	6.34	65.0	149
Th	21.0	6.40	19.1	4.52	10.4	37.8	24.2	6.90	23.9	5.20	9.49	40.3
Ti	4168	710	4350	513	2735	5409	4601	1072	4943	473	1382	6942
Tl	0.697	0.111	0.676	0.091	0.486	0.941	0.663	0.113	0.641	0.072	0.497	1.04
U	4.63	1.07	4.74	0.665	2.09	6.68	5.25	1.32	5.34	0.816	18.0	8.37
V	65.6	19.2	63.9	18.0	27.8	96.9	62.1	18.1	60.0	14.5	112.0	94.3
W	1.71	0.510	1.75	0.267	0.896	3.75	1.72	0.754	1.58	0.351	0.319	5.60
Y	16.9	3.58	17.3	2.17	8.81	23.7	17.8	4.48	18.2	3.18	5.56	26.9
Zn	84.8	18.7	83.9	14.5	49.7	124	67.3	17.9	66.7	12.9	30.2	102

The total content of As in the topsoil of sediments of the Teplá Vltava exceeded the "precautionary value" 20 $mg.kg^{-1}$ (Act No. 153/2016), indicating high soil contamination by As and a need to prevent further increases in soil As contents. Even the "indicative value" of 40 $mg.kg^{-1}$ (Act No. 153/2016) was exceeded in pits 1 and 3, and these high contamination loads represent a potential risk to the quality of farming products and a potential hazard to human and animal health. Total Be contents in the sediments of all pits exceeded the precautionary value of 2.0 $mg.kg^{-1}$. Precautionary values for Cd (0.5 $mg.kg^{-1}$) were exceeded in the sediment layers of pits 3, 4, 5 and 6 and for Pb (60 $mg.kg^{-1}$) in pits 3, 4 and 5. The precautionary value for total Zn (120 $mg.kg^{-1}$) was exceeded only in the topsoil of sediments in pit 3. Ecological risks associated with these sediment contamination levels will be discussed below.

Other studies have also found increased element contents near the Lenora glass works. MAŘÍKOVÁ (2008) reported significantly increased contents of total Hg and EDTA extractable Pb in the Teplá Vltava River bed sediments (0–20 cm) at a site near our pit 5. Comparing bed sediments up and down the river from Lenora, she found total Hg contents of 0.0358±0.0054 versus 0.0767±0.0026 $mg.kg^{-1}$. For the bed sediments of Řasnice, relative low total Hg contents between 0.0063 and 0.0079 $mg.kg^{-1}$ were found. In addition, respective total Hg contents of 0.1853 and 0.1603 $mg.kg^{-1}$ were measured in the H and A1 horizons of a coniferous forest near Lenora. NOVOTNA et al. (2016) published EDTA extractable Pb contents in forest soil and in H horizons at 8 sites within a 3 km distance around Lenora.

Considering the contamination of the topsoil to a depth of 30–35 cm by elements from the glass works operating for 186 years and the negligible natural vertical migration of these elements in sediments, the average sedimentation rate of sediments near Lenora is estimated to be only 0.161–0.188 $cm.year^{-1}$. The estimated sedimentation rate is lower than estimates obtained by activities of ^{137}Cs for the last 32 years.

Remaining elements

The second group of elements (e.g., Al, Ba, Be, Cs, K, La, Li, Nd, Sr, Th, Ti, Tl, U and Y) was characterised by a tendency of their contents to increase with sediment depth (Fig. 5c,d). The accumulation of these lithogenic elements in the subsoil is mainly caused by the aggradation of mineral particles of various size coming from weathered local bedrocks.

