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Recent Changes in Stable Lead Isotope Ratios in Sediments of Lake Zug, Switzerland

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In Switzerland, unleaded gasoline was introduced in 1985. In order to study the effects of decreasing lead emissions from gasoline on a lake sediment, profiles of lead concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios have been determined in cores from Lake Zug. Sediment samples were digested and analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Accurate dating of sediment cores was achieved using four independent methods showing the results within a range of <10%. Pb emissions in Switzerland and Pb concentrations in the sediment correlated well. Background Pb concentrations in pre-industrial sediments were 16 $\mu\text{g/g}$ in Lake Zug and 13 $\mu\text{g/g}$ in Lake Baldegg (for comparison); background $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were 1.20 in both lakes. In Lake Zug, lead concentrations reached a maximum of 110 $\mu\text{g/g}$ in a depth corresponding to ca. 1970, the time of highest lead emissions. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio profile provided additional information because this ratio of Pb used for gasoline additives in Europe ranges from 1.04 to 1.10, and the ratio of background Pb in central Europe is about 1.20. The ratios in the sediment had a minimum of 1.13 ca. 1980 and an increase up to 1.16 since ca. 1990. The isotope ratios reflected the fraction of Pb emissions from gasoline.

Introduction

During the last two decades, the worldwide reduction of lead additives in gasoline and the introduction of unleaded fuels in many countries have led to decreasing global Pb emissions. This has been confirmed by decreasing Pb concentrations in different time-resolved environmental reservoirs such as Greenland ice (1–3) and lake and estuarine sediments (4–6).

Pb isotopic ratios have been successfully used as tracers to identify Pb pollution sources. Methods include thermal ionization mass spectrometry (TIMS) (4, 6–9) and inductively coupled plasma mass spectrometry (ICP-MS) (5, 10–

12). Three of the four stable Pb isotopes are end products of a natural radioactive decay series: ^{204}Pb is non-radiogenic, ^{206}Pb results from the decay of ^{238}U , ^{207}Pb results from the decay of ^{235}U , and ^{208}Pb results from the decay of ^{232}Th . Their relative abundance depends on the age of formation of a certain Pb ore, e.g., the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreases with increasing geological age due to the faster decay of ^{235}U (13).

Most of these studies have focused on environmental systems in the United States, Canada, or Greenland. There are only few studies investigating the problem in Europe: one in the U.K. (5), one mainly in France (14), one in Finland (8), and one in Germany (11). Leaded fuels were curtailed in the United States around 1970 but not in most European countries until more than 10 years later (6). In Switzerland, unleaded gasoline was introduced in 1985. Lead ore used in gasoline additive production in Europe is mostly imported from Canada and Australia (Precambrian ores) with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between 1.04 and 1.10. Natural background Pb in central Europe is modern Pb with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of about 1.20 ± 0.015 (11, 13, 14).

For Switzerland, available data on lead pollution are sparse. The National Air Pollutant Observation Network (NABEL) reported that lead concentrations in dry deposition had decreased by more than 50% at five of six stations all over Switzerland between 1988 and 1993 (15).

Sediments were successfully used to investigate past deposition rates of Pb (4–6). Pb emitted by cars or by other sources such as waste incinerators or metallurgy is scattered by aeolian transport and subsequently deposited onto the lake surface or within the catchment area. In the lake, efficient scavenging by settling particles will transport Pb to the sediment (16). We assume that the flux of stable lead to the sediment is linearly related to the emissions, with a certain time lag. This is valid on the condition that no significant changes of pH, E_h , or other conditions in the lake occur that influence the scavenging efficiency or lead to postdepositional mobility in the pore water or to release from the sediment. Natural input is an additional, probably constant contribution of Pb.

The aim of this work was to analyze the response of Pb concentrations and Pb isotope ratios in Swiss lake sediment cores to the introduction of unleaded gasoline. Although the main investigation was focused on Lake Zug, additional sediment samples from Lake Baldegg were used to verify the natural background values of both Pb concentration and isotopic composition of the Pb.

