Origin of Lead in Eight Central European Peat Bogs Determined from Isotope Ratios, Strengths, and Operation Times of Regional Pollution Sources

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Lead originating from coal burning, gasoline burning, and ore smelting was identified in 210Pb-dated profiles through eight peat bogs distributed over an area of 60 000 km². The Sphagnum-dominated bogs were located mainly in mountainous regions of the Czech Republic bordering with Germany, Austria, and Poland. Basal peat 14C-dated at 11 000 years BP had a relatively high 206Pb/207Pb ratio (1.193). Peat deposited around 1800 AD had a lower 206Pb/207Pb ratio of 1.168–1.178, indicating that environmental lead in Central Europe had been largely affected by human activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution. Five of the sites exhibited a nearly constant 206Pb/207Pb activity (smelting) even before the beginning of the Industrial Revolution.

Introduction

More lead has been released into the environment since prehistory than any other metal (1). As late as 1990, 50% of the annual worldwide Pb production was still being lost to the atmosphere (2). Direct data concerning atmospheric Pb deposition rates cover only the past 30 years; data prior to this period must be reconstructed indirectly from geochemical records (3). Anthropogenic lead is mostly adsorbed on particles and scattered by aeolian transport, with sediments representing the ultimate sinks for Pb emissions. Ombrotrophic peat deposits have been used as relatively high-resolution archives of Pb pollution levels for the past 12 000 years, i.e., throughout the Holocene Epoch (4). In Europe, vertical peat profiles have been most extensively studied in three countries: U.K. (5), Sweden (6), and Switzerland (3, 4).

Here, we report on the origin of lead in eight 206Pb-dated peat cores from blanket bogs situated in Central Europe, mainly in the mountainous border regions of the Czech Republic. This area is known for its long history of silver and lead mining, sizable coal reserves, and belated phasing-out of leaded gasoline. The Bohemian Kingdom, predecessor of today’s Czech Republic, produced one-third of European silver at the end of the Middle Ages (7). In the 20th century, the Czech Republic was the third largest producer of soft coal in the world (8). Historical data on mining outputs dating back to the 13th century are preserved in Geofond, one of the oldest state-run mining archives in the world. Fortuitously, the centrally planned economy during the Communist era (1948–1989) involved accurate monitoring of nationwide metal, coal, and gasoline consumption. Therefore, the strengths and operation times of individual Pb pollution sources can be reconstructed quantitatively.

In addition to historical Pb emission inventories, we used Pb isotopes as pollution source indicators. Lead has four stable isotopes, the nonradiogenic isotope 204Pb, the two uranogenic isotopes 206Pb and 207Pb, and the thorogenic isotope 208Pb. The 206Pb/207Pb abundance ratio has been generally accepted as the most sensitive to change in environmental studies. The Pb isotope ratios depend on how Pb and its parents were together before the Pb was segregated into the mineral under study. The modern crustal lead is relatively highly radiogenic (206Pb/207Pb ≥ 1.20). The...
206Pb/207Pb ratio in Pb minerals with no uranium decreases with increasing geological age. For example, galena from the 1.7 billion year old deposits at Broken Hill, Australia, largely used for the production of alkyd lead gasoline additives, is characterized by a relatively low 206Pb/207Pb ratio of 1.04 (9).

It has been unclear whether car exhausts introduced this Precambrian lead into the environment of Central Europe when it was separated from the West by the Iron Curtain. It has also been unclear whether lead pollution from ore smelting and coal combustion in Central Europe can be isotopically distinguished. Because both local Ag–Pb ores and coal are Phanerozoic in age, it has been suggested that their Pb isotope signatures coincide and are of little use as source indicators (10). In this study, we have looked for the Australian Precambrian traffic-derived lead in Czech ecosystems and for Pb isotope differences between local ores and coal.

At a receptor site, a smooth shift in Pb isotope ratios should only rarely accompany constant Pb accumulation rates. It is unlikely that, while one isotopically distinct Pb source retreats and an isotopically different source builds up, the sum of their emission fluxes remains constant. Yet, such cases have been reported, usually with the conclusion that “there are discrepancies between isotopes and fluxes” (10–12). In this paper, we have focused on such discrepancies.

