

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 ratio (1.175) throughout the 19th century, resembling the “anthropogenic baseline” described in Northern Europe (1.17). At all sites, the ²⁰⁶Pb/²⁰⁷Pb ratio of peat decreased at least until 1980; at four sites, a reversal to more radiogenic values (higher ²⁰⁶Pb/²⁰⁷Pb), typical of easing pollution, was observed in the following decade (1980–1990). A time series of annual outputs for 14 different mining districts dispersing lead into the environment

has been constructed for the past 200 years. The production of Ag–Pb, coal, and leaded gasoline peaked in 1900, 1980, and 1980, respectively. In contrast to other European countries, no peak in annual Pb accumulation rates was found in 1900, the year of maximum ore smelting. The highest annual Pb accumulation rates in peat were consistent with the highest Pb emission rates from coal-fired power plants and traffic (1980). Although maximum coal and gasoline production coincided in time, their isotope ratios were unique. The mean measured ²⁰⁶Pb/²⁰⁷Pb ratios of local coal, ores, and gasoline were 1.19, 1.16, and 1.11, respectively. A considerable proportion of coal emissions, relative to gasoline emissions, was responsible for the higher ²⁰⁶Pb/²⁰⁷Pb ratios in the recent atmosphere (1.15) compared to Western Europe (1.10). As in West European countries, the gasoline sold in the Czech Republic during the Communist era (1948–1989) contained an admixture of low-radiogenic Precambrian lead from Australia.

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. Om-brotrophic 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 ²¹⁰Pb-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. Fortunately, 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 long 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

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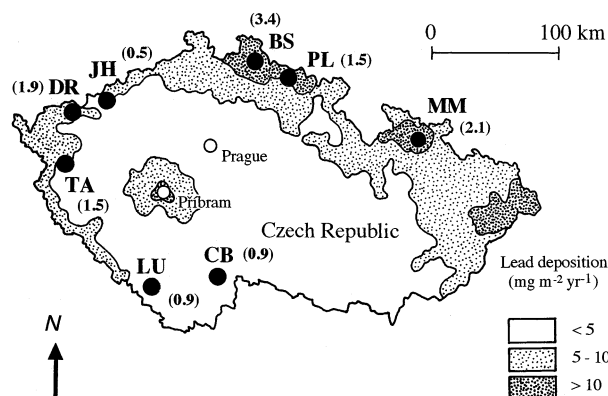


FIGURE 1. Study sites (solid circles). Contours denote annual atmospheric lead deposition in the 1990s. Data from the Czech Hydrometeorological Institute, Prague. Numbers in parentheses are cumulative Pb depositions since 1900 AD in grams per square meter.

$^{206}\text{Pb}/^{207}\text{Pb}$ 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 alkyl lead gasoline additives, is characterized by a relatively low $^{206}\text{Pb}/^{207}\text{Pb}$ 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 svatého Sebestiana 25 km northwest of DR (Figure 1). This basal peat

from the depth of 4.6 m below surface was ^{14}C -dated at $10\,930 \pm 140$ years BP. Lead isotope signatures of Central European coal were measured in samples collected at six major power plants (Tisova, Vresova, Uzin, Trmice, Melnik, and Chvaletice) 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 Strasceci, Kolesov, Verusicky, Karlovy Vary, Unesov, Pacov, Vysocany, Chlumec nad Cidlinou, and Vamberk). 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 $\text{HNO}_3/\text{H}_2\text{O}_2$ 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 ^{210}Pb -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 $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios higher than 1.199 for the early and mid-Holocene Epoch in Switzerland. In contrast, the oldest ^{210}Pb -datable peat layers (around 1860 AD) in Switzerland had a significantly lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (1.175–1.18). In the northern Czech Republic, we found a similar preanthropogenic, early Holocene $^{206}\text{Pb}/^{207}\text{Pb}$ signature of 1.193 (Figure 2). The oldest ^{210}Pb -datable peat throughout the Czech Republic (years 1780–1825) had a $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ value

