Origin and Evolution of Pb in Sediments of Lake Geneva (Switzerland−France). Establishing a Stable Pb Record

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Pb isotopes and Pb concentrations were measured in two
sediment cores sampled in Lake Geneva (i) at the center
of the basin (central plain) and (ii) in an area which receives
the effluents of the wastewater treatment plant of
Lausanne as well as runoff inputs. The presence of an
anthropogenic contribution is observed over all the sampled
period (~150 years), even at the center of the lake. At
both sites, the maximum contamination of Pb occurred in
the late 1970s, and has declined to present. The site
close to Lausanne received much more Pb than the one
at the center of the lake. Surprisingly, the Pb isotopes show
that gasoline-derived Pb has had a minor influence, at
least over the last 20 years. Instead, deposition of Pb from
industrial (and domestic) activities predominates. This
study demonstrates that one of the major limitations of
the isotopic method is the poor (or partial) knowledge of
how the isotopic compositions of potential sources have
evolved through the past. A simple method of sample
dissolution, based on HNO_3 leaching assisted by microwave,
is also presented. We believe that this sample preparation
can be extensively used because it provides a reliable
estimate of Pb having an anthropogenic origin.

Introduction

Pb added into gasoline as antiknock compounds was
considered for a long time to be the major source of Pb
contamination, with a maximum worldwide contamination
occurring in the mid-1970s (*1*). In Switzerland, unleaded
gasoline was introduced in 1985, and nowadays less than
20% of gasoline still contains leaded additives. The National
Air Pollutant Observation Network (NABEL) reported that,
between 1988 and 1993, the Pb dry deposition decreased by
more than 50% at five of six stations over Switzerland (*2*). As
a consequence, other sources such as industrial (or domestic)
activities may become relatively more important in the total
anthropogenic Pb budget (*3*). In addition, the presence of a
point-source, such as a wastewater treatment plant, an
industrial area, or runoff may locally dominate the pollutant
inputs.

Stable Pb isotope geochemistry in environmental studies
can be used for tracing the origin of Pb. This method is based
on the differences in isotopic abundance existing between
different groups of materials (e.g. local rocks, gasoline
additives, industrial emissions, etc.). The determination of
Pb isotopes in the sedimentary column allowed the recon-
structing of the history of Pb inputs (i.e. annual/decade scale
or more) in lakes (*4−10*) or marine/estuarine environments
(*11−16*). However, Pb in sediments is generally derived from
multiple sources. Contributions, as well as their isotopic
signatures, likely evolved through time, since the location of
input has frequently changed relative to the economic
condition (*17*). Such an isotopic database is unfortunately
either poor or nonexistent, depending on the country. In
addition, the study of a single binary mixing (e.g. natural,
anthropogenic) is relatively easy, whereas it becomes much
more ambiguous for multicomponent mixing, where several
anthropogenic end-members are involved.

The aim of this study was to investigate the origin and the
history of Pb inputs at an in-shore site potentially influenced
by industrial/domestic wastewater effluents and by urban
runoff, where gasoline-derived Pb should dominate. For
comparison a reference site was chosen in the center of the
lake, far from direct human inputs. The results were compared
to the few studies previously carried out in Switzerland: ice
from a high alpine site (*18, 19*), lake Zug sediments close to
Zurich (*10*). and peat bog in Jura Mountains (*20, 21*).

Setting

Lake Geneva is the largest freshwater body in Europe, with
a volume of 89 km³ (Figure 1). The Rhone River is its major
tributary and drains 70% of the lake watershed, including
industrial and urban sites, agricultural lands, glaciated areas,
pasture, and forests. The biggest city on the lake shore is
Lausanne, which releases treated domestic and industrial
wastewater into the Bay of Vidy (200 000 equiv inhabitants).
The wastewater treatment plant started in 1964 with biological
treatment, followed in 1971 by the implementation of a phase
for the phosphate elimination using $FeCl_3$. A pipe also drains
the runoff into the bay. A core (BV) has been sampled at
about 700 m from the plant effluent, at a depth of 51 m. For
comparison, another core (PC) has been recovered from the
central plain and deepest part of the lake (307 m).

Methodology

Sampling and Subsampling. The cores were recovered
using poly(vinyl chloride) liners (50 cm in length), from the
submersible F. A. Forel (*22*). Volume magnetic susceptibility
(VMS) was determined on the BV core using a Bartington
MS2. The subsampling of the PC core (44 cm long) was carried
out at an interval of 0.5 cm for the first 20 cm, and 1 cm for
the remaining section, whereas a 1 cm interval was used all
along the BV core (41 cm long). Samples were gently air-
dried at 60 °C for 2 days; the water content and porosity were
calculated following the method of Sugai et al. (*23*). The depth
scale was expressed in term of mass depth (g cm⁻²).

Analysis. Dating was based on ²¹⁰Pb and ¹³⁷Cs methods,
measured by α- and γ-ray spectrometry, respectively (*22*).
Excess Pb (²¹⁰Pb_xs) was obtained by subtracting the supported
activity, determined via measurement of the ²¹⁴Pb isotope
by γ-ray spectrometry. Loss on ignition (LOI), a surrogate
for organic matter content, was measured after 4 h at
550 °C.