In summary, our objectives were (i) to determine the sources of lead buried in Central European peat, (ii) to reconstruct Pb emissions in the region since 1800 AD, and (iii) to seek differences between the Central and Western European Pb pollution histories.

Methods

Samples. Seven ombrotrophic to weakly minerotrophic Sphagnum-dominated peat bogs were located on mountain plateaus within the Czech Republic (mean elevation of 950 m, mean annual precipitation of 1240 mm) near the borders with Germany, Austria, and Poland (Figure 1). The eighth peat bog (CB) was situated in a Miocene basin at an elevation of 440 m, receiving 580 mm of rainfall per year. The distance of the sampling sites from the nearest road was more than 600 m. Detailed site descriptions were given previously (13). One peat core was collected from each site in October 1992 using a 40-cm-long, 10-cm-diameter PVC cylinder. Each peat core was frozen, sectioned into 2-cm sections, freeze-dried, weighed, and homogenized. The amount of acid-insoluble ash averaged across all sites and all depths between 0 and 30 cm was 4.1 wt. %. Additionally, to investigate the preanthropogenic lead isotope signature in the area, we collected one 500-g sample of basal peat from Hora svateho Sebastiana 25 km northwest of DR (Figure 1). This basal peat from the depth of 4.6 m below surface was 14C-dated at 10 930 ± 140 years BP. Lead isotope signatures of Central European coal were measured in samples collected at six major power plants (Tisova, Vresova, Uzin, Trnice, Melnik, and Chvaletic) and one city heating plant (Strakonice). Lead isotope signatures of leaded gasoline were measured on 10 samples collected between June 1999 and December 2000 throughout the Czech Republic (Prague, Nove Straseci, Kolesov, Veru-sicky, Karlovy Vary, Unesov, Pacov, Vysocany, Chlumec nad Cidlinou, and Varnberk). Lead isotope ratios of 185 samples of Central European Ag–Pb ores were taken from ref 14.

Lead Analysis. The total Pb extraction used to prepare samples for both concentration and isotope measurements was described previously (multiple-step HNO3/H2O2 digestion combined with ashing (13)). Lead concentrations in peat were determined on a Perkin-Elmer atomic absorption spectrophotometer. The individual 2-cm peat increments were 210Pb-dated using an ORTEC 576A alpha spectrometer. The dates were estimated using the constant rate of supply model (15). Three different instruments were used to determine the 206Pb/207Pb and 208Pb/207Pb isotope ratios: ICP-MS Perkin-Elmer SCIEX ELAN 6000 (119 measurements on peat; continuous solution aspiration), ICP-MS-MC (14 peat samples), and TIMS (Finnigan MAT 262; coal and gasoline samples). During the ICP-MS measurements, the NIST-SRM 981 standard was frequently analyzed to monitor mass fractionation. The measured isotope ratios were corrected when the standard's ratio differed from the certified value by more than the relative standard deviation (RSD) of the analysis. Prior to analysis, the samples measured with the ICP-MS-MC and TIMS instruments underwent acid dissolution and preconcentration using anion-exchange columns (BioRed AG-1-x8 resin). For TIMS, the purified samples were loaded on Re filaments with silica gel and phosphoric acid. The isotopic ratios measured by the ICP-MS apparatus typically exhibited RSD values of less than 0.3%, whereas ratios for the TIMS and ICP-MS-MC instruments were near 0.02%.

Results and Discussion

Pb Accumulation in Peat. There was general agreement between the contemporary atmospheric Pb loads and cumulative Pb contents in the peat profiles since 1900 AD (Figure 1). The south of the Czech Republic (sites CB and LU) is a relatively unpolluted natural preserve area, remote from direct point sources of pollution. Both current Pb deposition rates and cumulative Pb deposition since 1900 at CB and LU were relatively low. In contrast, the north is part of the industrialized “Black Triangle Region” (16, 17). The cumulative Pb deposition since 1900 at the northern sites was, on average, 1.9 times higher than that in the south.

