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The Fate of Atmospherically Derived Pb in Central European Catchments: Insights from Spatial and Temporal Pollution Gradients and Pb Isotope Ratios

Leona Bohdalkova,^{†,§} Martin Novak,^{*,†} Marketa Stepanova,[†] Daniela Fottova,[†] Vladislav Chrastny,[†] Jitka Mikova,[†] and Ales A. Kubena[‡]

[†]Czech Geological Survey, Geologicka 6, 152 00 Prague 5, Czech Republic

[‡]Institute of Information Theory and Automation, Czech Academy of Sciences, Pod Vodarenskou Vezi 4, 182 00 Prague 8, Czech Republic

[§]Global Change Research Centre, Academy of Sciences of the Czech Republic, Belidla 986/4a, 60300 Brno, Czech Republic

Supporting Information

ABSTRACT: Soils in polluted regions are generally regarded as a delayed, longlasting source for Pb contamination of aquatic systems. Lead deposited on topsoil is slowly transported downward with particulate and colloidal organic matter, driven by infiltrating precipitation. Then, Pb is tightly retained in mineral soil. Lead export from catchments is extremely low and decoupled from the atmospheric input. We tested this hypothesis in 11 small catchments, differing in pollution levels. Input/ouput Pb fluxes were monitored for 14–15 years in an era of decreasing industrial Pb emission rates. Between 1996/1997 and 2010, Pb deposition fluxes decreased significantly, on average by 80%. At the beginning of the monitoring, Pb export constituted 2 to 58% of Pb input. At the end of the monitoring, Pb export constituted 2 to 95% of Pb input. Highly polluted sites in the northeast exported significantly more Pb than less polluted sites further south. The ²⁰⁶Pb/²⁰⁷Pb isotope ratios of runoff (1.16) were identical to those of



topsoil and present-day deposition, and different from mineral soil and bedrock. Lead isotope systematics and between-site flux comparisons indicated that a portion of the incoming Pb had a relatively short residence time in the catchments, on the order of decades.

INTRODUCTION

Upland forested catchments are a major source of drinking water. Following 200 years of high industrial Pb emissions, there are concerns that neurotoxic effects of Pb may negatively influence aquatic biota and human health.¹ A number of studies have calculated Pb input/output mass balances at the catchment level.²⁻⁵ Recently, processes controlling accumulation and release of Pb in forest ecosystems have been modeled, with a focus on competitive solid-solution partitioning, and chemical interactions in solutions.⁶ These models take into account a sharp decrease in Pb deposition, which started in the mid-1970s in Western Europe and North America, and in the late 1980s in Central Europe. Vertical profiles through peat deposits reveal that atmospheric Pb input in the 20th century was up to 1000 times higher compared to the early Holocene.⁷ A 10-fold drop in pollution in recent years means that atmospheric Pb deposition may still be 100 times higher than in prehistoric times. Only in a few studied areas, such as Arctic Scandinavia, present-day Pb deposition is nearly as low as in early Holocene.

In forested catchments, runoff outputs of Pb are much less than precipitation inputs.⁸ Forest ecosystems function as sinks for anthropogenic Pb.^{2–5} Substances with the highest affinity to Pb are organic matter, amorphous Fe-oxides, and clay minerals.⁹ Some Pb in groundwater may be geogenic. Lead isotopes have shown that weathering of granitic bedrock releases Pb into waters in two steps, first Pb from accessory minerals, and then Pb from the main rock-forming minerals.¹⁰

Tree bark, fine roots and foliage accumulate more Pb than xylem.¹¹ In forests, standing pools of Pb are much larger than annual hydrological Pb losses from catchments. Lead turnover through above-ground vegetation is rapid, on average only a few years.¹ Lead contained in litter is partly recycled into vegetation, but mainly retained in soil. Out of the total soil Pb pool, more than 75% are usually stored in humus, and less than 25% in mineral soil.¹¹ Lead isotopes have shown that even at remote northern locations, far from point sources of Pb pollution, over 90% of all Pb in the organic forest floor is pollution-derived, not geogenic.¹² The Pb pool in conifer soil tends to be higher than in nearby deciduous soil because of slower turnover of soil organic matter in coniferous stands.⁹ A

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minute, but measurable, downward translocation of pollutant Pb has been detected in forest soils using natural-abundance isotopes.^{13,14}