Methods

Site Description. Lake Zug is a sub-alpine hard-water lake, located 30 km south of Zurich. It is situated in a mainly rural region. There are three towns situated to the north of the lake: Zug (22 000 inhabitants), Baar (16 000), and Cham (10 000). The wastewaters of these towns are treated and then discharged into the Lorze River only after its outflow from the lake. The population density in the basin is less than 200/km². Lake Zug was formed by the last glaciation. It is subdivided into a shallow (40–60 m depth) North Basin and a 200 m deep South Basin by a highly hardened conglomerate ridge forming the Kiemen Pen-

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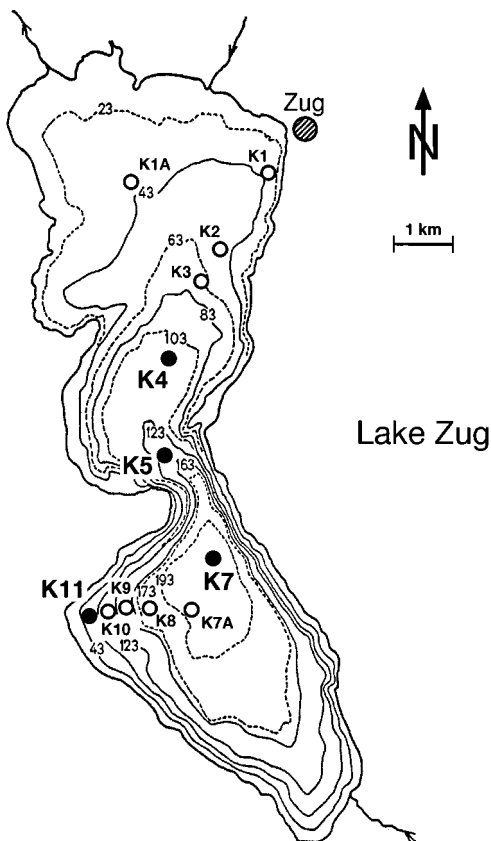


FIGURE 1. Map of Lake Zug including the sampling sites (depth of the contour lines in m). Sediment cores were taken at stations K1–K11.

insula. The North Basin contains lacustrine and deltaic sediments. The North Basin deepens to the south. The South Basin is broad and flat with very steep (20–45°) slopes; the littoral zone is very narrow. The local bedrock is mostly marls, sandstone, silt stones, and limestone. Lake Zug has no river flowing longitudinally through the basin. The mean outflow of $7\text{--}8\text{ m}^3\text{ s}^{-1}$ is very small compared to its volume of 3.2 km^3 ; the mean hydraulic residence time is approximately 14 yr. The South Basin is protected from wind by mountains reaching 400–1400 m above lake level. This protection from wind and the high eutrophic level since the beginning of this century are responsible for the meromictic state of the lake. As a consequence, seasonally anoxic conditions exist in a depth of 140–160 m and permanently below 160 m (17, 18). The coring sites are shown in Figure 1.

Lake Baldegg is also situated in the sub-alpine region, about 15 km northwest of Lake Zug. The catchment is even more rural and less populated. The bedrock in the Lake Baldegg catchment is the same as for Lake Zug. It is also a glacial lake. In contrast to Lake Zug, its morphology is very regular: from a central deep plain (66 m) the lake bottom rises evenly toward the shore. Detritus delivered to Lake Baldegg by the many small creeks draining the catchment area is derived from alluvial soils, marls, sandstone, silt stones, calcic limestone, and dolomite. Similarly to Lake Zug, it is eutrophic. Between 1940 and 1982, major parts of the deep water were permanently anoxic. Since 1982, the lake has been artificially aerated. This has shifted the deep water from an anoxic to an oxic state (19). Bathymetric and hydrological data for the two lakes are summarized in Table 1.

TABLE 1

Bathymetric and Hydrological Description of the Two Lakes

	Lake Zug ^a		Lake Baldegg ^b
	North Basin	South Basin	
position	47°10' N, 08°30' E		47°12' N, 08°17' E
surface area (km ²)	22	16	5.2
vol (km ³)	1.2	2.0	0.17
av depth (m)	52		34
max depth (m)	100	200	66

^a From ref 20. ^b From ref 21.