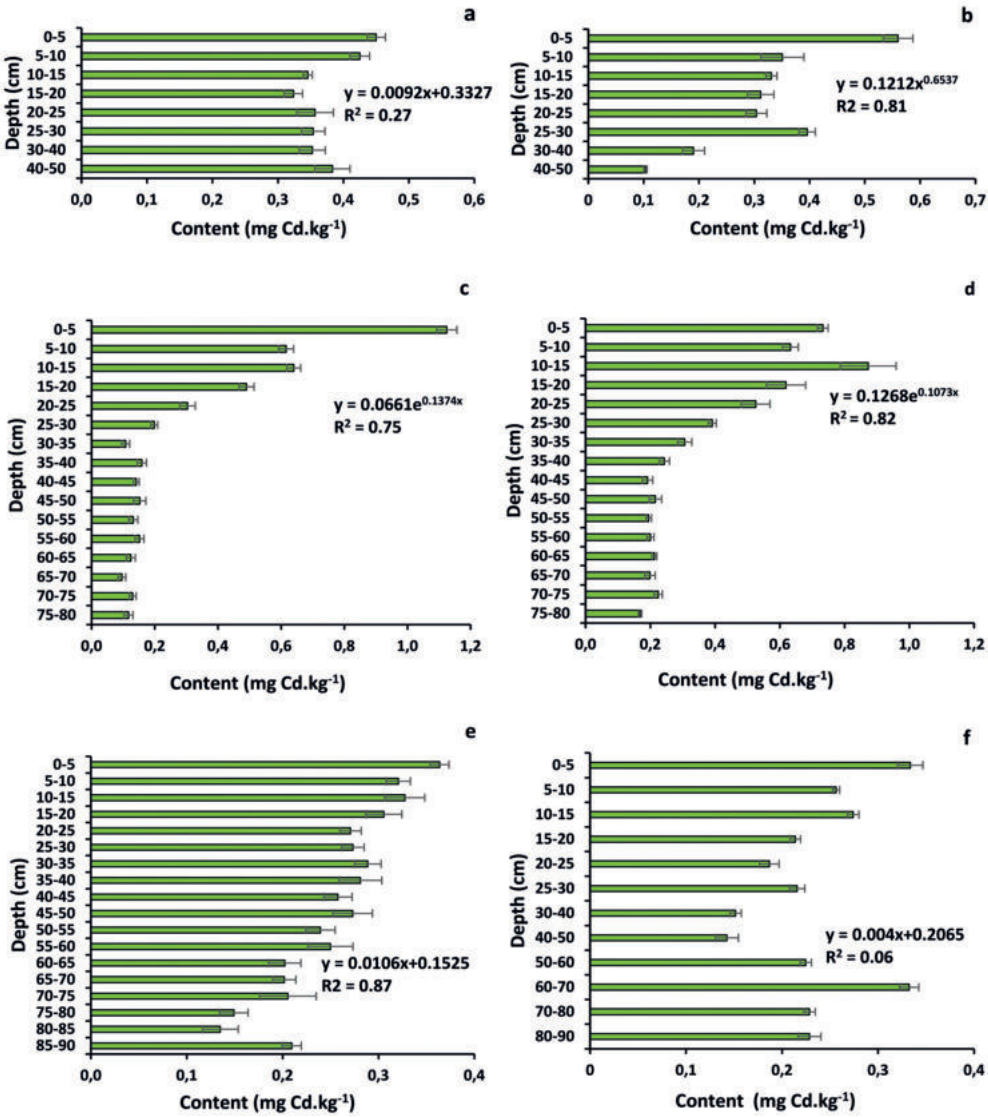

Fig. 6. Vertical distribution of medians of the total cadmium contents in profiles of pit 1 (a), 8 (b), 3 (c), 4 (d), 9 (e), and 7 (f). Error bars show ± median absolute deviations.

Similar content patterns are found in natural soils, where elements are released from bedrocks to the subsoil and at the same time elements from the topsoil partially migrate to the subsoil and similarly as the remaining elements they are partially absorbed from the topsoil by plants in a small amounts and annually removed by crop harvests.

For example, Rb is abundant in local two-mica granites and pegmatites and Ba in biotitic granites. There are also higher contents of lanthanides in both the Weinsberg and Eisgarn granites of Stážný pluton and in the monotonous group of migmatites and paragneisses in other parts of the river catchments, and Be is present in mineral beryl contained in pegmatites and granites, and in plagioclase and micas (NAVRÁTIL 2000, FINGER et al. 2003, PERTOLDOVÁ et al. 2010, RENÉ & HÁJEK 2010, 2011, POUR 2012, RENÉ 2012, 2020). The divergent geochemistry of the bedrock types in both catchments causes increased contents of As, Ba, Mg, U, V and W in the sediments of Teplá Vltava and increased Be, Ca, Cr, Na, Nd, Sr and Th contents in the Řasnice sediments.