It has already been demonstrated that anthropogenic
component can be partly separated from the total Pb by a
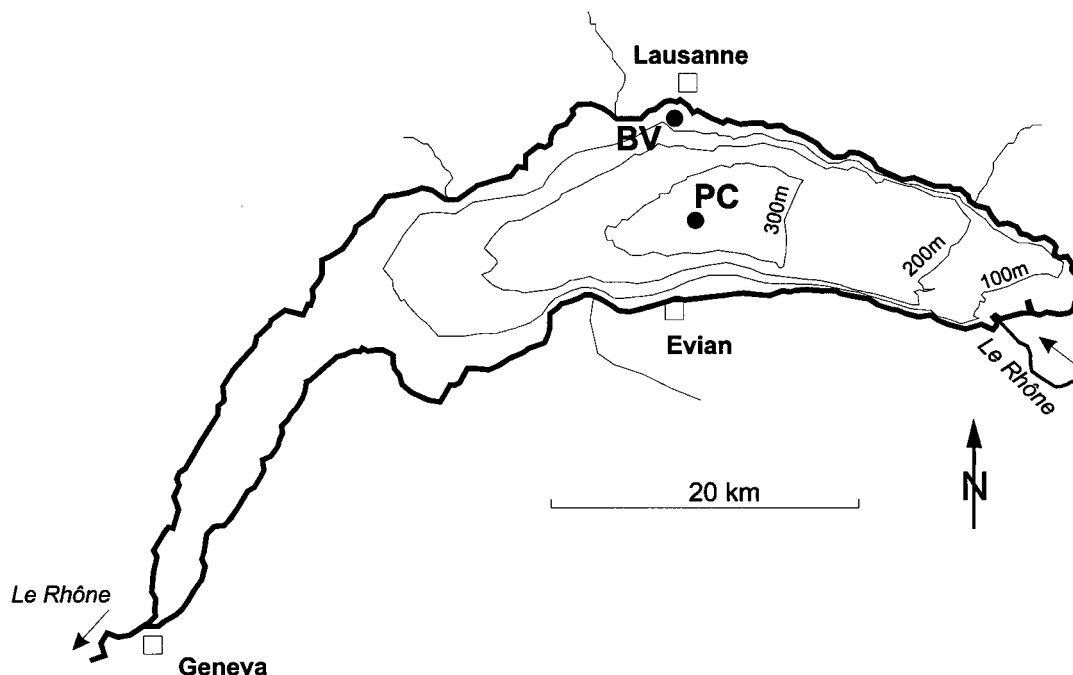dilute acid leaching (*5, 13, 24*). Graney et al. (1995) have also

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FIGURE 1. Map of lake Geneva with location of cores. Central Part of the lake (PC): 46°28′38″ N, 6°38′35″ E, depth = 307 m. Bay of Vidy (BV): 46°30′42″ N, 6°35′06″ E, depth = 51 m.

reported that the strength and the nature of acid (HCl or HNO_3) have only little effect on the concentration and isotopic ratios of leached Pb and that the leached fraction of a contaminated sediment are isotopically distinct from those removed from the silicate minerals after HF digestion (9). This does not mean that only anthropogenic Pb is removed by dilute acid, nor that the residue is totally free from some anthropogenic Pb persisting after leaching, but simply that dilute acid can be used to extract preferentially anthropogenic Pb from a contaminated sediment. Such a procedure was carried out here using nitric acid for evident reasons of convenience for further ICP-MS measurements. The procedure consisted of (i) a partial dissolution of about 500 mg of sediment with 10 mL of suprapure 2 N HNO_3 and (ii) the total dissolution of the residue of 14 selected samples with suprapure and concentrated $HF/HNO_3/HCl$ mixture (3 mL of each). The partial dissolution was carried out in closed, pressurized Teflon bombs, in a microwave assistance oven (ETHOS, Milestone) with the following settings: 5 min at 400 W, 2 min at 100 W, 10 min at 600 W, and finally 10 min at 700 W (magnetic stirring; pressure max, 20 bar). After centrifugation the residues were washed again with 10 mL of suprapure 2 N HNO_3 and centrifuged. Total dissolution was carried out using the settings above for the microwave. Chemical preparation was performed in a class $100-1000$ clean room. Pb concentrations were then measured by a quadrupole-based ICP-MS (POEMS1, TJA) using Rh/Re internal calibration. Reproducibility of Pb concentrations was better than 10% on the basis of numerous replicates. Blanks were systematically measured for each set of eight unknown samples and were always found to be negligible compared to Pb in samples.

Isotopic ratios were measured using the same quadrupole-based ICP-MS. Separation of Pb, mass bias correction via NBS 981 measurements, and typical settings are reported elsewhere (25, 26).

Results

Pb Isotopes. Leachates of Lake Geneva sediments are plotted on two diagrams of $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ (Figure 2). The measured changes in isotope ratios are much greater than the uncertainties in the

measurements and are significant in all cases. For both cores, the linear trends indicate an influence of one or more less radiogenic (anthropogenic) sources contaminating the naturally occurring Pb. In Figure 2a, the PC samples seem generally shifted to less thorogenic values (lower $^{208}Pb/^{204}Pb$ ratios), but this tendency does not appear in Figure 2b.

Bay of Vidy. The uppermost 22 cm ($0-10.9$ g cm^{-2}) are almost black, characterized by relatively constant porosity (except the uppermost 3 cm), high organic matter content, and high values of VMS (Figure 3a, Table 1). Below 22 cm, the sediments turn gray with numerous laminae in which the organic matter content and VMS remain steady at lower values. The ^{137}Cs profile exhibits two distinct peaks reaching 200 and 130 mBq g^{-1} at mass depths of 6 and 10.5 g cm^{-2}, respectively. The $^{210}Pb_{tot}$ activities increase from bottom to top, from about 59 to 170 mBq g^{-1}, following the same evolution as the porosity profile. The ^{214}Pb activities slightly decrease toward the top from 55 to 44 mBq g^{-1}.

Leached Pb. Relatively low Pb contents ($\sim$30 μg g^{-1}) are observed at the core bottom. They increase, slowly at first up to 10.9 g cm^{-2} ($\sim$ 90 μg g^{-1}) and then rapidly to reach a maximum at 8.4 g cm^{-2} ($\sim$ 300 μg g^{-1}). Finally, the Pb contents decline up to the surface ($\sim$120 μg g^{-1}). The BV core is characterized by a decrease of the $^{206}Pb/^{207}Pb$ ratios proceeding in four steps: (i) a decrease from $\sim$1.195 at the bottom to $\sim$1.170 at 16.3 g cm^{-2}, (ii) a stabilization up to 10.9 g cm^{-2}, (iii) another decline at about 1.150 up to 9 g cm^{-2}, and (iv) another stabilization up to the surface.

Residual Pb. It is always low comparatively to the total Pb content, but can vary between 5.1 and 17.8 μg g^{-1}; the highest value being recorded in the strongest contaminated layer. Its isotopic signature follows the same trend as the leachate fraction, but it is systematically more radiogenic.