Lead storage in soils has built up for over three thousand years. Several studies have concluded that more than 50% of the present-day Pb store in soils accumulated before the beginning of the Industrial Revolution.⁷ Within catchments, soils at higher elevations tend to store more Pb, due to higher precipitation totals.¹¹ The soil storage of Pb may be high enough to allow export of anthropogenic Pb for extremely long periods of time in the future, regardless of present-day deposition.¹⁵ Lead transport is governed by biogeochemical conditions, which have an impact on pH and on mobilization of organic substances.¹⁵ Mobility of Pb in forest ecosystems is strongly dependent on the solubility of organic matter.^{13,16} Hydrology, and other physical processes, such as erosion, also affect Pb mobility.¹⁷ Mean residence time of Pb in forest soil is believed to be on the centennial, or rather millenial, time scale.¹⁴ A lag in response of streamwater quality can be expected following reduction in industrial Pb emissions, and reduction in atmospheric Pb deposition rates.¹⁴

Some recent studies have suggested that it will take many decades before Pb concentration in runoff decreases appreciably.^{14,16,18} Due to a large Pb soil pool compared to export Pb flux, and due to high availability of Pb-binding sites in catchment soils, insensitivity of Pb export to decreasing pollution is postulated. Direct testing of such conclusion, however, has been rarely performed.¹⁶ It requires large spatial and/or temporal gradients in anthropogenic Pb loads.¹⁹ Here we present input/output Pb mass balances for a wide range of small forested catchments, differing in past and present pollution levels. Our 11 study sites were situated throughout the Czech Republic, Central Europe. The Pb mass balances are based on a long period (15 years) of hydrochemical monitoring. Our first objective was to test whether or not Pb runoff fluxes respond to decreasing Pb inputs. Our second objective was to isotopically fingerprint the source of presentday runoff Pb in all 11 catchments. Our third objective was to evaluate whether highly polluted sites exported more of the recently deposited Pb than relatively unpolluted sites.

MATERIALS AND METHODS

Site Description. All 11 sites (Figure 1; Table 1) were small headwater catchments, forming V-shaped valleys, forested mainly with Norway spruce. Sites situated near the northern border of the Czech Republic with Poland and Germany (*e.g.*, UHL and UDL) were affected by spruce die-back related to industrial pollution.^{20,21} Clearings date mostly to the early 1980s. In contrast, no spruce damage was visible at sites situated further south (e.g., LIZ and LES). The average catchment area was 130 ha, precipitation totals varied betwen 600 and 1700 mm yr⁻¹. Soils were relatively well developed, with thicknesses of 50–90 cm. Dystric cambisols and podzols predominated.²²

Sampling. For 15 hydrological years (November 1, 1996 to October 31, 2010), monitoring of water chemistry was carried out monthly in all 11 cachments. At one site, JEZ, the oldest available Pb data came from 1997 (14-year time series). The sampling procedures were identical in all catchments. The time span between two samplings was nearly constant, close to 30 days. Two rain collectors were used to sample open-area (bulk) deposition. Nine rain collectors, installed in a regular 10×10 m grid, were used to sample spruce canopy throughfall. In winter,



Figure 1. Location of the studied catchments in the Czech Republic (solid circles). The selected sites spanned a 27-fold Pb pollution gradient. Lead concentrations in the atmosphere in 1996 are based on unpublished data by the Czech Hydrometeorological Institute, Prague.

five snow collectors were used to collect spruce canopy throughfall, and two snow collectors were used to sample openarea deposition. Runoff fluxes were measured continuously by a pressure transducer (LIZ, UHL, MOD), or ultrasonically (CER, JEZ). All the other sites were equipped with a water level recorder ("float"). Stream water was collected monthly at the gauging station. Samples were collected manually and acidified with HNO₃ (Suprapur, Merck) to 2% (v/v). At each site, water within each sample type was pooled before analysis. In September and December 2010, samples of open-area deposition, spruce canopy throughfall, and runoff were collected in each catchment for Pb isotope analysis.