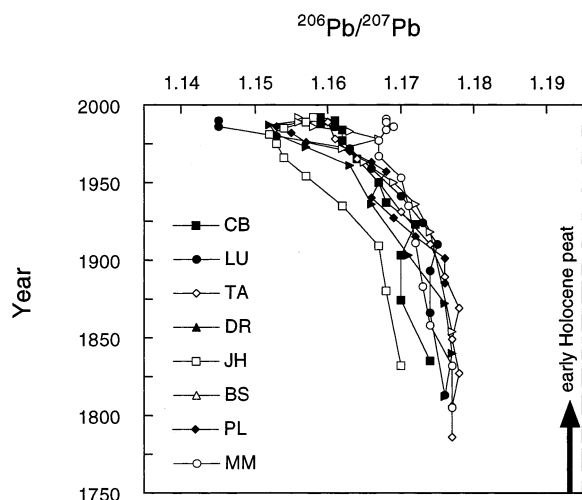


FIGURE 2. Temporal changes in $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in peat. Early Holocene peat was sampled at Hora svateho Sebastiana, located between DR and JH in the northern Czech Republic.

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 (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 (20 t 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 (Příbram and Jáchymov in Bohemia, Freiberg in Saxony; Figure 3) increased as of the 16th century. At Příbram, numerous small smelters were replaced by a large smelter in 1786. The Jáchymov (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}Pb -derived peat chronologies also date back to ca. 1800. The map also includes four historical Pb deposits with unknown or negligible Ag production (Stribro, Olovi, Harrachov, Horní Benesov). 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 \pm standard deviation). Figure 4a compares the all-time

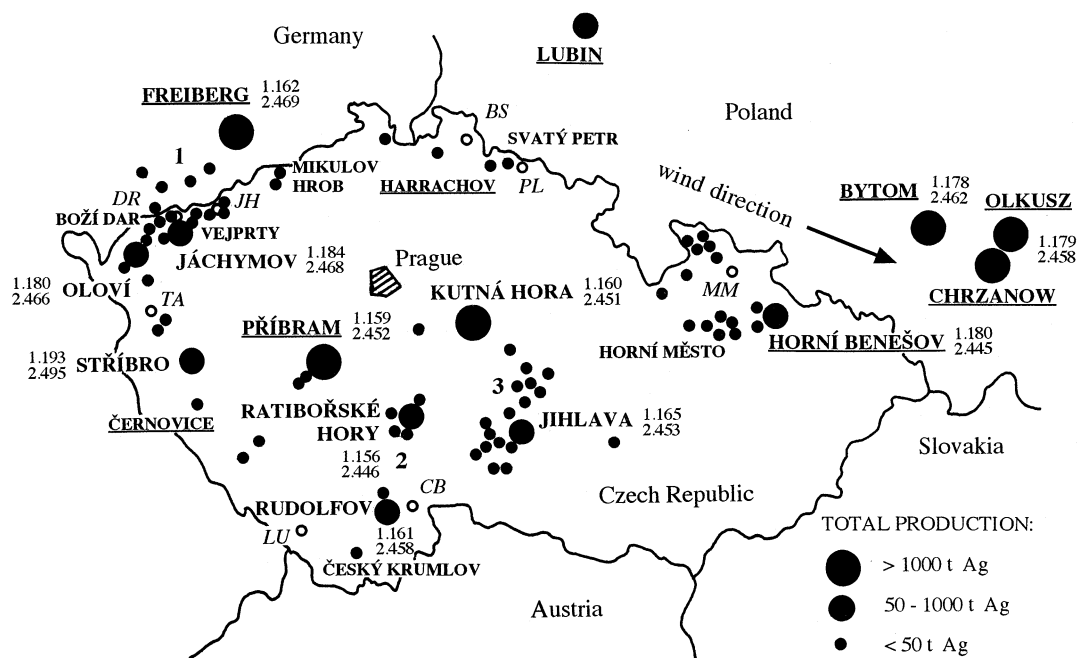


FIGURE 3. Location of Ag and Pb deposits in the Czech Republic, southeastern Germany, and southern Poland (solid circles). Sites are divided into three categories on the basis of all-time production. Numbers next to site names give $^{206}\text{Pb}/^{207}\text{Pb}$ (top) and $^{208}\text{Pb}/^{207}\text{Pb}$ (bottom) ratios of the ore. Sites with most production after 1800 AD are underlined. Small open circles are peat bogs under study. 1, deposits in the Saxon part of the Erzgebirge Mountains (Annaberg, Marienberg, Schwarzenberg, Schneeberg, Johangeorgenstadt); 2, the Blanice Furrow district; 3, the Bohemian–Moravian Highland district.