Central Plain. The porosity profile indicates a regular compaction with depth, except that shifts are observed at $\sim$1 and 4.3 g cm^{-2} (Figure 3b, Table 2). The organic matter content regularly decreases in the first 7 g cm^{-2} and then stabilizes around 4%. Two peaks of ^{137}Cs reaching 550 and 230 mBq g^{-1} are observed at 1.5 and 3.5 g cm^{-2}, respectively; whereas $^{210}Pb_{tot}$ activities increase from 50 mBq g^{-1} at the bottom, up to nearly 300 mBq g^{-1} at the surface. However, ^{137}Cs, $^{210}Pb_{total}$, and LOI profiles are perturbed in the low
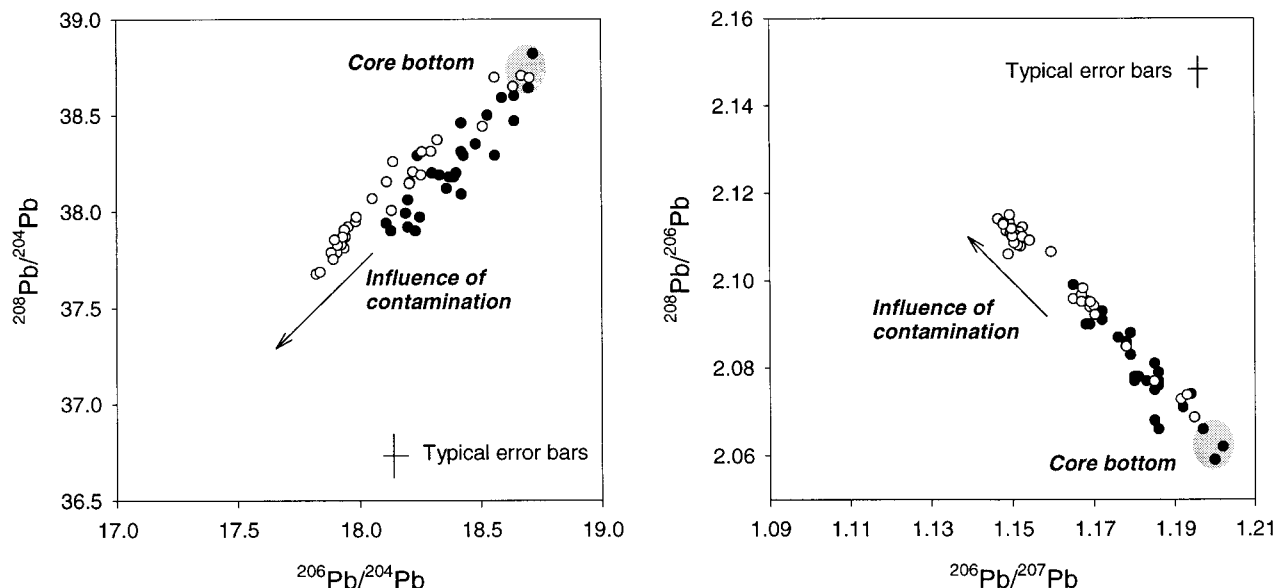
FIGURE 2. Pb isotopic compositions of leachates in the sediments coming from (○) BV core and (●) PC core.

porosity layers. Outside these horizons, the ^{214}Pb activities are fairly constant at about 45 mBq g^{-1}.

Leached Pb. In contrast to the BV site, the Pb content remains low and shows a two-step trend: (i) an increase from bottom to 2 g cm^{-2} (maximum 63 μg g^{-1}, about 5 times lower than at BV) and (ii) a decrease to the surface. The ^{206}Pb/^{207}Pb ratios decline more or less regularly from ~1.20 at the bottom, to a turning point at a mass depth of 2.3 g cm^{-2} (1.165), and then an increase to the surface (1.186).

Residual Pb. The Pb remaining in the residue is nearly constant along the core (Pb = 4 $\pm$ 1 μg g^{-1}). These values are similar to the lowest observed in the same fraction at BV. The ^{206}Pb/^{207}Pb ratios are fairly stable, varying in a narrow range: 1.198–1.205. Only the sample at 2.3 g cm^{-2} is slightly different, with a ^{206}Pb/^{207}Pb ratio of 1.180. It also presents the highest Pb content, 7.4 μg g^{-1}.

Discussion

Core Dating. The atypical low porosity and ^{210}Pb, ^{137}Cs, and organic matter values in few horizons of the PC core can be explained by rapid deposition of sediments, probably related to sporadic events such as turbidity currents or floods. This may considerably complicate the establishment of a reliable chronology. However, the two ^{137}Cs peaks allow an absolute dating of both 1963/64 and 1986 horizons, which correspond respectively to worldwide maximum deposition of Cs from nuclear weapon tests in the atmosphere and the Chernobyl accident. ^{210}Pb chronology was obtained using the CRS model (constant rate supply), which assumes that the variations of the ^{210}Pb deposition are negligible over the last 100 years (*27*). This model is generally well-adapted to a context of variable sedimentation rate (*28*). ^{137}Cs and ^{210}Pb data provide a compatible (and likely reliable) chronology in the PC core.

At the BV site, the ^{137}Cs peaks of 1986 and 1963/64 are clearly identified, but the ^{137}Cs Chernobyl inventory appears abnormally high as compared to data from the PC core and other sites in Lake Geneva (*29*). An explanation could be a slump, occurring shortly after 1986, which brought ^{137}Cs-rich material, initially deposited elsewhere around the coring area. Moreover, the high Chernobyl ^{137}Cs inventory may also result from the focusing of the runoff from the Lausanne agglomeration collected in the waterwater treatment plant and rejected into the lake close to the sampling site. The CRS model becomes invalid, because the hypothesis of the

constant ^{210}Pb$_{xs}$ supply no longer applies. Reported in a semilog diagram, the ^{210}Pb$_{xs}$ activity evolves linearly between 0 and 1.8 g cm^{-2}, and deeper than 5.2 g cm^{-2}. The CF:CS model (constant flux:constant rate) (*30, 31*) applied to these two sections gives sedimentation rates of 0.10 $\pm$ 0.01 g cm^{-2} a^{-1} (r^2 = 0.99) and 0.16 $\pm$ 0.02 g cm^{-2} a^{-1}. In this way, the ^{210}Pb$_{xs}$ and ^{137}Cs data provide a coherent time scale. In addition, the increase of VMS, which coincides with the introduction of FeCl$_2$ in the water treatment process in 1971 (*32*), gives an absolute indicator fitting well with the above dating.