The contents of some elements (e.g., Be, Ca, Cs, Fe, Ga, Ge, La, Li, Nd, Rb, Si, Sr, Ti, Tl, U and Y) had even or irregular courses along the sediment vertical profiles (Fig. 5e,f). However, some elements can have both atmogenic and geogenic origins. Such irregularities in element contents can be explained by the variable deposition rates of particles with various sizes carrying different elements, such as, feldspar and mica particles, clay minerals, Fe/Al hydroxides and organic matter during floods. On the other hand, natural as well as anthropogenic turbation of sediment covers contributes to the vertical homogenization of element contents mainly in the sediment topsoils.

The total contents of some elements (e.g., Ba, Be, Ce, Fe, La, Li, Na, Nd, Pr, Rb, Th, Tl, U and V) at least in some parts of the sediment profiles were higher than typical total element contents reported for European flood sediments (SALMINEN et al. 2005, DE VOS et al. 2006). These higher contents were likely caused by the geochemistry of local bedrocks, mainly granites that are rich in minerals containing these elements.

Element content correlations

Strong correlations between element contents indicate their similar properties, including similar emission sources, atmospheric transport, deposition rates and adsorption by similar components of the soil matrix.

A mutual correlation matrix for 46 median element contents of all analysed samples (data not shown), showed the highest numbers of significant correlations for Ag, Na, Se, V, Ni, Si, W, Sb and As contents with the remaining elements. On the other hand, the least number or correlations were found for N, C, Mn, Be, Ba, Th, La, Pb, Mg and Li. The most significant and negative correlations were found for Si and alkaline elements (Na, K, Ca and Sr). The other anthropophile elements As, Cd, Hg, Sb and Sn were very strongly correlated ($r \geq 0.70$) with each other due to their possible common origin from the glass works. Total contents of V, Co and Ge also strongly correlated with anthropophile elements. Mutual strong positive correlations were found among many lithophilic elements and Ce. Lanthanides occurring together in minerals always correlated nearly perfectly ($r \geq 0.95$). The very strong correlations of elements associated with soil organic matter, such as C, N, P, S and Hg, and in contrast the negative correlations of K contents with these elements, indicates a dominant inorganic origin of K (e.g., from feldspar debris).

Stronger correlations were found for anthropophile and geogenic elements in the topsoil and subsoil, respectively. For example, the highest total number of significant positive correlations were for Ag, Na, Se, V, Ni, Si, W, Sb, Pb and As, while the most significant and negative correlations were found for Na, Si, K, Ca and Sr in the sediment subsoil.

pH($CaCl_2$) values, which are a proxy of the current saturation degree of the soil sorption complex, significantly and positively correlated with median contents of Ag, As, Co, Cr, Cu, Fe, Ge, Mg, Mn, Mo, Ni, Sn, Ti, V, W, Y and Zn, while significantly and negatively correlated with Al, Be, Bi, Ca, Cs, K, Na, Rb, Th and Tl, probably due to a larger presence of the latter elements in nonextractable forms.

Pb isotope ratios

Lead from industrial sources has lower $^{206}Pb/^{207}Pb$ ratios than Pb from natural sources, such as bedrocks, and the vertical migration of Pb from industrial sources in coniferous forests is low, estimated to about 0.30 cm.year^{-1} (e.g., ETTLER et al. 2004).

Obvious accumulation of total Pb was found in the topsoil of the sediments studied here, followed by an exponential decrease of Pb content in the subsoil of pits 3, 4, 5, 6 and 7. A slow linear decrease in Pb content was seen in sediments of pits 2 and 8 (i.e. a lower contamination of the topsoil by Pb). The $^{206}Pb/^{207}Pb$ ratio increased and $^{208}Pb/^{206}Pb$ ratio decreased with the sediment depth mainly in the pits close to the glass works highly contaminated by Pb (Table 5). The total lead content and relevant $^{206}Pb/^{207}Pb$ ratios in sediment profiles in pit 5 (Fig. 7) confirmed the industrial origin of Pb in the topsoil. A peak of Pb with a lower $^{206}Pb/^{207}Pb$ ratio was found in a deeper sediment layer 25–30 cm below the surface in pit 9, possibly due to aggradation of less Pb contaminated sediments by more recent floods or the deposition of material from river bed deepening.