Pb Isotopes in Peat. Shotyk et al. (4) were among the first to show that environmental Pb isotope ratios at the beginning of the industrial revolution (ca. 1800 AD in Central Europe) were far from preanthropogenic values. They found 206Pb/207Pb ratios higher than 1.199 for the early and middle-Holocene Epoch in Switzerland. In contrast, the oldest 210Pb-datable peat layers (around 1860 AD) in Switzerland had a significantly lower 206Pb/207Pb ratio (1.175–1.181). In the northern Czech Republic, we found a similar preanthropogenic, early Holocene 206Pb/207Pb signature of 1.193 (Figure 2). The oldest 210Pb-datable peat throughout the Czech Republic (years 1780–1825) had a 206Pb/207Pb ratio between 1.168 and 1.178. Clearly, in both countries dispersion of anthropogenic Pb was responsible for the offset toward less radiogenic Pb even prior to the Industrial Revolution. Since around the year 1800 no gasoline and practically no coal were burned in the region, ore smelting was the probable source of pollution. The preanthropogenic 206Pb/207Pb value...
of 1.193 in the northern Czech Republic measured in basal peat is close to the value for the B/C horizon of forest soils in the same region (1.20 ± 0.18).

The $^{206}\text{Pb} / ^{207}\text{Pb}$ ratio of atmospheric deposition decreased consistently since ca. 1830 until the end of the observation period (1992) at four sites (CB, LU, TA, BS). At the remaining four sites (DR, JH, PL, MM), the decrease ended around 1980, and the $^{206}\text{Pb} / ^{207}\text{Pb}$ ratio returned to slightly higher (more radiogenic) values in the following decade (Figure 2). The decrease in $^{206}\text{Pb} / ^{207}\text{Pb}$ spanning most of the 19th and 20th centuries became steeper over time. The major difference between the Swiss and Czech Pb isotope patterns over time was in the magnitude of the negative $^{206}\text{Pb} / ^{207}\text{Pb}$ shift: while in Switzerland the minimum values (encountered in 1980) were around 1.12, in the Czech Republic, the minimum values were mostly higher than 1.15. We will further interpret the $^{206}\text{Pb} / ^{207}\text{Pb}$ time series from Figure 2 in light of the amounts and isotope composition of Pb emitted from the three major polluters: ore smelters, coal-burning power plants, and traffic.

**Ag-Pb Mining.** For more than 5000 years, silver has been extracted from Pb ores by a technique called cupellation. Originally, because Pb was a byproduct, every effort was made to convert most of it into smoke (1). In the Central European region, the consumption of Pb for silver smelting was sizable (50 kg of Pb per 1 kg of Ag (19)). However, not all Pb was lost in the form of emissions, the resulting solid PbO was deposited on dumps. In the Bohemian Kingdom, starting from the 12th century, tens of tons of Ag were produced annually until the early 19th century. In contrast, extensive Pb mining commenced only after 1500 AD. In Figure 3, silver mines (solid circles) are divided into three groups according to their total production. The largest Medieval silver mining district was at Kutna Hora (201 year-1). Following the district’s decline (1528), one smelter continued operation near Kutna Hora, processing ores from 20 different localities. The silver production at the other three large mining districts (Pribram and Jachymov in Bohemia, Freiberg in Saxony; Figure 3) increased as of the 16th century. At Pribram, numerous small smelters were replaced by a large smelter in 1786. The Jachymov (Joachimstal) production peaked in the 16th century, and the smelter was closed in 1897. In Figure 3, all sites with maximum metal production after the year 1800 are underlined. We will further focus on these sites, because our $^{210}\text{Pb}$-derived peat chronologies also date back to ca. 1800. The map also includes four historical Pb deposits with unknown or negligible Ag production (Stříbro, Olovi, Harrachov, Horni Benešov). It is clearly seen that each of the studied peat bogs (open circles in Figure 3) are located close to Ag-Pb mines (not more than 30 km). Next to the major site names, Figure 3 is supplemented with $^{206}\text{Pb} / ^{207}\text{Pb}$ (top) and $^{208}\text{Pb} / ^{207}\text{Pb}$ (bottom) isotope ratios (14). The $^{206}\text{Pb} / ^{207}\text{Pb}$ and $^{208}\text{Pb} / ^{207}\text{Pb}$ ratios of Czech and Saxon Ag-Pb ores (n = 185) were 1.172 ± 0.02 and 2.454 ± 0.018, respectively (mean ± standard deviation). Figure 4a compares the all-time...
Coal Burning. During combustion, lead is more easily volatilized than common refractory elements. Modern emission-control systems in power plants capture more than 99.5% of the Pb-enriched fly-ash particles (20). Still, the smallest respirable particles emitted from coal exhibit the highest concentrations of lead among all types of particles found in the atmosphere (21). Burning of Czech lignite produces 5% of fly ash containing as much as 3000 ppm Pb. Despite such high concentrations of Pb in the fly ash, Wedepohl et al. (21) estimated that annual Pb emissions from coal were 10 times lower than those from automobiles. Figure 5 shows the main coal-mining districts in the Czech Republic. Coal-burning power plants were built in each of the mining districts, with the exception of Plzen. The main cluster of 11 coal-burning power plants (up to 50 years old) is situated between Most and Sokolov in the northern Czech Republic. By far, the Most basin has produced the highest amount of coal (over 3 billion tons), followed by Ostrava-Karvina and Sokolov (Figure 5). The maximum coal production in the region occurred in the year 1980 (Figure 6; the contributions of Kladno, Plzen, South Moravia, and Zacler were negligible). The maximum coal production in Central Europe thus occurred 50 years later than that in the United Kingdom (years 1980 and 1930, respectively (22)).