Sampling and Sample Preparation. Twelve cores from Lake Zug were retrieved on July 1, 1993, on a transect from north to south with a gravity corer and PVC liners with a diameter of 6.3 cm (22). The cores were kept cooled at 4 °C and stored in upright position for the transport. In the laboratory, the PVC tubes were cut longitudinally in half using Cu–bronze blades, photographed, described, and subsequently sectioned at 0.5-cm intervals to a depth of 15 cm. The samples were immediately freeze-dried using a Leybold Heraeus Lyvac GTZ. From the dried and homogenized samples, subsamples of 50 mg were digested in pressurized PTFE bombs with 4 mL of nitric acid and 1 mL of hydrogen peroxide in a microwave digestion device Milestone MLS 1200 Mega. Samples and blanks were handled further under class 100 clean-bench conditions. Procedure blanks corresponded to Pb concentrations of 0.18–0.70 $\mu\text{g/g}$ sediment.

Thirty-eight cores were retrieved from Lake Baldegg in October 1992 using the same equipment and following the same procedures as for Lake Zug. Details of the procedure are reported elsewhere (23).

Sediment Dating. Four different, independent methods were applied to estimate accurate rates of sediment accumulation. (a) A Ge well-type detector was used to determine the fallout of Chernobyl (April 26, 1986); γ -measurements of each samples were performed for 24 h with freeze-dried material. Activities were calculated for the radionuclides ¹³⁴Cs and ¹³⁷Cs; ⁷Be was used to check for total recovery of the topmost sediments in the cores. (b) Results of cylindrical sediment traps, deployed in the North and the South Basin of Lake Zug in 1982 and 1983, were used to calculate particle flux rates for the two different basins; traps had an active surface area of 68 cm² and an aspect ratio of 1:10. (c) Distinctive marker beds were measured directly on fresh cores, immediately after splitting of the cores and on core photographs. (d) Varves (annual laminations) were first checked to prove their annual character (24, 25) and then counted both on fresh cores and on core photographs.

Pb Analyses. An inductively coupled plasma-mass spectrometer (ICP-MS) ELAN 5000 from Perkin Elmer Sciex was used for both the determination of Pb concentrations and the determination of ²⁰⁶Pb/²⁰⁷Pb isotopic ratios. Triplicate measurements with acquisition times of 30 s for ²⁰⁶Pb and ²⁰⁷Pb (in order to achieve a high precision of the isotope ratios) and of 1.5 s for ²⁰⁵Tl and ²⁰⁸Pb were performed. Pb concentrations were determined measuring the isotope ²⁰⁸Pb. Signal fluctuations and instrument drift due to a slight clogging of the sampler and skimmer cones were corrected using ²⁰⁵Tl as an internal standard. Tl was

added to all samples and standards to reach a final concentration of 50 $\mu\text{g/L}$. The relative standard deviation of three replicates was always below 2%. The accuracy was checked by digesting and analyzing five subsamples of NIST Standard Reference Material 2704 (Buffalo River sediment) following the same procedure as for the sediment samples of Lakes Zug and Baldegg. The value found for Pb was $156.3 \pm 8.6 \mu\text{g/g}$, whereas the certified value is $161 \pm 17 \mu\text{g/g}$; uncertainties are given as 95% confidence intervals. Detection limits, calculated as 3 standard deviations of four laboratory blanks, were below 0.01 $\mu\text{g/L}$, i.e., below 0.01 $\mu\text{g/g}$ sediment.

Isotope Ratio Measurements. Isotopic ratios were normalized using a standard solution prepared using the standard reference material NIST SRM 981 (common Pb isotopic standard) to correct for mass discrimination. Therefore, a solution of 50 $\mu\text{g/L}$ of the isotopic standard ($^{206}\text{Pb}/^{207}\text{Pb} = 1.0933$) was analyzed within every batch of 10 samples. A correction factor in accordance with the measured isotopic composition of the standard was determined. The correction factors ranged from 0.9893 to 1.0004, i.e., the raw $^{206}\text{Pb}/^{207}\text{Pb}$ ratios before normalization ranged from 99.96 to 101.08%. Precision was checked by daily measurements of nine standard solutions prepared from the same stock solution, but with three different Pb concentrations in the same range as the samples (10, 50, 100 $\mu\text{g/L}$). Relative standard deviations of the nine determinations ranged from 0.11% to 0.50% with a median value of 0.32%.

Results

Natural Background Values. The natural background concentration of Pb in Lake Zug was estimated from core K5, which is the only core that covers about 200 yr in the uppermost 15 cm (see next paragraph). Pb concentrations are about 16 $\mu\text{g/g}$ in a depth of 15 cm. The Pb background concentration in Lake Baldegg was determined from nine pre-industrial sediment samples (sediment depth > 35 cm) of nine different cores from different parts of the lake. The concentrations range from 6.4 to 16 $\mu\text{g/g}$ with a median value of 13 $\mu\text{g/g}$.