One exception to these trends was an increased content of Pb with a lower $^{206}Pb/^{207}Pb$ ratio at the sediment surface in pit 8. We can speculate rather about partially archived anthropogenic Pb from more distant industrial sources coming from long-range transport, as archived in local peats (e.g., ZUNA et al. 2011) than about all Pb from the outlying Lenora glassworks.

Sediments in pit 1 were least affected by industrial Pb, showing only a weak decrease with depth ($Pb = -2.26 \times cm + 91.742$, $R^2 = 0.23$). Small peaks in Pb contents appeared in the depths of 20–25 and 5–10 cm. However, the minimal and maximal $^{206}Pb/^{207}Pb$ ratios were found in the depths of 20–25 cm and 30–40 cm, respectively, but the $^{206}Pb/^{207}Pb$ ratios only negligibly differed among layers. The upper and deeper Pb peaks could reflect decreased Pb emissions from the glass works in the corresponding time period.

The history of Pb deposition rates caused by the long-range transport of Pb from distant industrial sources and the combustion of leaded petrol is archived in peat profiles and tree rings. In the Bohemian Forest, maximal contents of industrial Pb with $^{206}Pb/^{207}Pb$ ratios between 1.16 and 1.17 in peat and wood cores correspond to the 1960s / 1970s (ZUNA et al. 2011). The $^{206}Pb/^{207}Pb$ ratios in current atmospheric Pb deposition are about 1.160 (CIMOVA et al. 2016).

MAŘÍKOVÁ (2008) reported low $^{206}Pb/^{207}Pb$ ratios of 1.1626–1.1751 and 1.1387–1.1487 in the river bed sediments up and down the river from Lenora, respectively. She also found $^{206}Pb/^{207}Pb$ ratios of 1.1491 and 1.1623 for forest floor humus and A1 soil horizon near Lenora, respectively. The corresponding $^{208}Pb/^{206}Pb$ ratios in river bed sediments up and down

Table 5. Ranges of median lead contents Pbtot (mg.kg^{-1}), $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in the topsoil (0–30 cm) and subsoil (>30 cm) in sediment layers of 9 pits.

Depth	0–30 cm		
Pit	Pb_{tot}	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
1	29.5–35.1	1.1701–1.1823	2.0806–2.0935
2	24.4–49.5	1.1745–1.1871	2.0777–2.0897
3	30.2–100	1.1501–1.1714	2.0898–2.1016
4	38.6–71.0	1.1636–1.1732	2.0857–2.0961
5	77.0–106	1.1642–1.1710	2.0900–2.0957
6	45.2–54.4	1.1630–1.1808	2.0819–2.0988
7	23.5–40.1	1.1778–1.1986	2.0714–2.0852
8	33.8–42.9	1.1794–1.1903	2.0747–2.0866
9	29.1–37.9	1.1783–1.1868	2.0750–2.0863

Depth	>30 cm		
Pit	Pb_{tot}	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
1	26.6–28.9	1.1844–1.1857	2.0832–2.0845
2	19.1–27.0	1.1864–1.2078	2.0637–2.0791
3	20.2–22.8	1.1795–1.2093	2.0646–2.0866
4	21.0–23.9	1.1732–1.2136	2.0600–2.0814
5	21.2–59.5	1.1708–1.2095	2.0675–2.0903
6	19.9–47.1	1.1863–1.2202	2.0557–2.0799
7	20.6–29.6	1.1925–1.2026	2.0691–2.0784
8	24.6–27.5	1.1852–1.1986	2.0722–2.0807
9	23.0–34.6	1.1833–1.2012	2.0704–2.0801

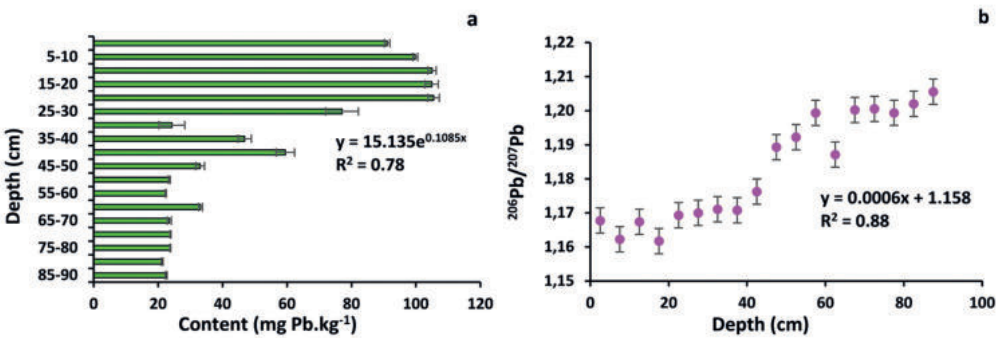

Fig. 7. Median total Pb contents (a) and median $^{206}Pb/^{207}Pb$ ratios (b) in sediment profiles of pit 5. Error bars show ± median absolute deviations.