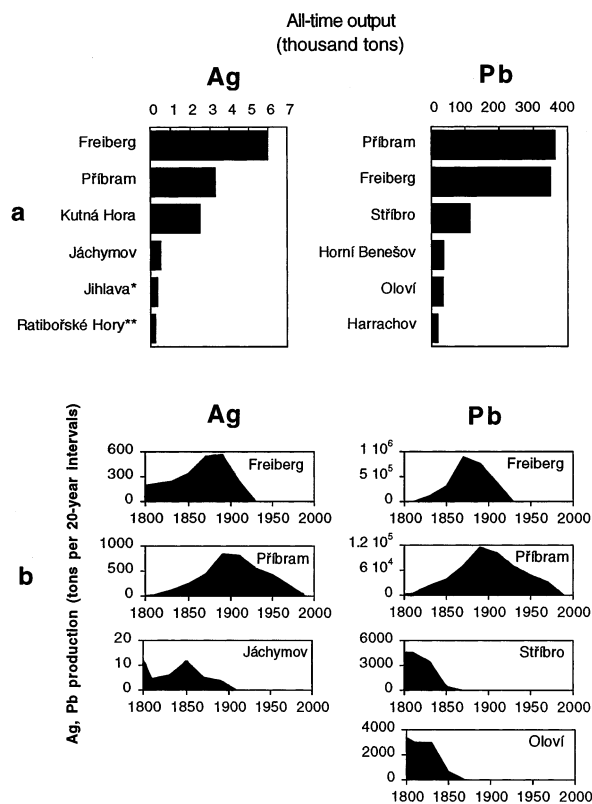


FIGURE 4. (a) All-time outputs of Ag and Pb. For site location see Figure 3. * indicates that all deposits in the Bohemian–Moravian Highland are included; ** indicates that all deposits in the Blanice Furrow (Rudolfov, Český Krumlov) are included. Off scale: Vejprty, Nove Zvolani, 3 t of Ag; Boží Dar, 2–3 t of Ag; Svatoj Petr, 1.5 t of Ag; Mikulov, Hrob, 1 t of Ag; Cernovice, Stankov, Merklín, 4600 t of Pb; Horní Město near Rymanov, 1000 t of Pb. (b) Time series of Ag and Pb production.

outputs among individual Ag and Pb mining districts. Importantly, the two largest Pb polluters in the region, Příbram and Freiberg, had lower Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$ of 1.16) than the regional mean. Whereas Ag output at Freiberg exceeded that at Příbram, Pb output at Příbram exceeded that at Freiberg. We estimate that the total production from all Czech plus Saxon deposits between 1200 and 2000 AD was 16 000 tons of Ag and 1 million tons of Pb. Figure 4b details the time series of Ag (left) and Pb (right) production for the period 1800–2000. The large output maxima at Freiberg and Příbram fell uniformly in a short period between 1880 and 1900. Output maxima prior to 1860 at Jáchymov, Stříbro, and Oloví were quantitatively insignificant compared to those at Freiberg and Příbram. Thus, we hypothesized that a major peak in annual Pb accumulation rates should be seen in peat profiles between 1880 and 1900, accompanied by a $^{206}\text{Pb}/^{207}\text{Pb}$ trend toward 1.16 throughout the 19th century.