It has been shown that radioactive equilibrium U–Pb is preserved in most coals (20). Therefore, the expected Pb isotope ratios in coal should be close to the average values for the upper continental crust. The measured 206Pb/207Pb and 208Pb/207Pb ratios of the Czech coals in this study were 1.190 ± 0.006 and 2.465 ± 0.006, respectively (n = 7). The encountered values were, indeed, close to the average crustal lead values (1.20 and 2.47). Czech stone coal previously analyzed by Aberg (unpublished results) exhibited a 206Pb/207Pb ratio of 1.178. In interpretations of Pb isotope compositions in peat, we will use the isotope ratio 206Pb/207Pb = 1.17 as the minimum value observed for coal (cf. 3, 10, 21). The two diagnostic features of coal-derived lead in Czech peat bogs should be increasing annual Pb accumulation rates up to 1980, followed by a decrease, and relatively radiogenic Pb isotope signatures (high 206Pb/207Pb ratios of more than 1.17 near stone-coal districts and around 1.19 in the vicinity of soft-coal-fired power plants).
lead played a major role in the production of gasoline lead additives sold in the European Union. Data on Pb isotope compositions of 10 samples of leaded gasoline collected throughout the Czech Republic in 2000. The results indicated that low-radiogenic Australian Pb represented a significant proportion of gasoline additives used in Central Europe: the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was $1.11 \pm 0.016$, and the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio was $2.37 \pm 0.018$ (mean ± standard deviation). These data are consistent with East German data from the period following German reunification (26). The sole East German producer of alkyl lead in the 1990s, Novooctan GmbH, used 50% of Australian ore and 50% of local ore from Freiberg, resulting in a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.10. The East German gasoline was used in the region directly upwind from the Czech Republic and contained isotopically similar Pb.

In summary, alkyl lead in the Czech Republic contains a significant proportion of low-radiogenic Australian Pb, similarly to West European countries. In peat, we expected traffic-derived Pb to exhibit low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios ($1.11 \pm 0.02$) and increasing annual Pb accumulation rates between 1950 and 1978, followed by a decrease. Gasoline Pb was isotopically different from that of both coal and local ores, but its maximum input into peat coincided with the maximum input of coal-derived lead.

**Site-Specific Pb Record in Peat.** Lead isotope ratios are compared to annual Pb accumulation rates in Figure 7. For each site, the annual Pb accumulation rates (thick line) are given together with Pb/Al ratios (thin line) in the graph on the left. Vertical $^{206}\text{Pb}/^{207}\text{Pb}$ patterns (solid circles) are shown along with isotope signatures of potential Pb sources (graphs on the right). For further interpretation, we will use the $^{210}\text{Pb}$-based accumulation rates rather than the Pb/Al ratios, whose usefulness has been questioned (27).