The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in Lake Zug (core K5; 15 cm) is 1.196. The average ratio from the nine samples from Lake Baldegg is 1.198, with a relative standard deviation of 0.45%, which corresponds to the precision of the method. Both are in good agreement with the literature values of 1.20 \pm 0.015 for Pb of European origin (11, 13, 14).

Dating of Sediment Cores. Since the sediment column is compacting, it would be preferable to discuss the sediment formation in accumulation rates ($\text{g m}^{-2} \text{a}^{-1}$) rather than in sedimentation rates in (cm a^{-1}). On the other hand, only the method b (sediment traps) will produce real accumulation rates, whereas the measurements applying methods a, c, and d give results in cm a^{-1} and therefore would require a transformation according to eq 1. We prefer to give the water content of core K4, which will be discussed in detail, in Table 2 and renounce to convert the results in accumulation rates, since finally the sedimentation rates are needed to establish a time scale in cm a^{-1} . For comparison, the result of method b will be converted in a sedimentation rate in cm a^{-1} .

The results of the four methods agree quite well: (a) measurement of the depth of the peaks of ^{134}Cs and ^{137}Cs from the Chernobyl accident in 1986 in core K4 resulting

TABLE 2

Water Content of Uppermost 15 cm of Core K4, Lake Zug

depth, cm	water, %	depth, cm	water, %
0.60	98.5	9.00	76.5
1.80	93.4	10.20	75.6
3.00	89.7	11.40	78.4
4.20	85.5	12.60	77.0
5.40	83.5	13.80	72.1
6.60	82.3	15.00	68.0
7.80	79.7		

in a sedimentation rate of $S_y = 0.393 \text{ cm a}^{-1}$ since 1986; (b) using 1982–1983 sediment traps and calculation of the sedimentation rate

$$S_y = \frac{R_y}{(1 - \Phi)\rho_s} \quad (1)$$

with a porosity Φ of 0.91, a density ρ_s of 2.5 g cm^{-3} , and an accumulation rate of R_y of $866 \text{ g m}^{-2} \text{a}^{-1}$ (26). The rate is $S_y = 0.385 \text{ cm a}^{-1}$. (c) comparison of the depth of two black marker layers in core K2 and in a core from 1982 taken at the same station. The layers were found in a depth of 14.5 and 30.5 cm in 1993 and in a depth of 10.5 and 26.5 cm in 1982. This corresponds to a sedimentation rate of $S_y = 0.364 \text{ cm a}^{-1}$ between 1982 and 1993; (d) varve counting in core K4. Eleven varves were counted between 2.0 and 6.0 cm, resulting in a sedimentation rate of $S_y = 0.36 \text{ cm a}^{-1}$.

The results of these four independent methods are within a range of 10% with highest values determined by the radionuclide method. These high values can be explained by the fact that Chernobyl nuclides have been measured in the uppermost 5 cm of the cores, where water saturation of the sediments is highest. The values are additionally confirmed by a previous investigation by Kelts, who reported a sedimentation rate of $S_y = 0.4 \text{ cm a}^{-1}$ using marker layers (17).

For core K4, a time scale was established for the sediment before 1986 (2.5 cm, peaks of ^{134}Cs and ^{137}Cs). A linear scale was applied using the sedimentation rate determined by varve counting. This is justified since the sedimentation rate determined by the shift of the marker layers (method (c), which takes into account the sediment compaction below a depth of ca. 10 cm, gives no significantly lower value than the other methods and the fact that the distance between the two indicator layers remained constant during 11 yr.

An attempt was made to date core K5 between the two basins measuring the profiles of ^{134}Cs , ^{137}Cs , and ^{210}Pb . The Chernobyl peak of ^{134}Cs and ^{137}Cs was found in the top layer (0–0.5 cm). The sedimentation rate was much smaller than in the North Basin. The ^{210}Pb profile confirmed that the first 15 cm of the core represent nearly 200 yr (27). The reason for this unique situation is the sampling site, which is situated on a ridge between the two basins and therefore is strongly affected by resuspension of organic matter or a lack of sedimentation.