Isotopic Signatures of the Potential Sources. The Pb added to Swiss gasoline today comes predominantly from Precambrian ore deposits of Australia and Canada (*18*). A mean ^{206}Pb/^{207}Pb ratio of 1.117 was measured in gasoline at Bern in 1995 (*33*), while ^{206}Pb/^{207}Pb variations between 1.101 and 1.124 were observed during 1996/97 in gasoline at Geneva (avg. 1.116) (*34*). To our knowledge, only one early measurement was done in Bern in the early 1970s (^{206}Pb/^{207}Pb $\approx$ 1.145) (*35*).

The emissions from waste incinerators contain lead with a representative average of man-made material (*3, 18, 36*). ^{206}Pb/^{207}Pb ratios of ~1.15 were measured in 1995 in the exhausts of an incinerator at Bern (*18*). To evaluate the local influence of the sewage treatment plant of Lausanne on the BV site, particles from its effluent were also measured (^{206}Pb/^{207}Pb, 1.146–1.149, n = 3). All these values are more radiogenic than modern gasoline-derived Pb, and they are quite similar to those reported for industrial sources in other countries (*3, 36, 37*).

Another source is the geogenic Pb. Theoretically, the analysis of residues should reflect the natural/local Pb source, because the anthropogenic (acid soluble) Pb should have been removed by preliminary HNO$_3$ leaching. Unfortunately, even if the isotopic compositions of the residues are systematically more radiogenic than in the associated leachates (that indicates a greater proportion of geogenic Pb), they depict large variations. This is particularly clear in the BV core, where the residual ^{206}Pb/^{207}Pb ratios vary between 1.157 and 1.197, while the Pb content concomitantly varies between 17.8 and 5.1 μg per gram of untreated bulk sediment. This strongly suggests that some residues may be still contaminated by a less radiogenic anthropogenic Pb, despite a second washing step. Nonetheless, the geogenic input can be assessed with the most radiogenic residues of the PC
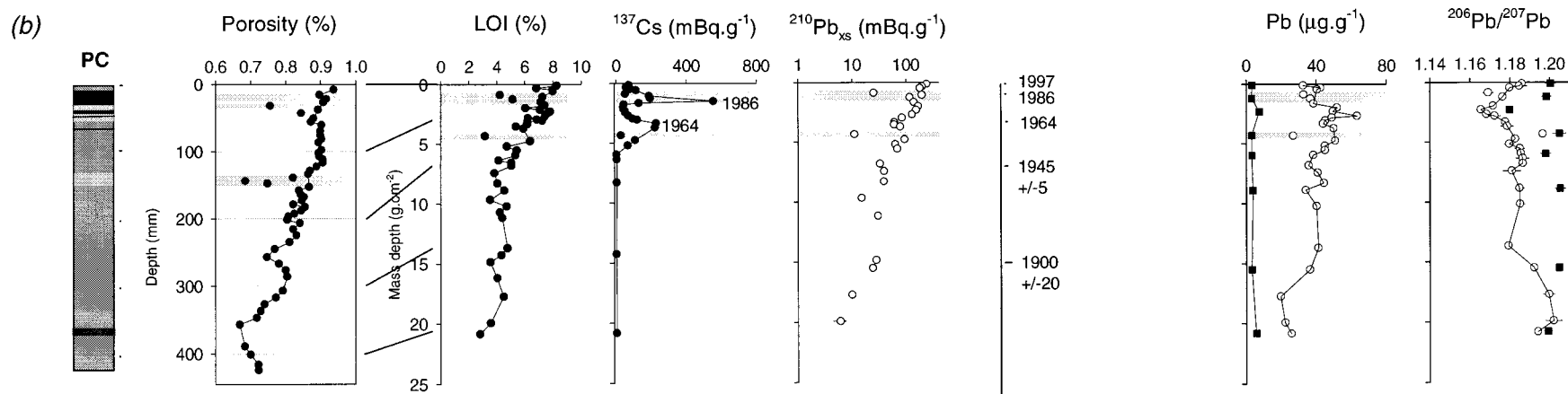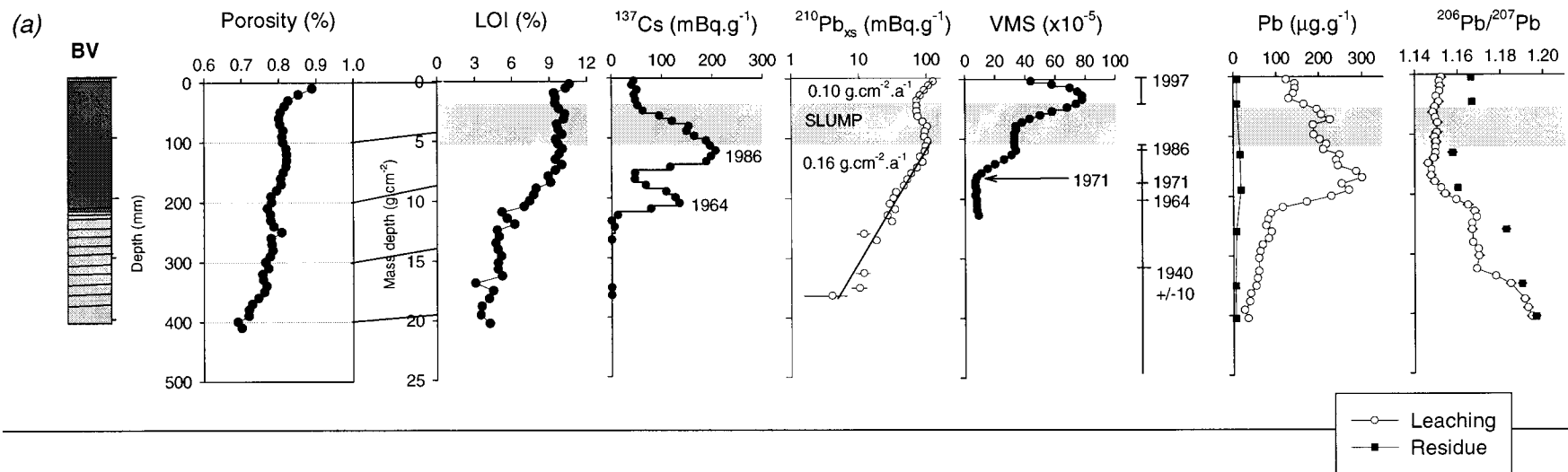
FIGURE 3. Profiles of porosity, LOI, ^{137}Cs, ^{210}Pb, SMV, Pb contents, and ^{206}Pb/^{207}Pb ratios in BV (a) and PC (b) cores.