Table 6. Geoaccumulation indices (I_{geo}), indicating moderately (not marked) and strongly (marked *) polluted sediment layers along the sediment profiles of 9 pits for the elements listed. The number intervals represent the thickness of the polluted zones in the corresponding depths under the sediment surface (cm).

Pit	1	2	3	4	5	6	7	8	9
Ag								0–30	65–75
As	0–30	0–20	0–45	0–50	0–35	25–35		0–30*	0–90*
Bi			0–10		0–10	30–40	0–20	0–30*	0–20
Cd	0–50	0–20	0–25*	0–35*	0–30* 35–85	0–55	0–10 70–90	0–30	0–50
Cr									0–90
Cu									0–35
Hg	20–40		0–30	0–40	0–30 35–65	0–55	0–10	0–30	15–35
Ni									20–40
Pb			0–20	0–25	0–30 40–50	0–25			
S			0–10	0–25	0–15 45–80	0–10 25–45		0–10	
Sb	0–10		0–80	0–30*	0–30* 35–65	0–40		0–30	0–35
Sn			0–25*	0–30	0–30* 35–50	15–25		0–10	
Th					0–90			0–30	35–50
V									20–45 55–65

the river from Lenora were 2.0828–2.1078, and 2.0991–2.1279, respectively, and in humus and A1 horizons in the forest near Lenora were 2.1124 and 2.0984. These ratios are approaching our values in bank sediments.

Sediment pollution loads

Geoaccumulation indices

For our 52 investigated sediment samples and 46 element contents, Igeo values ranged between 2.0 and 2.5. The sediments layers were moderately to strongly polluted by Ag, As, Bi, Cd, Cr, Cu, Hg, Ni, Pb, S, Sb, Sn, Th and V, which are mainly anthropophile elements that are most likely associated with the operation of the glass works. The topsoil layers of all pits were most polluted, but increased pollution was also found in the subsoil in pits 5, 6 and 9 near Lenora (Table 6). The polluted deeper layers in pits 5 and 6 included the layers of

buried charcoal material, which can effectively adsorb elements from the soil solution. Surprisingly, increased Pb pollution of sediments was only indicated in the topsoil of pits 3, 4, 5 and 6, while Cd contaminated the topsoil in all pits. Topsoil pollution by As and Hg was also indicated in nearly in all pits. On the contrary, Ag, Cr, Cu, Ni and V (both chalcophile and lithophile elements) polluted bank sediments only in two pits along the Řasnice, indicating an increased accumulation of elements derived from the local bedrock in the Řasnice catchment in contrast to along the Teplá Vltava.

Enrichment factors

Table 7 shows data for the sediment layers in pits for which EFs indicated an enrichment of the corresponding elements. The absolute highest EF values (14–23) were found for Sb in the surface layers of pit 3. In comparison to the I_{geo} values, 35 elements had EF values exceeding 1, including Ba, Be, Ce, Co, Cs, Fe, La, Li, Mn, Mo, Na, Nd, Pr, Rb, Se, U, W, Y and Zn, lithophilous elements of bedrock origin that enriched sediments mainly along the Řasnice River. Sediments of pits 1 and 2 were the least enriched by anthropophile elements released from the glass works compared to the remaining pits along the Teplá Vltava River.

Ecological risk assessment

Computed PTRI levels for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in sediment layer profiles at 9 sites are given in Table 8. The most severe ecological risk was represented by surface sediments close the former glass works at sites 3, 5 and 4, with PERI values exceeding 500, and by deeper layers of sediments rich in charcoal materials with adsorbed potential toxic elements.