No core from the South Basin could be radiometrically dated since there were too many turbidite layers. Varve counting was possible in two cores: in core K9, 9 varves were counted between 2.7 and 5.5 cm; and in core K7A, 9 varves were counted between 3.1 and 5.9 cm. This results

in a sedimentation rate of $S_y = 0.31 \text{ cm a}^{-1}$ for both cores. The same value of $S_y = 0.314 \text{ cm a}^{-1}$ was found using sediment traps and calculating the rate by eq 1 (18).

Postdepositional Pb Mobility. Pb is generally regarded as an element that is efficiently scavenged under oxic and anoxic conditions and showing little tendency to be remobilized. Several authors did not observe any remobilization in lakes with seasonally anoxic bottom waters, presumably due to the sulfide precipitation (28–30). However, there are some studies that reported release of Pb from the sediments due to reductive dissolution of (hydr)oxides of Fe and Mn in Lake Greifen, a hard-water lake in Switzerland (31) or Bickford Reservoir, a soft-water lake in Massachusetts (32, 33).

Within the last 100 yr, the water column was permanently oxic above cores K1, K1A, K2, K3, K4, K10, and K11; seasonally anoxic above cores K5 and K9; and permanently anoxic above cores K7, K7A, and K8. The pore water has been anoxic in all cores since about 1950 (18). If post-depositional mobility was important, it would affect the various isotopes similarly and therefore lead to an increased mixing of neighbor layers. In the concentration and isotope ratio profiles of the stable Pb isotopes, we would expect a broadening of the marked peaks and eventually qualitative differences between the profiles of cores from oxic and anoxic regions. None of these effects was observed. This is supported by the calculations of Benoit and Hemond (32), which predicted a decreasing importance of pore water diffusion when sedimentation rates exceed 0.1 cm a^{-1} ; however, it is not clear how far these results can be extrapolated to a different type of lake. Since sedimentation rates are above 0.3 cm a^{-1} in both basins, this would apply to 11 of the 12 cores. Release from the sediment has to eventually be taken into account for the discussion of core K5, where the sedimentation rate was extremely low and anoxic conditions occurred seasonally.

Profiles of Pb in Sediment Cores. The profiles of Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of cores K4, K5, K7, and K11 including the time scale for core K4 are shown in Figure 2. These four cores represent the four different types of profiles of Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios that were found in the 12 cores. Cores K1, K1A, K3, and K4 from the North Basin showed essentially the same patterns. K4 was chosen as a typical example because dating was most reliable for this core. Core K5 between the two basins showed quite unique results and is discussed separately. Both cores from the deepest part of the lake (in the South Basin), K7 and K7A, had turbidites. The cores K8, K9, K10, and K11 from the South Basin were similar. K11 was chosen as representative because it was the uppermost core from a flat near-shore region and therefore least affected by turbidites, which are typical for the cores from the South Basin.

From a depth of 15 cm, the Pb concentrations of core K4 and K11 increase to a maximum in a depth at about 8 cm and then decrease toward the top. In the North Basin, the isotopic ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ show a minimum at a depth of about 5 cm. In the South Basin, there is a zone of minimal values between 6.5 and 1.5 cm. The tops of all 12 cores show a significant shift towards higher isotope ratios.

In core K5, a maximum Pb concentration and a minimum isotopic ratio are found at about 1 cm, much higher than in the other cores. At 15 cm, both profiles have