TABLE 1. Core for Bay of Vidy (BV)

sample name/depth (cm)	mass depth[a]	^{214}Pb*	^{210}Pb$_{tot}$*	^{137}Cs*	Pb	^{206}Pb/^{204}Pb**	^{208}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{206}Pb
BV: 0-1	0.2		170 ± 5	44 ± 2	124	17.95 ± 0.04	37.92 ± 0.09	1.153 ± 0.002	2.112 ± 0.004
BV: 1-2	0.6	44 ± 6	152 ± 5	41 ± 1	144	17.98 ± 0.03	37.95 ± 0.07	1.152 ± 0.001	2.110 ± 0.003
BV: 1-2 R					8.2	18.32 ± 0.02	38.55 ± 0.08	1.167 ± 0.001	2.097 ± 0.003
BV: 2-3	1.0		137 ± 4	50 ± 3	144			1.152 ± 0.002	2.108 ± 0.004
BV: 3-4	1.4		125 ± 5	45 ± 2	141	17.99 ± 0.03	37.97 ± 0.03	1.152 ± 0.001	2.111 ± 0.002
BV: 4-5	1.8		116 ± 3	48 ± 2	130	17.93 ± 0.05	37.84 ± 0.03	1.150 ± 0.001	2.111 ± 0.003
BV: 5-6	2.3		116 ± 4	52 ± 2	165	17.94 ± 0.04	37.81 ± 0.08	1.151 ± 0.002	2.108 ± 0.005
BV: 5-6 R					8.1	18.34 ± 0.02	38.49 ± 0.08	1.167 ± 0.001	2.099 ± 0.003
BV: 6-7	2.7		116 ± 4	62 ± 2	196			1.150 ± 0.002	2.111 ± 0.004
BV: 7-8	3.2	49 ± 7	123 ± 3	96 ± 2	206	17.93 ± 0.05	37.86 ± 0.09	1.149 ± 0.002	2.111 ± 0.005
BV: 8-9	3.6		137 ± 4	120 ± 3	226	17.94 ± 0.04	37.87 ± 0.09	1.150 ± 0.001	2.111 ± 0.004
BV: 9-10	4.0		150 ± 4	153 ± 5	187	17.92 ± 0.05	37.83 ± 0.10	1.151 ± 0.002	2.110 ± 0.003
BV: 10-11	4.4		143 ± 3	150 ± 4					
BV: 11-12	4.8		141 ± 5	165 ± 5	189	18.05 ± 0.04	38.07 ± 0.10	1.151 ± 0.002	2.109 ± 0.003
BV: 12-13	5.2		152 ± 5	187 ± 3	202	17.94 ± 0.03	37.90 ± 0.06	1.149 ± 0.002	2.113 ± 0.003
BV: 13-14	5.7	50 ± 7	146 ± 4	196 ± 4	218	17.91 ± 0.03	37.79 ± 0.10	1.150 ± 0.002	2.110 ± 0.004
BV: 14-15	6.1	-	143 ± 4	207 ± 4	211	17.91 ± 0.04	37.82 ± 0.09	1.150 ± 0.001	2.112 ± 0.003
BV: 15-16	6.5	45 ± 6	128 ± 4	197 ± 4	248	17.93 ± 0.03	37.87 ± 0.05	1.150 ± 0.002	2.112 ± 0.003
BV: 15-16 R					15.5	18.21 ± 0.04	38.31 ± 0.10	1.158 ± 0.002	2.104 ± 0.004
BV: 16-17	7.0		135 ± 3	234 ± 5	241			1.149 ± 0.002	2.106 ± 0.005
BV: 17-18	7.4		121 ± 4	117 ± 2	244	17.82 ± 0.05	37.68 ± 0.10	1.147 ± 0.002	2.114 ± 0.004
BV: 18-19	7.9		108 ± 3	47 ± 2	286	17.88 ± 0.03	37.79 ± 0.07	1.148 ± 0.002	2.113 ± 0.003
BV: 19-20	8.4	51 ± 7	100 ± 3	47 ± 1	301	17.84 ± 0.06	37.69 ± 0.06	1.148 ± 0.002	2.113 ± 0.005
BV: 20-21	9.0		97 ± 4	68 ± 2	252	17.90 ± 0.03	37.85 ± 0.10	1.149 ± 0.002	2.115 ± 0.004
BV: 21-22	9.5		84 ± 2	109 ± 3	270	17.89 ± 0.05	37.75 ± 0.08	1.153 ± 0.001	2.110 ± 0.003
BV: 21-22 R					17.8	18.30 ± 0.03	38.47 ± 0.08	1.160 ± 0.001	2.105 ± 0.002
BV: 22-23	10.0		80 ± 2	127 ± 4	230	18.14 ± 0.04	38.26 ± 0.07	1.154 ± 0.002	2.109 ± 0.002
BV: 23-24	10.5		77 ± 2	135 ± 4	172	18.11 ± 0.03	38.15 ± 0.05	1.160 ± 0.001	2.107 ± 0.004
BV: 24-25	10.9	52 ± 7	83 ± 3	78 ± 2	115	18.13 ± 0.06	38.00 ± 0.14	1.165 ± 0.002	2.096 ± 0.004
BV: 25-26	11.4		75 ± 3	12 ± 1	87	18.21 ± 0.03	38.15 ± 0.07	1.168 ± 0.002	2.095 ± 0.002
BV: 26-27	11.9	-	79 ± 4		81	18.30 ± 0.04	38.31 ± 0.07	1.169 ± 0.001	2.094 ± 0.002
BV: 27-28	12.4			6 ± 3	77	18.22 ± 0.03	38.21 ± 0.09	1.167 ± 0.002	2.097 ± 0.005
BV: 28-29	13.0	55 ± 8	67 ± 3		90	18.21 ± 0.04	38.15 ± 0.08	1.167 ± 0.002	2.095 ± 0.002
BV: 28-29 R					6.7	18.68 ± 0.05	38.86 ± 0.10	1.183 ± 0.002	2.080 ± 0.004
BV: 29-30	13.5		73 ± 3		83				
BV: 30-31	14.0				69	18.26 ± 0.05	38.31 ± 0.09	1.167 ± 0.001	2.098 ± 0.002
BV: 31-32	14.6				63	18.32 ± 0.04	38.37 ± 0.07	1.170 ± 0.001	2.094 ± 0.003
BV: 32-33	15.2				60	18.25 ± 0.05	38.19 ± 0.10	1.170 ± 0.002	2.092 ± 0.003
BV: 34-35	16.3		67 ± 3		60			1.169 ± 0.001	2.095 ± 0.004
BV: 35-36	16.9				56	18.56 ± 0.03	38.70 ± 0.07	1.178 ± 0.001	2.085 ± 0.003
BV: 36-37	17.5		66 ± 3		53	18.51 ± 0.04	38.44 ± 0.07	1.185 ± 0.002	2.077 ± 0.002
BV: 36-37 R					5.1	18.78 ± 0.04	38.93 ± 0.08	1.190 ± 0.002	2.072 ± 0.003
BV: 37-38	18.2	56 ± 8	59 ± 3		40				
BV: 38-39	18.8				38	18.67 ± 0.06	38.70 ± 0.09	1.192 ± 0.002	2.073 ± 0.004
BV: 39-40	19.5				26	18.64 ± 0.04	38.65 ± 0.08	1.193 ± 0.002	2.074 ± 0.004
BV: 40-41	20.2				34	18.70 ± 0.03	38.69 ± 0.08	1.195 ± 0.002	2.069 ± 0.002
BV: 40-41 R					5.4	18.98 ± 0.06	39.23 ± 0.10	1.197 ± 0.002	2.067 ± 0.004