Seven sites exhibited a clear-cut subsurface peak in Pb accumulation rates corresponding to the years 1970–1980; one site (TA) showed a steady increase in Pb accumulation rates until 1992 (year of peat sampling). Such pollution history contrasts with that of other European countries, where typically one additional Pb accumulation maximum in peat (but also in tree rings, herbarium collections, ice cores and lake sediments) was found around 1900 (28). A horizontal shaded band in Figure 7 running across both graphs reveals a discrepancy between Pb fluxes and isotope trends. The band marks the years of maximum Pb input into the peat bog (left graph), but it intersects the $^{206}\text{Pb}/^{207}\text{Pb}$ curve (right graph) in the middle of a smooth steady shift to less radiogenic values upward (CB, LU, DR, BS, PL, MM). This is an unlikely
combination, because, after the maximum Pb input is reached, the Pb isotope signature of the dominant pollution source should also retreat. This expected response of Pb isotopes to decreasing accumulation rates in the years following pollution maximum, indeed, was observed at one site, JH (Figure 7). At JH, increasing Pb accumulation rates corresponded to decreasing $^{206}\text{Pb} / ^{207}\text{Pb}$ ratios and vice versa.

A number of alternative scenarios would be more likely than the steady fall in $^{206}\text{Pb} / ^{207}\text{Pb}$ beyond the Pb accumulation maximum observed at our six sites (CB, LU, DR, BS, PL, MM). For example, the $^{206}\text{Pb} / ^{207}\text{Pb}$ ratio would remain roughly constant following the Pb input maximum if only one dominant Pb source caused the maximum and all other pollution sources were orders of magnitude weaker. A large open circle in Figure 7 marks peak consumption of leaded gasoline and peak coal production (1978–1980). At all but one site (DR), the open circle coincided with the maximum Pb accumulation rate (shaded band). From fluxes
alone, it follows that the Pb accumulation maximum in peat was caused mainly by a mixture of emissions from traffic and coal burning (emissions from ore smelting were negligible in 1980, Figure 4b). Isotopes can help to quantify the contribution of both major Pb sources: Given that the average $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of coal and gasoline are equal to 1.19 and 1.11, respectively, an isotope mass balance gives different percentages for various sites, depending on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the peat. For example, at LU ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.155 in 1980), the proportion was 56% of coal and 44% of gasoline Pb. A similar calculation can illustrate the flux—isotopes discrepancy seen in Figure 7: Ten years after the maximum Pb input at LU (around 1990, the topmost sample with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.142), the isotope mass balance gives 41% of coal and 59% of gasoline Pb. However, a calculation using Pb fluxes would give a different result. Over the same 10 years, the Pb emissions from coal burning and traffic in the broader region decreased to 54 and 23%, respectively (13), and the Pb input into LU decreased to one-third (Figure 7). If we assume that the proportions of Pb from both major sources (coal and traffic) were correctly calculated for 1980 (56 and 44%, respectively), a subsequent calculation using the decreasing fluxes would indicate that, in 1990, Pb was made up of 75% coal Pb and 25% gasoline Pb. Such a result does not agree with the isotope-based calculation (41% coal, 59% gasoline). The cited reduction in Pb emissions (13) referred to an area of ca. 80 000 km$^2$. The discrepancy for a receptor site (LU) illustrates that dispersions of atmospheric Pb, and thus manifestations of a reduction in Pb emissions from various anthropogenic sources, are not uniform over Central Europe.

Solid left arrows in Figure 7 denote the year 1900 when ore smelting reached a regional maximum. At none of the sites was there a corresponding maximum in annual Pb accumulation rates. Instead, the left arrow falls in the middle of a steady increase in Pb accumulation rates, between the beginning of coal mining (1860, marked c) and the beginning of the use of leaded gasoline (1950, marked a). This absence of a peak in Pb input around 1900 in the Czech peat bogs is surprising in the European, or at least Central European, context (28).