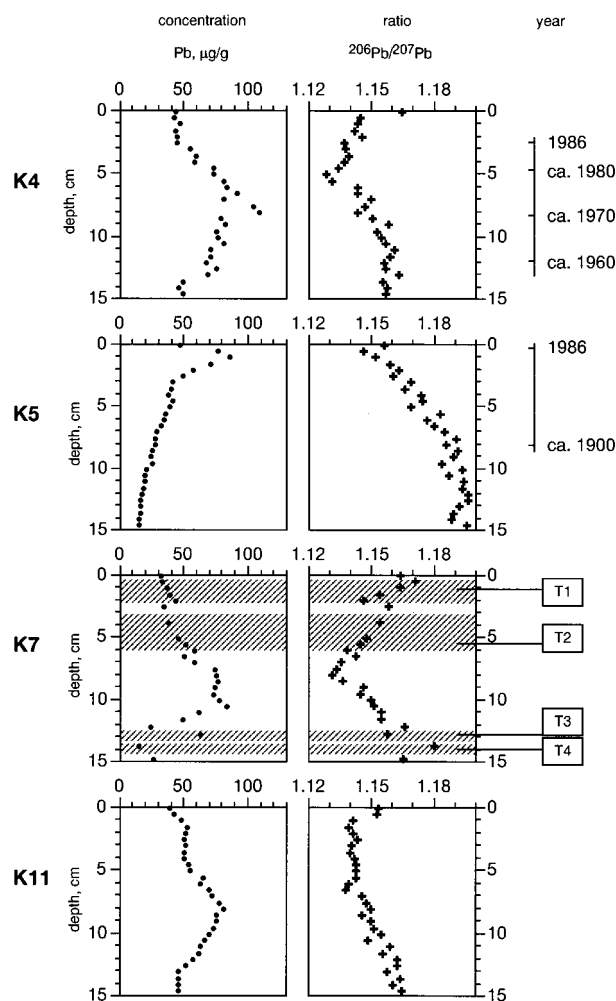


FIGURE 2. Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in four sediment cores from Lake Zug. Depth of the sampling stations: K4, 117 m; K5, 140 m; K7, 200 m; K11, 40 m. Dating: see text. K7: T1–T4 are turbidites that disturb the regular layers.

values that are typical for the natural background. This confirmed the assumption of an extremely low sedimentation rate at this special site. The profiles show the growing anthropogenic Pb input into the lake during the 20th century, which is accompanied by a shift in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio from 1.185 to 1.130. As for all other cores, the most recent sediment layer shows decreasing Pb concentrations and an increase of the isotopic ratio. The profiles of this core might be distorted to a certain extent by diffusion of Pb in the pore water. The concentration decrease at the top could be due to Pb release into the deep water, but not the simultaneous increase of the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio since the release would affect all Pb isotopes to the same degree.

Core K7 from the deepest part of the lake contained turbidite layers, which do not allow the calculation of a constant mean sedimentation rate. In Figure 2, the parts of the profile of core K7 that are not affected by turbidite layers (white background) show a profile similar to the normally layered cores K4 or K11 both for concentrations and for isotopic ratios; however, it is not possible to directly compare the depth and age of a certain layer. In core K7, the minimum $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is found about 2.5 cm higher than the concentration maximum. In core K4, this difference is slightly larger, around 3 cm; in core K11 it is 1.5 cm. The comparison is limited by the temporal resolution of the 0.5-cm slices.

TABLE 3

Lead Emissions (in T) in Switzerland between 1950 and 1990 (34)^a

	year								
	1950	1955	1960	1965	1970	1975	1980	1984	1990 ^b
gasoline	200	340	590	990	1200	1100	1100	510	290
other sources	210	270	370	420	580	360	400	180	150
total	410	610	960	1410	1780	1460	1500	690	440

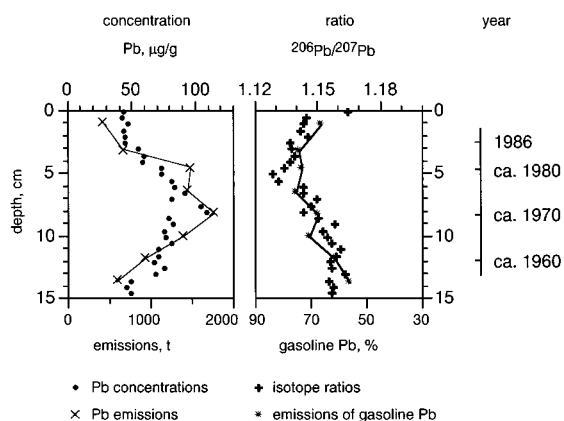
^a Switzerland has a population of 6.9 million (1990) and an area of 41 300 km². ^b Estimated values (34).

FIGURE 3. Total Pb emissions in Switzerland versus Pb concentration profile (left) and share of Pb from gasoline combustion in the total emissions compared to the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (right) in core K4 (the scale of percentage is depicted vice versa in order to facilitate the comparison). Emission data are displayed in the corresponding depth. The Pb concentration profile reflects the sum of the emissions, whereas the isotope ratio profile is an indicator for the traffic's share in the Pb emissions.