It is important to note that, among Czech Ag deposits, only Příbram (30% of the regional Ag production) had a sufficient amount of its own Pb needed for Ag smelting. Unpublished archived materials revealed a complicated pattern of Pb import routes to Czech Ag smelters in the past. The main three Pb suppliers included Rammelsberg (Harz, Germany), Bleiberg (Korinthia, Austria), and Bytom-Tarnów (Silesia, Poland). We estimate that the total Pb imports for Ag smelting amounted to at least 200 000 tons. These Pb imports could influence the amount of emissions from the Czech smelters, especially before 1800, but their Pb isotope signatures differed from those of local ores by less than 0.01 (3).

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 Plzeň. 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, Plzeň, South Moravia, and Znojmo 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 $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.178. In interpretations of Pb isotope compositions in peat, we will use the isotope ratio $^{206}\text{Pb}/^{207}\text{Pb} = 1.17$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of more than 1.17 near stone-coal districts and around 1.19 in the vicinity of soft-coal-fired power plants).

Gasoline-Engined Vehicles. Widespread use of automobiles on the territory of today's Czech Republic started in the 1950s, simultaneously with such European countries as Sweden (23) and Switzerland (3). It has been shown that lead emissions from car tail pipes in the Czech Republic intensified until 1978 and decreased thereafter (13). The maximum Pb emission rates from mobile sources in the Czech Republic coincided with those in Western countries (9). The use of alkyl lead was discontinued first in the U.S. (1988), then in Western Europe (1999) and the Czech Republic (2000). It is important to note that total sales of leaded gasoline are not a good measure of Pb emissions from traffic. The reason was an administrative effort in many countries to reduce Pb content in gasoline several years before the sales of leaded gasoline actually dropped. As in Western Europe, Czech gasoline contained around 0.60 g of Pb L^{-1} between 1960 and 1983. In 1984, the Pb contents were reduced to 0.40 g L^{-1} . Further reduction to 0.15 g of Pb L^{-1} in 1989 effectively meant compliance with the West European regulation. The reduction to 0.15 g of Pb L^{-1} occurred in the Czech Republic 3 years later than in the U.K. (1989 vs 1986). With respect to the U.S., there was an only 2-year delay in the reduction of Pb content in the Czech gasoline below 0.25 g L^{-1} (years 1984 and 1986, respectively).

There is limited information in the open literature regarding the geological origin of Pb used in fuel additives (24). The typical $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of urban aerosol in Western Europe is 1.10 (25), indicating that Australian Precambrian



FIGURE 5. Locations of coal basins in the Czech Republic and all-time coal production in these basins. Open circles represent the studied peat bogs. The prevailing wind direction is eastward.

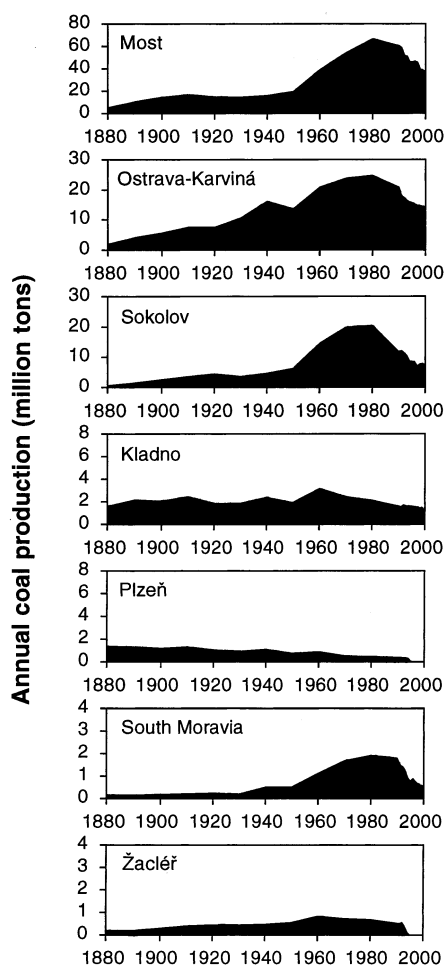


FIGURE 6. Time series of coal production.