Analysis. Unfiltered samples were analyzed. Care was taken to prevent contamination of water samples. All PE labware was cleaned by 20% HNO₃ (Suprapur, Mercks) for 48 h, samples for analysis of Pb isotopes were handled in a laminar flow box (class 7). Lead concentrations were determined by atomic absorption spectrometry with electrothermic atomization (ETAAS; Perkin-Elmer 4100). The detection limit was 0.4 μ g Pb L^{-1} . All procedural blanks had Pb concentrations below this detection limit. The inlet tubing in ETAAS had an inner diameter of 1 mm. Acidified samples were well shaken before introduction into the spectrometer, so that Pb-containing colloids and small organic particles were also analyzed. Lead isotope ratios (²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁷Pb) were determined on a mass spectrometer with inductively coupled plasma (ICP MS X-series, Thermo Fisher Scientific) with a Meinhard concentric nebulizer. The accuracy of the Pb isotope measurements was checked by measuring an AGV-2 standard $(^{206}Pb/^{207}Pb =$ 1.2085 ± 0.0006 , ²⁰⁸Pb/²⁰⁷Pb = 2.4671 ± 0.003). The standard error for Pb isotope measurements did not exceed 0.4% RSD (10 replicates). Calibration against the NIST SRM 981 standard was performed after every two samples.

Thoughout the study, we used acid-washed 100 mL LD PE bottles for water samples. Supporting Information (SI) Figure S1 gives a time-series of Pb concentations of a QC-1 standard with a certified value of 4 μ g L⁻¹. The standard was kept in LD PE bottles identical to those used in our sampling. Lead recovery was quantitative.

Calculation of Pb Fluxes. Catchment-level Pb input fluxes were calculated as a sum of area-weighted contributions of spruce throughfall and open-area deposition. Runoff Pb fluxes

Table 1. Study Site Characteristics

catchment	location	elevation (m a.s.l.)	area (ha)	% spruce forested	bedrock	soil type	mean winter-time/annual/summer- time temperature (°C)	annual precipitation (mm)
ANE	49°34′ N, 15°05′ E	480-540	27	88	paragneiss	distric cambisol	-3.0/ + 6.9/ +16.7	644
CER	49°27′ N, 18°23′ E	640-961	185	85	sandstone	distric cambisol	-3.8/ + 6.2/ +15.5	1155
JEZ	50°32′ N, 13°28′ E	475-924	261	18	gneiss	distric cambisol	-3.9/ + 5.0/ +14.3	934
LES	49°58′ N, 14°49′ E	400-495	70	44	granite	distric cambisol	-3.0/ + 7.0/ +17.0	613
LIZ	49°04′ N, 13°41′ E	828-1024	99	63	paragneiss	distric cambisol	-3.4/ + 4.9/ +13.6	905
LKV	49° 38′ N, 15°21′ E	472-658	66	100	granite	distric cambisol	-3.2/ + 6.9/ +16.0	715
MOD	50°42′ N, 15°42′ E	1010-1554	262	18	mica-shist	cambic podzol	-5.9/ + 2.9/ +12.1	1666
РОМ	49°47′ N, 15°45′ E	512-640	69	91	gneiss	stagno-gleyic cambiosol	-3.6/ + 6.3/ +16.0	695
SAL	49°31′ N, 14°59′ E	557-744	168	100	paragneiss	stagno-gleyic cambiosol	-4.5/ + 6.0/ +16.5	572
UDL	50°13′ N, 16°29′ E	880-950	33	67	gneiss	cambic podzol	-4.0/ + 5.0/ +15.0	1308
UHL	50°49′ N, 15°08′ E	780-870	187	50	granite	cambic podzol	-4.8/ + 4.0/ +13.8	1231

were calculated from the known water fluxes and Pb concentrations by interpolation.

Statistics. The PASW software by SPSS (Version 18) was used for the statistical treatment of the data. Temporal trends in Pb monthly input and runoff fluxes were evaluated using mixed models with AR(1) covariance type. The same method was used to compare Pb fluxes at the four highly polluted northeastern sites (UDL, UHL, MOD, and CER) with the remaining seven sites.

RESULTS AND DISCUSSION

Pb Concentrations. A decrease in mean annual Pb concentrations was observed in all three sample types (SI Table S1). At UDL, the most polluted site situated in the northeast, mean Pb concentrations in spruce canopy throughfall decreased from 29 in 1996 to 1.6 μ g L⁻¹ in 2010, that is, 18 times. In 1996, Pb concentrations in open-area deposition at UDL (15 μ g L⁻¹) were about half of those in throughfall. In 1996, none of the sites had mean Pb concentrations in throughfall lower than 2.8 μ g L⁻¹. In 2010, none of the sites had mean Pb concentrations in throughfall higher than 2.8 μ g L^{-1} . UDL runoff contained slightly less than 3 μ g L^{-1} Pb in 1996. UDL runoff Pb concentrations were lower by ca. 50% in 2010, compared to 1996. Lead concentrations in atmospheric deposition in the polluted northeast occasionally exceeded the drinking water limit $(10 \ \mu g \ L^{-1})^{23}$ at the beginning, but not at the end of the observation period.