In the $^{206}\text{Pb}/^{207}\text{Pb}$ graphs (Figure 7, right), the solid left arrows (year 1900) mark the end of nearly constant Pb isotope composition and the beginning of a steady fall (typically at TA; in all, at five sites, including also DR, JH, LU, and PL). In contrast, at other sites (typically at CB, but also at BS), the solid left arrows fall in the middle of a steadily falling $^{206}\text{Pb}/^{207}\text{Pb}$ curve. We would have predicted that the CB-type gradient would be more common during the 19th century, as the growing ore production should increasingly control the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio at the expense of relatively high values of crustal dust. Instead, at the majority of the sites (the TA-type gradient), there was a nearly constant $^{206}\text{Pb}/^{207}\text{Pb}$ ratio throughout the 19th century, resembling nearly constant ratios observed for the same period in Scotland (12) and Scandinavia (29). Whereas, in Scotland and Scandinavia, the constant $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the 19th century was close to 1.17, that in Central Europe was slightly higher (1.175). A shaded up arrow in Figure 7 marks the $^{206}\text{Pb}/^{207}\text{Pb}$ composition of the largest ore producers in the region (Pribram, Freiberg). At three of the sites (CB, TA, MM), the falling $^{206}\text{Pb}/^{207}\text{Pb}$ curve never reached a value as low as it did at Pribram and Freiberg. At the remaining sites (typically at LU), the $^{206}\text{Pb}/^{207}\text{Pb}$ curve dropped to even lower values during the 20th century. The segment between the years 1900 and 1950 (solid left arrow and the letter a marking the advent of leaded gasoline) on the $^{206}\text{Pb}/^{207}\text{Pb}$ curves (Figure 7) illustrates yet another aspect of the flux—isotopes discrepancy. Why did the atmospheric $^{206}\text{Pb}/^{207}\text{Pb}$ signature decrease between 1900 and 1950, when there was no leaded gasoline containing Precambrian lead? The vertical dotted line in Figure 7 marks the minimum $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of coal. Coal production in the early 20th century increased or stagnated (Figure 6), but the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was too high to explain the $^{206}\text{Pb}/^{207}\text{Pb}$ drop in the atmosphere. The decreasing air-borne $^{206}\text{Pb}/^{207}\text{Pb}$ ratio approached the ratios of two pollutants, ores and leaded gasoline. However, neither of these two sources provides a good explanation for the decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ trend (isotope signature of ores could not increasingly dominate at a time of rapidly declining mining outputs; vehicles did not use leaded fuel). A similar trend has been reported from the U.K. (30), Switzerland (3), and Sweden (29). After 1900, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in atmospheric deposition in these countries decreased, more or less linearly, even before the introduction of leaded gasoline. This decrease was explained by imports of Australian Pb ores for industry and therefore not perceived as a discrepancy. There were no imports of Precambrian lead into Central Europe at that time; however, the most frequent wind direction is from the west to the east (31). We conclude that long-range transboundary transport of industrial lead from Western Europe is currently the only possible explanation of decreasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the atmosphere of Central Europe soon after 1900.

As seen in Figure 7, there was considerable site-to-site variation in the $^{206}\text{Pb}/^{207}\text{Pb}$ patterns in the youngest (uppermost) peat layers: whereas at three sites (DR, JH, PL) a reversal toward higher (more radiogenic) values typical of easing pollution (cf. ref 3) was observed, five sites lacked such a trend. The question arises whether such a high degree of site-specific control in $^{206}\text{Pb}/^{207}\text{Pb}$ patterns in peat after 1980 is consistent with the concept of a regionally uniform manifestation of long-range imports of Precambrian lead from Western Europe after 1900.

Three-Isotope Plots. In a $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ plot (Figure 8a), the peat samples form a distinct triangle. The oldest samples (ca. 1800 AD) fall near the top right point, the youngest samples near the bottom side of the triangle. The explanation of the triangular shape of the $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ plot for Central Europe is in Figure 8b. Lead isotope ratios of peat (shaded triangle downscaled from Figure 8a) are given in the context of natural and anthropogenic lead sources. The lead isotope compositions of Pb—Ag ores ($\times$), coal (•), and alkyl lead gasoline additives (○) fall outside the triangle representing Czech peats. Ores and coal form two distinct clusters that envelope peat in the upper one-half of the triangle. Clearly, the lead isotope compositions of Ag—Pb ores and coal can be used as diagnostic tools for source apportionment in the environment of Central Europe. The high emissions of Pb from coal burning are responsible for the triangular plot for the Czech peats (Figure 8). The highest proportion of coal Pb is seen in MM (open circles in Figure 8a), a site located near the large coal district Ostrava-Karvina. MM forms the bottom right point of the triangle in Figure 8a.