Discussion

Comparison of Sediment Data and Pb Emissions. Sources of Pb in sediments of sub-alpine lakes are natural input from erosion in the drainage basin and input of anthropogenic Pb by dry or wet deposition (14). Because of the large difference of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios between Pb from gasoline additives and from other sources such as industry or waste incineration, the profile of the isotope ratios should reflect the fraction of Pb that was emitted by combustion of leaded gasoline (Table 3).

The temporal development of Pb emissions compared to the sediment data of core K4 is illustrated in Figure 3. The emissions reached their maximum around 1970. This correlates well with the concentration peak in the sediment. The minimum $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the depth profiles corresponds to the years before 1980 when the traffic emissions were the largest source of Pb. The sharp increase toward a more natural ratio in the top layer is interpreted as the result of the phasing in of unleaded gasoline beginning at 1985. These results are in accordance with other studies (1–6, 13) and consistent with our expectations.

In order to demonstrate the difference of the temporal development of Pb emissions from gasoline additives and Pb from other sources, a factor model as described by Gobeil et al. (4) was applied. Two Pb sources were taken into consideration since two different types of Pb contribute to the isotopic composition of the sediments. Gasoline lead was regarded as a source with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.10. All other sources including the natural input were treated as a second source with an European $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.20 (11, 13, 14). Depth profiles of the four cores are shown

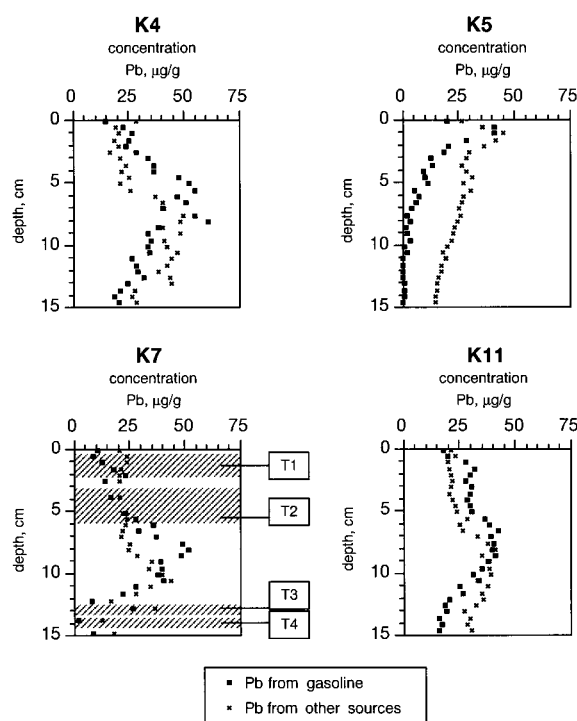


FIGURE 4. Pb concentration profiles of the individual sources in core K4, K5, K7, and K11, calculated using a two-source model with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.10 for gasoline lead and 1.20 for other sources.

in Figure 4 for both sources separately. Since the absolute values of the assumed $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are uncertain, it is important to mention that slight variations of these values only affect the concentrations of the individual sources, but not their temporal development. Core K4 and K11 reveal that the maximum Pb input from the gasoline source occurred several years later than the maximum of the Pb input from other sources. The profiles of core K5 show that as early as at the end of the last century (in a depth of ca. 8 cm) there was a remarkable anthropogenic Pb input, assuming that the Pb concentration of 16 $\mu\text{g/g}$ in a depth of 15 cm represents the natural background. The share of gasoline Pb phases in during the 20th century. However, both profiles of this core might suffer from a certain peak broadening due to pore water diffusion. The situation of core K7 containing turbidite layers is special. It is obvious that the slumping caused layer T3 and T4 affected both Pb sources, whereas in layers T1 and T2 only the gasoline fraction is affected. However, a further interpretation of core K7 is not possible with the present data.

The isotopic pattern provides important information about the pollution sources. The profiles of isotope ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ show that gasoline combustion was the main Pb source until ca. 1990. Since then, the isotope ratio is increasing toward European Pb. Although unleaded fuel had been already introduced in 1985, there was a lag of 5

yr until this source lost its importance. This lag is partially due to the simultaneous reduction of lead emissions from other sources and partially to a transport delay because Pb is deposited not only directly onto the lake surface but also on the whole drainage basin area. The concentration and $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of the recent sediment are similar to the values of ca. 1950. The trend toward natural background values is still in progress.

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