The decreasing Pb concentrations in catchment inputs reflect decreasing anthropogenic emission rates in the Czech Republic. Both major sources of environmental Pb, gasoline combustion (a smaller source, Figure 2a) and coal combustion (a larger source, Figure 2b) peaked in the 1980s, and then experienced a dramatic decrease.²⁴ Mining and processing of Pb–Ag ores in the region had peaked already in 1890 and did not contribute significantly to recent Pb emissions.²⁴

We hypothesized that Pb export via runoff was mainly mediated by dissolved, colloidal and particulate organic matter.^{13,16,25} Therefore, we measured total organic cabon



Figure 2. History of Pb pollution in the Czech Republic. (a,b) Pb emission rates, 23 (c) 206 Pb/ 207 Pb of organic soils in 10 vertical peat profiles, 23,28 (d) 206 Pb/ 207 Pb of spruce xylem in the catchment JEZ. 26

(TOC) concentrations in runoff, starting in 2005. SI Figure S2 plots Pb concentrations in runoff in two highly polluted



Figure 3. Time-series of vegetation-type weighted annual Pb input and runoff fluxes in 11 small forested catchments in the Czech Republic. Note the different scales on the y-axis. R^2 , coefficient of determination.

catchments, UDL and UHL, vs TOC concentrations in runoff. There was no correlation between Pb and TOC at UDL ($R^2 = 0.022$, p = 0.127). At UHL, a significant positive correlation was observed ($R^2 = 0.114$, p = 0.0.006). In contrast to some other studies in the literature,^{13,16,24} TOC availability in runoff did not control Pb export at all our sites. Interestingly, no correlation between TOC and Pb concentrations ($R^2 = 0.022$) and $R^2 = 0.022$ and $R^2 = 0.022$.

0.034, p = 0.278) was found in a recent survey of surface water chemistry on the territory of the entire Czech Republic (1016 samples; area of 80 000 km²).²⁶

Catchment-Level Pb Input. Time-series of vegetationtype weighted Pb input fluxes are given in Figure 3 (solid circles). Over the monitoring period, atmospheric Pb inputs decreased significantly at all 11 sites (p < 0.001), on average by 80% (from 49 to 10 g Pb ha⁻¹ yr⁻¹). Our study began in 1996/ 1997, approximately 10 years after the industrial Pb emissions started to decrease (1987, Figure 2a, b). The year 1996 also marks completion of installation of dust-removing devices in 15 large Czech lignite-burning power plants.²² At the same time, dust removing devices were not yet part of Polish coal burning power plants, situated north of UDL, UHL, MOD, and CER. Indeed, as seen in Figure 4a, it was these northeastern sites



Figure 4. Comparisons between Pb input and runoff fluxes in the studied small catchments at the beginning and the end of the monitoring (a). All sites exhibited lower Pb input in 2010 compared to 1996/7 (p = 0.004). The most polluted sites UDL, UHL, and MOD exhibited the largest decrease in Pb runoff flux between 1996 and 2010 (b).

which received the largest amounts of atmospheric Pb. There was a sharp spatial pollution gradient in 1996, with the most polluted site UDL in the northeast receiving 27 times more Pb than the least polluted site LES located further south (Figure 4a).

Pb Export via Runoff. Pb runoff fluxes are given in Figure 3 (open circles). Across the sites, the Pb runoff flux was $6.1 \pm$ 2.5 g ha⁻¹ in 1996 (mean \pm SE). In 2010, the Pb runoff flux was 3.4 ± 1.4 g ha⁻¹. At the beginning of the study, catchment output at individual sites was between 2 and 58% of atmospheric input. At the end of the study, the catchment output was between 2 and 95% of atmospheric input. The highest Pb export of 95%, relative to the atmospheric Pb input, was observed at the most polluted site UDL. Over the duration of the study, the percentage of the Pb output relative to Pb input increased on average from 13 to 35%. This percentage was higher than in studies performed in less polluted countries.^{3,16} Over the duration of the study, and across the sites, Pb runoff decreased by 44%. Statistically, however, this decrease was insignificant at the 0.05 level (p = 0.87). This may have been due to large interannual variability in runoff Pb fluxes.