[a] Mass depth expressed in g cm^{-2}, radiochemical data (^{137}Cs and ^{210}Pb and ^{214}Pb) in mBq g^{-1}, Pb Contents in μg g^{-1} (error ~ 10%) Pb isotopic compositions are of leachates, except for Residues (R). Errors: *66% at confidence level and **95% confidence level.

core: ^{206}Pb/^{207}Pb ∼ 1.203 ± 0.002, assumed free of human contribution, because of their very low Pb contents (3.1−3.8 μg g^{-1}). This signature is in good agreement with the literature values characterizing the background Pb in central and western Europe (10, 20, 21, 38, 39).

The leachate fraction should mostly contain Pb desorbed from oxyhydroxide surfaces but also integrate Pb primarily hosted by carbonates, organic matter, or simply adsorbed to the particle surface (40, 41).

Even in the deepest horizons, the leachates are slightly less radiogenic than their associated residues, suggesting a contribution of a low radiogenic anthropogenic source. That is in agreement with what was previously observed in an ombrothrophic bog in the Jura (20, 21) and in the Thau basin (41).

The isotopic signature of the anthropogenic Pb added to the sediment can be obtained by subtracting the natural (background) leachable component from the total leached Pb. The mathematical formulation is the same that was reported elsewhere (9):

$$^{206}\text{Pb}/^{207}\text{Pb anthropogenic Pb component} = [(^{206}\text{Pb}/^{207}\text{Pb TL}) (\text{ppm Pb TL}) - (^{206}\text{Pb}/^{207}\text{Pb BC}) (\text{ppm Pb BC})]/(\text{ppm Pb TL} - \text{ppm Pb BC}) \quad (1)$$

where TL = total leach and BC = background leachable component.

The amount of leachable natural Pb was assumed to be about 23 ± 3 μg g^{-1}. This value was obtained by averaging the concentrations in leaches of the three deepest and the least polluted horizons of the PC core.

Although 95% of anthropogenic Pb are removed by leaching, up to 5% may remain in the residue which results in a considerable change in Pb isotopic compositions. However, the procedure of leaching proposed here appears highly convenient for rapid and reliable assessment of the anthropogenic component. In addition, it presents the advantage of being fairly reproducible (better than 10%) and

TABLE 2. Core for Central Part of the Lake (PC)