Composite PTRI values are calculated from the sums of potential ecological risk indices for individual element contents. The highest ecological risk levels (E_r^i) were found for Cd contamination of sediments at sites 1–5, with E_r^i values between 87 and 440, and Hg contamination at sites 6–9, with E_r^i values 60–267. E_r^i values for Hg and pits 1–5 were 110–231, and E_r^i for Cd and pits 6–9 were 57–197. The third element most contributing to PTRI was As, with E_r^i = 12–56 at all sites. The PTRI values decreased with the distance of the pits from the Lenora glass works. Ecological risk levels of single element pollution have been defined as follows: E_r^i <40 low risk, $40 \leq E_r^i < 80$ moderate risk, $80 \leq E_r^i < 160$ higher risk, $160 \leq E_r^i < 320$ high risk and $320 \leq E_r^i$ serious ecological risk (GUO et al. 2010). At our sites, E_r^i values decreased in the order Cd>Hg>As>Pb>Cu>Ni>Cr>Zn and Hg>Cd>As>Pb>Cu≥Ni>Cr>Zn for pits 1–5 and 6–7, respectively. A similarly decreasing order of E_r^i values was found for sediments along the Řasnice River (pits 8–9): Hg>As>Cu>Ni>Pb≥Cr>Zn. Surprisingly, relative low ecological risk levels were found for the Pb contamination of sediments, even in the vicinity of the glass works. One reason may be the low value of the toxicity coefficient (T_r^i) for Pb in comparison to the Hg, Cd and As. It should also be kept in mind that potential ecological risk levels for Sb, Bi, Sn, V and other elements could not be estimated due to the lack of coefficients of toxicity for these elements, even though they have evident ecological effects.

Table 7. Enrichment factors (EFs), indicating minimal (not marked), moderate (*), significant (**) and very high (***) enrichment of the listed elements in the sediment profiles of 9 pits. The number intervals represent the thickness of polluted zones in the corresponding depths under the sediment surface (cm).

Pit	1	2	3	4	5	6	7	8	9
Ag			0–50		40–45		50–70	0–30	0–75
As	0–25* 30–50	0–10* 10–40	0–50* 50–65	0–50* 50–80	0–35* 35–45 60–65	25–40	0–10 50–70	0–25* 25–40	0–75* 75–85
Ba			0–40				30–80	10–20	
Be			0–40		25–50		0–10 60–80	0–25	
Bi		0–15	0–10* 10–60	0–50	0–50	35–55	0–10* 10–60 60–65*	0–30* 30–40	10–40
Cd	0–10* 10–20 20–50*	0–15* 15–40	0–10** 10–60	0–15** 15–35* 35–65	0–20* 20–25** 25–90*	0–10* 10–35 35–40** 40–55*	0–5* 5–20 25–60 60–70* 70–90	0–30	0–30
Ce								0–30	0–85
Co	0–20	0–10		0–50	20–30			0–30	20–70
Cr								0–25* 25–30	0–15 15–40* 40–85
Cs						0–15 25–80		0–10 10–25* 25–30	15–30
Cu			0–5* 5–30 35–50	0–25	20–50			0–30	0–15 15–30* 30–85
Fe									0–85
Hg		0–40	0–10** 10–60	0–35* 35–60	0–65* 65–80	0–15 15–35* 35–35** 35–40* 40–55	0–10* 10–15 50–60 60–70* 70–80	0–30	
La								0–30	0–80
Li								0–30	

Table 7. Continued.

Pit	1	2	3	4	5	6	7	8	9
Mn	0–15	0–10	0–20	0–50				0–10 10–30*	0–30** 30–35 35–85*
Mo		0–10	0–5* 5–55	0–50	0–10 40–65	35–45	0–5	0–25* 25–40	0–40
Na							0–15 25–70		
Nd								0–30	0–75
Ni			0–5					0–30	0–85
P			0–25	0–15	40–65		0–10 50–70	0–30	
Pb	0–10 20–30	0–5* 5–40	0–5** 5–25* 25–55	0–25* 25–35	0–45* 45–75	0–15 35–45	0–15 25–80	0–30	15–30
Pr								0–30	
Rb							0–15 25–80		0–90**
S	0–5 20–50	0–20	0–15* 15–50	0–5* 5–35	0–40 40–80*	0–10 30–45* 45–55	0–15	0–30	
Sb	0–30	0–40	0–10*** 10–15** 15–30* 30–50	0–15** 15–30* 30–40	0–15* 15–25** 25–65* 65–80	0–35 35–40* 40–45	0–10 50–70	0–20* 20–30	0–20 20–30* 30–40
Se			0–10					0–30	30–40
Sn	0–30	0–10	0–20** 20–30* 30–60	0–30* 30–50	0–20* 20–25** 25–45* 45–80	5–25 35–50	0–60 60–80*	0–30	15–35
Th								0–10 10–20* 20–30	0–75
Tl		0–10	0–55	0–35	25–50	35–45	0–70	15–25	
U								0–30	0–20 20–25* 25–90

Table 7. Continued.