Across the sites, the percentage of Pb concentration measurements which were below the detection limit (4 μ g L⁻¹) was high (53%). Across the sites, the percentage of Pb concentration measurements which yielded values lower than 3 times the detection limit (12 μ g L⁻¹) was also high (82%). In such cases, trace element data should be treated with caution. In our study, the frequency of Pb concentration measurements below one and three detection limits significantly increased with time (p = 0.006, and p = 0.012, respectively). These trends add credibility to the presented Pb runoff data.

A possible correlation of Pb export from catchments with runoff pH could not be evaluated. There was no statistically significant temporal change in runoff pH over the duration of the study, and across the sites (SI Figure S3).

Lead Isotope Systematics in the Environment of Central Europe. Several authors studied Pb isotope signatures of Central European sources of pollution.^{24,27–30} The main



Figure 5. Mean Pb isotope signatures in the environment of the Czech Republic (Central Europe). A three-isotope plot. Data from refs 23,27-30. Small black oval marks catchment inputs and outputs, given in more detail in Figure 6

polluters are plotted in a three-isotope graph in Figure 5. The 206 Pb/ 207 Pb ratio increased in the order: gasoline (mean of 1.11) < Pb-Ag ores (1.17) < coal (1.19). Variscan bedrock had the highest, most radiogenic 206 Pb/ 207 Pb signature of 1.22. These mean values differed from each other sufficiently for a meaningful source apportionment. The large light-gray triangle in Figure 5 marks Pb isotope ratio of vertical peat profiles in the Czech Republic since the beginning of the Industrial Revolution (AD1800).²⁴

Lead Isotopes in Catchment Inputs/Outputs and soil. In contrast to the large range of Pb isotope ratios of peat, all values for atmospheric deposition and runoff in the 11 studied catchments fell into a very narrow range (small black oval in Figure 5). The ²⁰⁶Pb/²⁰⁷Pb ratios of catchment fluxes were all close to 1.16. As seen in Figure 6a, b, there was no systematic trend between ²⁰⁶Pb/²⁰⁷Pb of spruce throughfall, open-area deposition, and runoff.

Several authors have studied vertical profiles in upland forest soils in the Czech Republic (e.g., refs 28 and 31). Throughout the country, the 206 Pb/ 207 Pb trends in well-aerated forest soils were very similar (Figure 6c). Typically, the O+A horizons had a 206 Pb/ 207 Pb ratio of 1.16. Lead became more radiogenic in deeper soil horizons, with 206 Pb/ 207 Pb of 1.19 in the B horizon, and around 1.22 in the C horizon. The relatively high value for the C horizon was identical to bedrock (*cf.*, Figure 6c and Figure 5).

Clearly, the Pb isotope signal of catchment inputs, topsoil and catchment outputs (1.16) was anthropogenic. It resulted from mixing of ore Pb (peak production in the 19th century), partly industrially recycled ore Pb (throughout the 20th century), coal combustion (1860–present) and gasoline combustion (1940–2000; adding alkyl Pb to gasoline was banned in 2000). The 208 Pb/ 207 Pb ratios on the vertical axis in Figure 5 helped to define the main mixing lines: Pb isotope ratios of various types of catchment waters lay close to the gasoline-ores-coal mixing lines, but were offset relative to any mixing lines involving bedrock. Our observation that presentday atmospheric inputs and runoff outputs in Czech forested CER

2.446

2 444

2.442

2 4 4 0

2.438

2.436

2.434

2.432

2,430

2.428

2.446

2 4 4 4

2.442

1.152

b

²⁰⁸Pb/²⁰⁷Pb

а





Figure 6. Lead isotope ratios of spruce throughfall, open-area deposition and runoff in late summer (a) and early winter (b) of 2010. For site location see Figure 1. Vertical trend in ²⁰⁶Pb/²⁰⁷Pb in Czech soils (c). Means for soils in the northern, central, and southern Czech Republic (refs 27, 30, and references therein).

catchments contain isotopically identical Pb agrees well with a previous study in Scotland.³²