sample name/depth (cm)	mass depth[a]	^{214}Pb*	^{210}Pb$_{tot}$*	^{137}Cs*	Pb	^{206}Pb/^{204}Pb**	^{208}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{208}Pb/^{206}Pb
PC:0-1	0.1		283 ± 13	72 ± 3	32.6	18.59 ± 0.04	38.59 ± 0.09	1.186 ± 0.001	2.076 ± 0.002
PC:0-1 R					3.2			1.200 ± 0.003	2.059 ± 0.005
PC:1-2	0.3		242 ± 8	57 ± 5	42.6	18.42 ± 0.06	38.09 ± 0.10	1.185 ± 0.004	2.068 ± 0.008
PC:2-2.5	0.5		226 ± 6	82 ± 3	40.5	18.23 ± 0.05	37.90 ± 0.14	1.180 ± 0.001	2.077 ± 0.006
PC:2.5-3	0.6			114 ± 2					
PC:3-3.5	0.9	28 ± 4		52 ± 5	32.8	18.19 ± 0.03	37.99 ± 0.14	1.169 ± 0.003	2.090 ± 0.008
PC:3.5-4	1.0		241 ± 6	188 ± 5					
PC:4-4.5	1.2		162 ± 7	194 ± 14	36.7	18.42 ± 0.03	38.46 ± 0.08	1.176 ± 0.001	2.087 ± 0.004
PC:4-4.5 R					3.1			1.198 ± 0.002	2.062 ± 0.003
PC:4.5-5	1.5			553 ± 5					
PC:5-5.5	1.6		184 ± 6	130 ± 2	38.6				
PC:5.5-6	1.8			44 ± 2					
PC:6-7	2.0		212 ± 6	40 ± 5	51.9	18.20 ± 0.02	38.06 ± 0.12	1.172 ± 0.002	2.091 ± 0.005
PC:7-7.5	2.1	52 ± 6		42 ± 2					
PC:7.5-8.5	2.3		198 ± 5	50 ± 3	49.5	18.24 ± 0.03	38.29 ± 0.07	1.165 ± 0.001	2.099 ± 0.002
PC:7.5-8.5 R					7.4			1.180 ± 0.002	2.078± 0.003
PC:8.5-9	2.4			52 ± 3					
PC:9-10	2.7		174 ± 5	69 ± 3	63.3	18.13 ± 0.07	37.90 ± 0.16	1.168 ± 0.001	2.090 ± 0.004
PC:10-10.5	2.8				49.0	18.11 ± 0.06	37.94 ± 0.17	1.172 ± 0.003	2.093 ± 0.009
PC:10.5-11	3.0		129 ± 4	95 ± 3					
PC:11-11.5	3.0			120 ± 3	45.2				
PC:12-12.5	3.3		106 ± 4	228 ± 10	44.0	18.33 ± 0.05	38.19 ± 0.15	1.178 ± 0.002	2.086 ± 0.006
PC:12.5-13	3.5		105 ± 3						
PC:13-13.5	3.7	62 ± 8	123 ± 3	222 ± 9	49.8	18.20 ± 0.07	37.92 ± 0.07	1.179 ± 0.003	2.083 ± 0.006
PC:14-14.5	4.3		56 ± 2	27 ± 1	26.9	18.70 ± 0.02	38.64 ± 0.07	1.197 ± 0.001	2.066 ± 0.002
PC:14-14.5 R					3.0			1.205 ± 0.003	2.051 ± 0.006
PC:15-15.5	4.7		139 ± 4	109 ± 2	50.8	18.25 ± 0.06	37.97 ± 0.11	1.183 ± 0.002	2.077 ± 0.007
PC:16-16.5	5.2		108 ± 3	67 ± 2	45.0	18.36 ± 0.07	38.12 ± 0.08	1.180 ± 0.002	2.078 ± 0.008
PC:17-17.5	5.5		114 ± 4		45.0	18.39 ± 0.07	38.18 ± 0.13	1.185 ± 0.002	2.077 ± 0.005
PC:18-18.5	6.0			3 ± 0.8	38.4	18.53 ± 0.02	38.50 ± 0.09	1.186 ± 0.001	2.077 ± 0.003
PC:18-18.5 R					3.2			1.198 ± 0.003	2.065 ± 0.006
PC:19-19.5	6.4	41 ± 5		4 ± 2		18.40 ± 0.04	38.20 ± 0.09	1.186 ± 0.003	2.066 ± 0.006
PC:20-20.5	6.8		78 ± 3		35.7	18.43 ± 0.06	38.29 ± 0.16	1.186 ± 0.002	2.079 ± 0.006
PC:21-22	7.4		84 ± 3		40.9	18.37 ± 0.05	38.18 ± 0.15	1.181 ± 0.004	2.078 ± 0.006
PC:23-24	8.3	45 ± 5	84 ± 3	5 ± 1	44.3				
PC:24-25	8.9				34.0	18.48 ± 0.04	38.35 ± 0.11	1.185 ± 0.002	2.075 ± 0.008
PC:24-25 R					3.8			1.205 ± 0.003	2.052 ± 0.005
PC:25-26	9.6		60 ± 2						
PC:26-27	10.2				40.2	18.42 ± 0.05	38.31 ± 0.12	1.185 ± 0.002	2.081 ± 0.004
PC:28-29	11.2		75 ± 3						
PC:29-30	13.7				41.2	18.30 ± 0.05	38.20 ± 0.05	1.179 ± 0.002	2.088 ± 0.005
PC:30-31	14.3	50 ± 6		1.5 ± 0.3					
PC:31-32	14.8		73 ± 2						
PC:32-33	15.5		69 ± 2		36.5	18.64 ± 0.04	38.60 ± 0.09	1.192 ± 0.001	2.071 ± 0.002
PC:32-33 R					3.2			1.205 ± 0.001	2.052 ± 0.003
PC:35-36	17.7		55 ± 2		19.6	18.56 ± 0.04	38.29 ± 0.07	1.200 ± 0.003	2.059 ± 0.004
PC:38-39	19.9		51 ± 2		22.1	18.64 ± 0.03	38.47 ± 0.10	1.202 ± 0.004	2.062 ± 0.003
PC:39-40	20.8	40 ± 5		4 ± 0.7	25.7	18.72 ± 0.03	38.82 ± 0.06	1.194 ± 0.001	2.074 ± 0.003

[a] Mass depth expressed in g cm^{-2}, radiochemical data (^{137}Cs, ^{210}Pb, and ^{214}Pb) in mBq g^{-1}. Pb contents in μg g^{-1} (error ~10%). Pb isotopic compositions of leachates, except for residues (R) Errors: *at 66% confidence level and **at 95% confidence level.

to be in a medium (HNO$_3$) that allows the direct measurement of concentrations by ICP-MS.

Fluxes and Origin of Pb. The anthropogenic flux of Pb, $F(t)$, can be assessed as follows:

$$F(t) = (\text{ppm Pb TL} - \text{ppm Pb BC})R(t) \qquad (2)$$

where $R(t)$ is the sedimentation rate. For both sites, a peak of contamination occurred in the late 1970s (Figure 4). Afterward, the anthropogenic inputs declined likely under the implementation of environmental policies. However, at the Bay of Vidy, the Pb fluxes were at least 1 order of magnitude higher than at the center of the lake. A sharp increase is recorded when the water treatment plant of Lausanne started in 1964, because of the proximity of the sampling site to the input source. The amount of Pb (and other metals, Pardos, Personal Communication) buried at that bay is considerable and may constitute a potential hazard for biota in the bay.