lead played a major role in the production of gasoline lead additives sold in the European Union. Data on Pb isotope compositions of gasoline in the Communist countries before 1989 are scanty. A high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.17 was measured in one sample from Poland in 1988 (24). A mixture of 50, 30, and 20% of Pb from Freiberg, the Soviet Union, and the West, respectively, resulted in a mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.13 in East German gasolines during the 1980s (26). It has been speculated that Central European gasolines at present contain

local and Russian lead [$^{206}\text{Pb}/^{207}\text{Pb}$ of 1.17 (10)]. We measured 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 ± 0.016 , and the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio was 2.37 ± 0.018 (mean \pm 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 ± 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}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

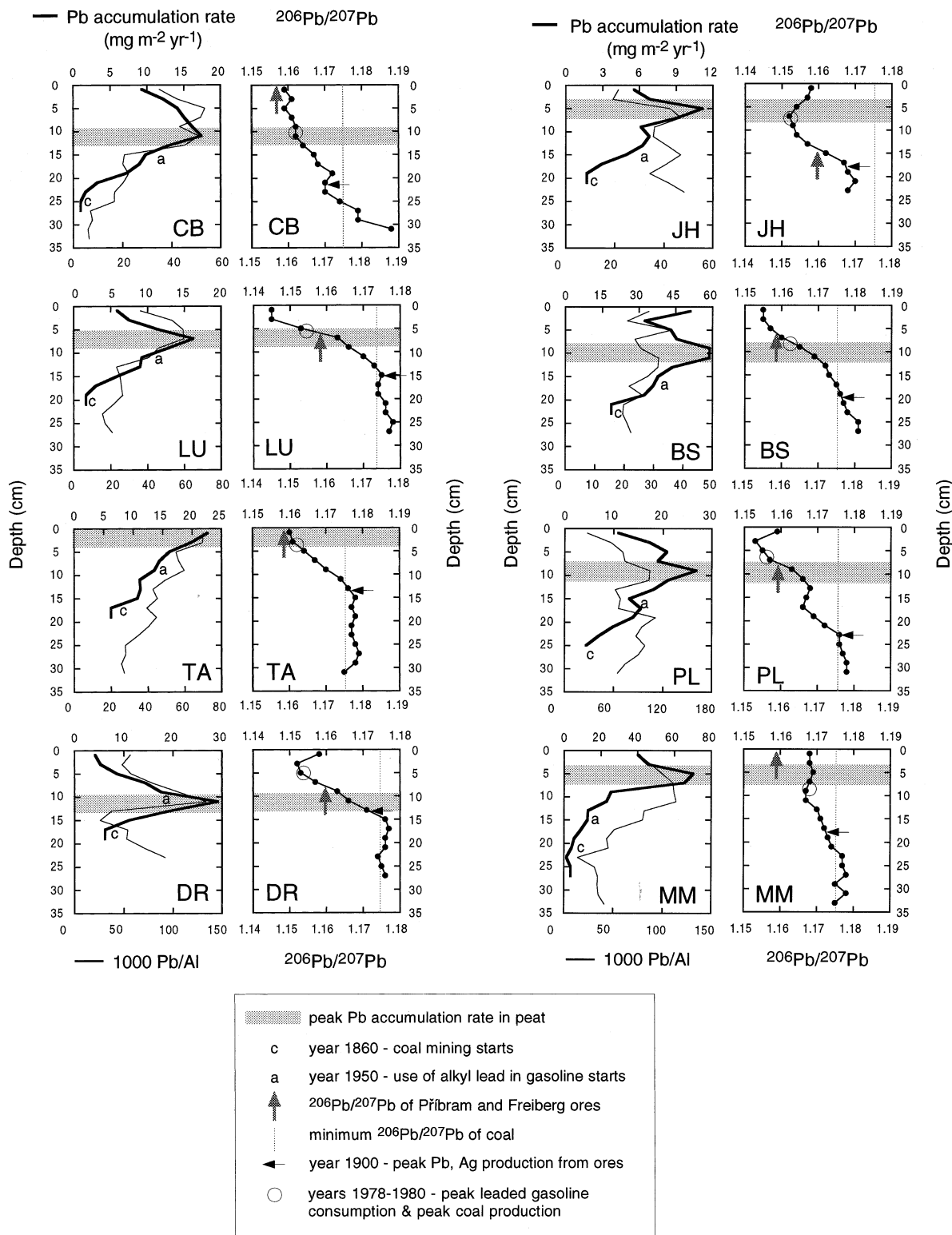


FIGURE 7. Site-specific record of ^{210}Pb -dated peat cores. See text for explanation. Vertical immobility of Pb assumed according to refs 36 and 37.