Pit	1	2	3	4	5	6	7	8	9
V			0–5 25–70	0–35				0–5 5–20* 20–30	0–20 20–25* 25–90
W	25–50		0–50		30–50	35–45	0–15 50–70	0–30	0–85
Y								0–30	0–85
Zn		0–10	0–10	0–5	5–25			10–25	

Conclusion

Results showed that the sediments of Teplá Vltava and Řasnice were mainly affected by a local glass works operating between 1834 and 1995. Buried charcoal material accumulated in a thick layer of the sediment subsoil in two pits down river from the glass works distinctly affected the physical and chemical characteristics of sediments in this layer, as charcoal can adsorb elements from the soil solution. However, despite ^{14}C dating of the charcoal remnants, the origin and reason for this accumulation is not clear. The topsoil in all pits was contaminated by anthropophile elements, mostly by As, Cd, Hg, Pb, Sb, Sn and Zn originating mainly from the glass works. However, Pb contamination loads in sediments were lower than expected. An increased accumulation of anthropophile elements in the subsoil was found mainly in pits situated close the glass works. Contaminated sediments were transported and aggraded down river from Lenora. Overall, the contamination gradient in sediment profiles decreased with the distance from the glass works. A high content of As in sediments near Borová Lada was mainly caused by geogenic As accompanying nearby gold deposits. I_{geo} and EF indices indicated a higher than background accumulation of anthropophile as well as some lithophile elements in sediment profiles. The enrichment of sediment layers by lithophile elements is likely caused by the sedimentation of local bedrock weathering products during floods. The proportion of lithophile element contents in sediments of both catchments differs due to variations in the geology of the catchments. Lower $^{206}Pb/^{207}Pb$ isotopic ratios in the topsoil compared to the subsoil confirmed the mainly industrial origin of Pb in the topsoil. Potential toxicity response indices implied a moderate to serious potential toxicity of sediments, mainly in the topsoil but also in the whole sediment profile of pits situated close the former glass works. Cd, Hg, As and Pb contents had the highest contribution to the total ecological risks. However, elements for which toxicity coefficients have not been established were not included in this toxicity estimation. Total contents of As, Be, Cd and Zn in topsoil sediments reached or exceeded legal limits for the protection of health, quality of crops and soil. The heavily contaminated bank sediments near Lenora represent a potential risk for water biota if larger amounts of sediment material are released, for example by catastrophic floods or during large bank earthworks.

Table 8. Computed potential toxic response index (PTRI) values for the vertical bank sediment profiles in 9 pits, indicating moderate (*), severe (**) and serious (***) potential toxicity.

Depth / Pits	1	2	3	4	5	6	7	8	9
0–5 cm	278*	259*	547**	408**	521**	401**	246**	282*	177*
5–10 cm	273*	233*	441**	387**	531**	360**	192*	233*	167*
10–15 cm	220*	215*	469**	446**	490**	363**	192*	212*	179*
15–20 cm	247*	180*	395**	369**	563**	348**	146	198*	190*
20–25 cm	275*	164*	249*	326**	727***	367**	124	200*	190*
25–30 cm	255*	139	217*	258*	356**	296*	126	169*	199*
30–35 cm		153*	124	229*	177*	339**			203*
35–40 cm	202*	139	190*	202*	287*	496*	90	98	176*
40–45 cm		106	166*	186*	379**	304**			160*
45–50 cm	248*	140	150	179*	321**	242*	85	55	160*
50–55 cm		145	134	158*	245*	239*			147
55–60 cm		152*	136	151*	212*	127	142		151*
60–65 cm			121	150	276*	105			155*
65–70 cm			100	131	166*	102	190*		152*
70–75 cm			106	143	174*	110			142
75–80 cm			98	116	169*	142	136		110
80–85 cm					151*				118
85–90 cm					158*		137		140

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