The isotopic compositions of the anthropogenic component generally follow the same evolution at both sites. Obviously, as already noticed by Graney et al. (9), the anthropogenic Pb signature is less well resolved in the PC core than in BV, because of the higher contribution of the lithogenic end-member. The discrimination of both industrial and gasoline components in both cores is however complicated by the lack of details concerning the evolution of the isotopic compositions of the anthropogenic sources through the past. As previously mentioned, the ^{206}Pb/^{207}Pb signatures of the gasoline component have varied widely, at least between 1.145 in the early 1970s (35) and 1.10−1.12 at the present (34). In addition only recent data are available for the industrial sources. Nonetheless, by analogy with the neighboring countries, where the primary sources, of Pb have changed only little over the last 15−20 years (3, 42), we can reasonably assume that the Swiss leaded gasoline and industrial-derived Pb have remained steady since the early
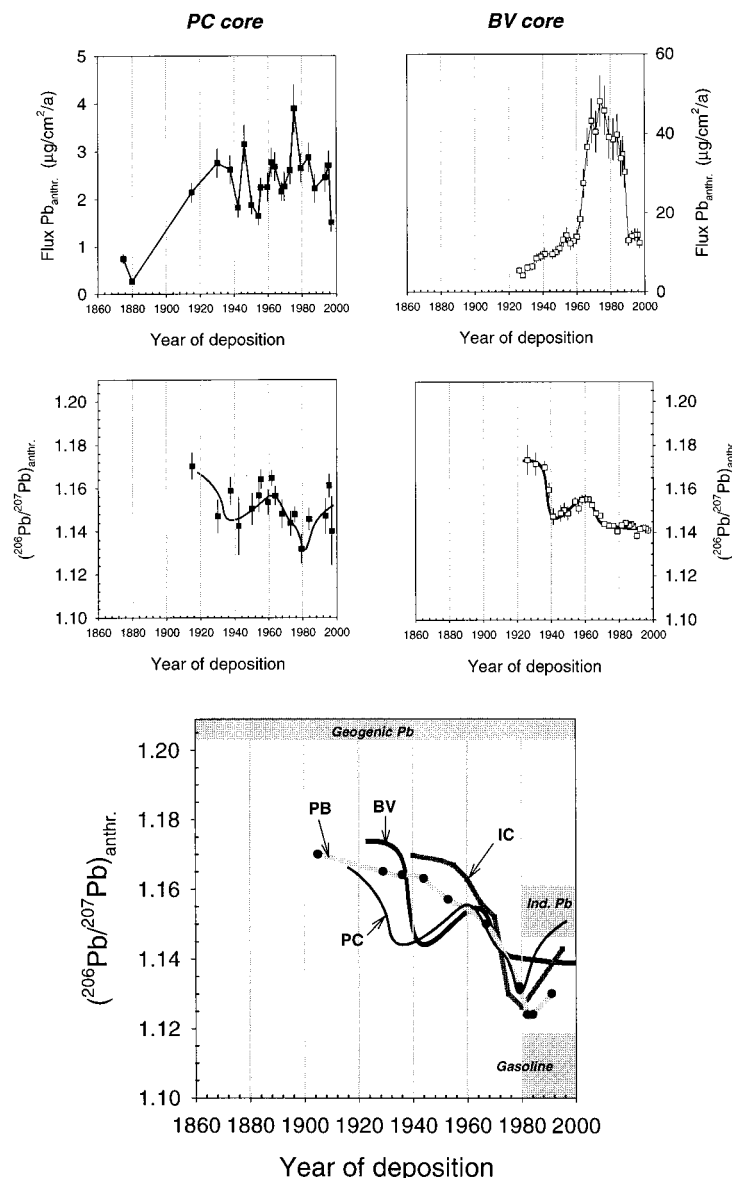
FIGURE 4. Fluxes of Pb, expressed in μg cm^{-2} a^{-1}, and ^{206}Pb/^{207}Pb ratios of the anthropogenic sources through the last century, at (■) PC site and (□) BV site. For comparative purpose, Pb isotopes recorded in an ice core at an high alpine site (IC) (*19*) and in a peat bog in the Jura Mountains (PB) (*20, 21*) are also reported.

1980s with ^{206}Pb/^{207}Pb ratios at 1.11 ± 0.01 and 1.15 ± 0.01, respectively. With such an assumption, it becomes possible to roughly assess the origin of Pb, at least over the last 20 years. At the Bay of Vidy, the Pb isotopes demonstrated a large predominance of industrial/domestic—derived Pb, with maybe a small contribution from leaded gasoline which did not exceed 10%. As a consequence, most of the Pb originated from wastewater inputs. The storm runoff, which mainly removes car-derived aerosols from roads and streets, has never played an important role. The center of the lake received industrial/domestic Pb as well, except in the early 1980s, where the relative contribution from gasoline seemed to be a little bit more important.

In the 1920s, the isotopic composition of the anthropogenic end-member was more radiogenic (^{206}Pb/^{207}Pb ~ 1.17). This corresponded to a mix of industrial emissions and coal burning. It should be remembered that, at those times, industrial Pb mainly came from the major European Pb ore deposits characterized by ^{206}Pb/^{207}Pb ratios of about 1.16—1.18 (*43, 44*). A drop in ^{206}Pb/^{207}Pb ratios occurred later in the 1930s through the 1940s. Such a change has already been noted approximately at the same period in the UK and was

explained as an increased use of imported ores and coal with lower isotope ratios, or possibly as the reduced use of relatively radiogenic coal (*17, 45*). Historical knowledge well supports such an explanation. Indeed in Switzerland, coal imports averaged 230 000 t/a during 1850—1870; that values increased to 2.7 Mt/a from 1900 to 1920, and from 1930, with the introduction of heating oil, came the gradual replacement of coal (*46*).

All these data can be compared to a few isotopic studies previously undertaken in Switzerland. Similar isotopic trends were observed in an ice core sampled in a high alpine site (*19*) and a peat bog in the Jura Mountains (*20, 21*), with however more pronounced variations (Figure 4). In the early 1980s, the relative contribution of gasoline-derived Pb was more important in ices and peat bog than at the PC site. Actually, this discrepancy can be easily explained by the fact that ice integrates only the atmospheric deposition (mainly coming from automotive and industrial exhausts), while lake sediments record both atmospheric and fluvial inputs (including domestic and industrial effluents as well). One can imagine that the Rhône river, which drains numerous industrial effluents, was one of the major sources of pollution

in Lake Geneva, at least in the zones far from the direct human contributions such as Bay of Vidy. That could explain also why a major influence of leaded gasoline was observed in Lake Zug (close to Zurich) (*10*) and not in Lake Geneva.

This study also proves that the Pb isotopic method, combined with dilute acid leaching, is efficient for identifying the anthropogenic component in relatively contaminated sediments. However its power of discrimination is limited by the establishment of a reliable and complete database describing the isotopic evolution of the main anthropogenic sources through the past. This lack of data was recognized by several authors (*3, 17, 39*), and efforts should be undertaken to rectify this situation.

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