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 km². 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 (Příbram, 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 Příbram 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 (x), 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.

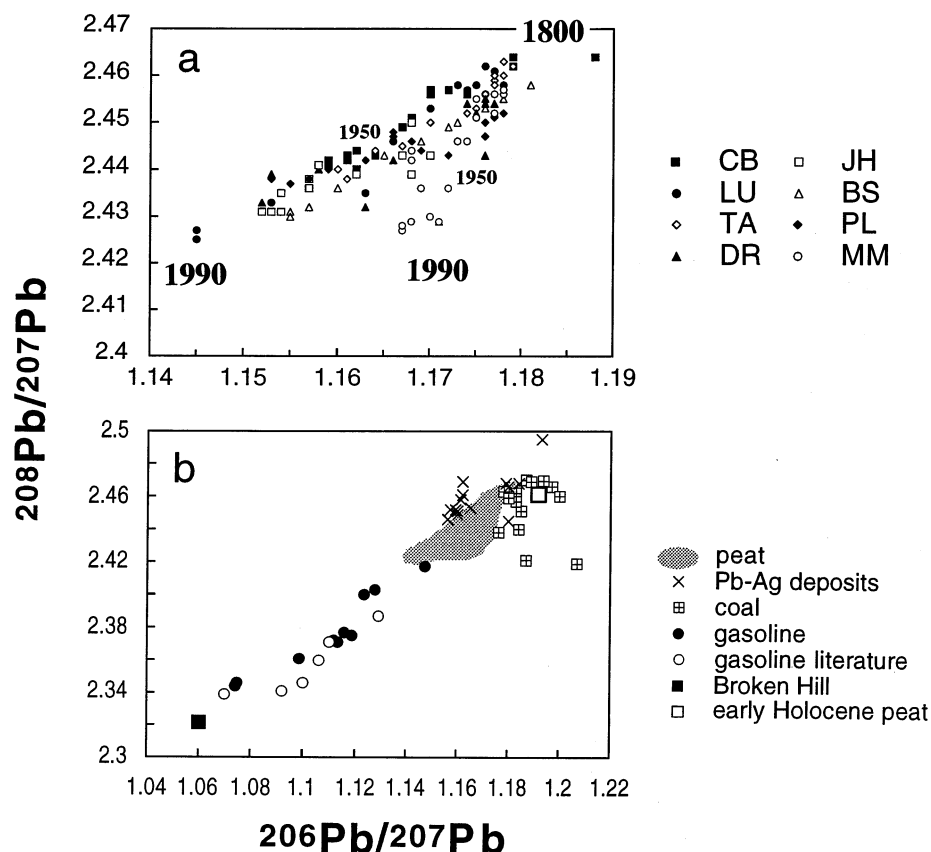


FIGURE 8. Three-isotope plots for (a) Czech peats and (b) lead pollution sources. Literature data on gasoline were taken from refs 24 and 26.

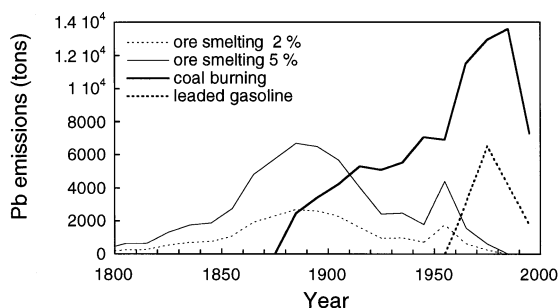


FIGURE 9. Lead emissions in the Czech Republic.

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), lead 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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