Figure 2c and d provide an insight into temporal changes in ²⁰⁶Pb/²⁰⁷Pb of deposited Pb in the Czech Republic. Lead-210 dated peat profiles (Figure 2c) and tree rings (Figure 2d) were used as archives of past pollution. Two-hundred years ago, peat recorded a relatively high 206Pb/207Pb ratio of 1.18, slightly lower than ²⁰⁶Pb/²⁰⁷Pb of unpolluted modern crustal Pb (1.20–1.23). By then, lowering of the ${}^{206}\text{Pb}/{}^{207}\text{Pb}$ ratio was caused by centuries-long processing of Ag and Pb ores. After AD1800, ²⁰⁶Pb/²⁰⁷Pb further decreased and became more variable.^{24,29,30} The lowest values of 1.14 were found in peat bogs close to roads (alkyl-Pb in gasoline with ²⁰⁶Pb/²⁰⁷Pb ratios around 1.11). The highest values were found close to coal burning power plants. Interestingly, input/output data from the studied catchments (illustrated by a solid vertical line near the

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right-hand-side axis in Figure 2c) fell into a twice narrower range than peat (dots in Figure 2c). The catchment data were collected 10 years after cessation of usage of alkyl-Pb in traffic (2010 vs 2000), and may reflect further homogenization of atmospheric Pb with 206 Pb/ 207 Pb = 1.16, as pollution eases.

Origin of Pb in Runoff. Our Pb isotope inventory has shown that practically all exported Pb came either directly from the atmosphere, or from the topmost soil horizons. Bedrock Pb did not contribute significantly to runoff Pb (206Pb/207Pb of bedrock was too high, more than 1.20). A negligible contribution of bedrock Pb to runoff was predicted already from flux data (Figure 4). If bedrock Pb dominated runoff, a 44% decrease in runoff Pb flux within 15 years would have been unlikelv.

Even though the range of ²⁰⁶Pb/²⁰⁷Pb ratios of inputs/ outputs was minute, we did observe a difference between late summer (Figure 6a) and winter (Figure 6b). The range of summer $^{2\dot{0}\dot{6}}\breve{P}b/^{207}Pb$ ratios was wider (compare the width of gray bands in Figure 6a and b). Runoff Pb at LKV and LES was more radiogenic than atmospheric input in the same month, but also when compared with winter-time Pb fluxes. One possible explanation is that in summer exported Pb came from deeper soil horizons with higher ²⁰⁶Pb/²⁰⁷Pb than in winter.

Arctic soils exhibit climate-change triggered export of old contaminants, such as Pb, via runoff.³³ Given that forested catchments around Europe report increasing DOC export, our data on Pb fluxes should be examined in light of possible climate-change effects. SI Figure S4 shows that mean annual temperatures in Czech catchments have been increasing since the beginning of the 1960s. Hruska et al.³⁴ have shown that the studied catchments in the Czech Republic export increasing amounts of DOC. Yet, Figures 3 and 4a show that climatic warming has not resulted in increasing export of Pb from the soil into streamwater.

Several recent studies in Western Europe and North America have used Pb isotopes to constrain Pb origin in catchment runoff. Dawson et al.35 found contrasting trajectories of atmospherically derived Pb in wetland soil and aerated mineral soil. Whereas Pb was exported from near surface layers of peat, mineral soil was characterized by immobilization of Pb in deep soil horizons. Vinogradoff et al.³² calculated that a studied catchment in Scotland was still a sink for pollutant Pb, but reported measurable release of legacy Pb under high-flow conditions. Friedland et al.³⁶ resampled forest floor 10 years after an initial sampling campaign, and found decreasing Pb contents. These were not matched by water Pb loss, which continued to be minute. The authors concluded that the missing Pb pool must be located in deep soil horizons. Similarly, Johnson et al.³⁷ concluded that, between 1926 and 1987, up to 30% of atmospherically derived Pb was leached from organic soil horizons, immobilized in deep soil horizons, but partly also exported via runoff.