Whereas the upper half of the peat triangle (prior to 1950) is explained by mixing of preanthropogenic lead (large open square in Figure 8b), ore- and coal-derived lead, the lower half (after 1950), requires mixing with a fourth Pb source, gasoline. The lead isotope compositions of gasolines (solid circles in Figure 8b denote samples measured in this study; open circles are literature data for the period 1980—1990) indicate the presence of a low-radiogenic Precambrian component (large solid square) in lead dispersed from mobile sources in Central Europe. Atmospheric deposition into peat exhibits increasing proportions of gasoline-derived Pb after 1950; the Pb isotope compositions at the receptor sites converge to that of gasoline. In summary, Figure 8b provides a consistent overall picture that satisfactorily identifies the sources of lead found in the studied peat.
No direct data are available on the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of gasolines used in Central Europe in the early Communist years (after 1950). Figure 8 provides evidence that, even before the fall of the Berlin Wall (1989), there was an Australian Precambrian component in alkyl lead. This is because Pb buried in peat after 1950 fell outside the local ore-coal envelope (Figure 8b).

**Total Pb Emissions in the Years 1800–2000.** Using the annual outputs of silver, lead, and coal; sales of leaded gasoline; and lead concentrations in coal and gasoline, we calculated total regional Pb emission rates (Figure 9). To estimate the percentage of the produced lead that was actually released into the atmosphere, we used previously published experimental data (19, 22, 32, 33). We used two scenarios for ore smelting (2 and 5%) and the upper limit of the published ranges for coal (55%) and gasoline (66%).

The most striking feature of the regional Pb emission rates in Figure 9 is that coal-derived lead dominated over lead from both smelting and traffic. Emission rates of lead derived from ore smelting might have reached values in 1890 similar to those of traffic-related lead emissions in 1980. However, coal-derived lead emissions in 1980 were twice as high. We note that, in other parts of Europe, Pb emissions from coal peaked long before those in the Czech Republic. In most Western European countries, as well as in the U.S., alkyl lead emissions appeared to exceed those from ore smelting and coal burning throughout the 1970s and 1980s (34). Lead isotope data from Central European peat bogs in Figure 8 indicate that alkyl lead was about equally represented in the atmosphere as coal-derived lead. If the typical air-borne $^{206}\text{Pb}/^{207}\text{Pb}$ isotope signature was 1.15 in 1980, the proportions of gasoline (1.11) and coal (1.19) lead were 50% each. Again, the Pb isotope record in peat seems to contradict the available regional data on historical Pb fluxes. The most detailed previous attempt to reconcile Pb isotope data with independent regional Pb flux estimates was reported from the United States by Graney et al. (34). The study showed a similar type of discrepancy.

In constructing Pb emission rates in Figure 9, we chose not to include coal-derived Pb from upwind East German sources. (The Leipzig and Lusatian districts with maximum coal output around 1980; in contrast, East German ores were included.) The inclusion of East German coal-fired power plants would even enhance the dominance of coal-derived Pb over gasoline in the second half of the 20th century. We suggest that the apparent inconsistency between the isotope data (Figure 8) and the regional Pb fluxes (Figure 9) might be solved by careful evaluation of the relative roles of regional and local pollution. It has been generally accepted that, because of the long residence time of aerosols (5–10 days), Pb can be dispersed over thousands of kilometers (35). However, more field data are needed to calibrate the maximum transport distance for individual types of Pb pollution and types of landscape. In general, lead from gasoline tends to be associated with smaller particles than lead originating from coal and smelting (35). If so, longer
transport distances for traffic-related Pb might have contributed to its dominance over coal-derived particles in Central European mountain-top peat bogs. Additionally, we propose that, over the past 50 years, the Czech coal-burning power plants might have captured, on average, a larger proportion of fly ash than previously assumed and thus a larger proportion of particle-reactive Pb than the 45–55% reported in the literature (22). This would have been paradoxical in a region where over 600 km² of spruce forests perished as a result of industrial pollution during the Communist era, but perhaps realistic in light of the well-constrained annual coal productions and Pb concentrations in coal used for constructing Figure 9.

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