Evidence for a Relatively Short Residence Time of Pb in the Catchments. Even though the 44% decrease in runoff Pb fluxes (Figure 4) was statistically insignificant (p > 0.05), we propose three lines of evidence for a relatively short residence time of some Pb in the catchments, on the order of decades: (i) Pb isotopes (Figures 5 and 6) indicated either direct runoff of recently deposited rainfall, or export of legacy Pb that had accumulated in the topsoil, to a great extent, during the second half of the 20th century. (ii) The percentage of runoff Pb flux relative to atmospheric input was rather high, averaging 35% in 2010. The most polluted site UDL even released an equivalent

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of 95% of present-day Pb input. Both fluxes at UDL had the same Pb isotope composition, different from the mineral soil. Previous studies from less polluted parts of the world reported smaller percentages of exported Pb, compared to our data. For example, Finnish forest ecosystems studied by Ukonmaanaho et al. ³ immobilized 94–97% of all incoming Pb in the mineral soil, and released an equivalent of less than 6% of contemporary input. We explain higher amounts of Pb in present-day runoff at the Czech sites, especially in the northeast, by higher recent atmospheric Pb input with a short residence time in the catchment. (iii) There was a statistically significant difference between the magnitude of the Pb runoff flux at the extremely polluted four sites in the northeast (UDL, UHL, MOD, and CER), and the remaining seven sites further south (p = 0.015). The northeastern sites exported up to 24 g Pb $ha^{-1}yr^{-1}$, more than the southern sites. This may be causally related to the proximity of Polish coal-burning power plants. Since these were put in operation only in the 1950s-1970s, the residence time of some of the exported pollutant Pb in the nearby catchments must have been less than 60 years.

At two sites in the polluted northeast, we found a significant positive correlation between Pb runoff fluxes and water runoff fluxes (SI Figure S5; p = 0.040 at UDL, and p = 0.012 at UHL). It appears that, under high pollution levels, Pb export was hydrologically controlled. No such relationship was found at the less polluted sites. Some of the deposited Pb may have had a short residence time in the catchments, due to little contact between dry-deposited particulate Pb on snow cover, and the soil. During the vegetation season, major precipitation events may lower the efficiency of the seepage of the incoming Pb into soil, and some deposited Pb may be rapidly exported via runoff.

Our results agree with the previous studies in that some old anthropogenic Pb may remain stored in the catchment for centuries or millenia. We add that in extremely polluted regions a sizable portion of the incoming Pb may have a shorter residence time in the catchment, not exceeding several decades. A time-series longer than in this study would be needed to assess whether or not Pb export significantly responds to decreasing atmospheric inputs.

We cannot directly evaluate whether the found relatively short residence time of Pb in Czech catchments is consistent with other studies. The reason is that other studies^{14,32,33,38-40} were performed in less polluted areas than the northern Czech Republic (UDL and UHL). Burning of Czech lignite produces 5% of fly ash, including respirable nanoparticles. These particles contain up to 3000 ppm Pb. We suggest that fine coal-derived particles released in the Czech power stations may be responsible for the relatively short residence time of Pb in the catchments. To the best of our knowledge, none of the previous studies of the behavior of Pb in headwater catchments was performed in an area with more than 50% pollutant Pb coming from coal burning. Plentiful evidence suggests that, in Western Europe, Pb pollution in the second half of the 20th century was mainly caused by the use of leaded gasoline.⁴¹ The exact mechanism of why coal-derived (nano)particles in catchments might contribute to lowering the mean residence time of Pb in the ecosystem remains uncertain.

Long-term hydrochemical monitoring in an era of climate change and easing pollution is vital to predictions of trends in environmental quality. Concerns have been raised that export of legacy Pb via runoff may negative affect drinking water supply in densely populated areas, such as Central Europe or northeastern U.S. (e.g., ref 36). Our data indicate that Pb from the anthropogenic soil pool may continue to be released in an extremely diluted form. The release of legacy Pb from the soil may not lead to increasing water pollution over time even in heavily industrialized areas.

ASSOCIATED CONTENT

S Supporting Information

Figure S1 shows full recovery of Pb from solutes in LD PE bottles, used in this study (the horizontal gray band represents the permitted reproducibility of a certified standard Pb concentration of 4 μ g L⁻¹). Figure S2 plots TOC vs Pb concentrations in runoff. All Pearson's correlation coefficients were low ($R^2 < 0.12$). Figure S3 is a compilation of 15 years of monthly pH values of catchment runoff (Fottova et al., unpublished database, 11 sites). Figure S4 shows mean temperatures at selected study sites. Figure S5 compares runoff water flux with Pb export flux. Table S1 gives mean annual Pb concentration in catchment inputs and outputs. Table S2 compares water fluxes in 1996 and 2010. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: +420-251085333; fax: +420-251818748; e-mail: martin.novak@geology.cz.

Notes

The authors declare no competing financial interest.

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