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Modeling Lead Input and Output in Soils Using Lead Isotopic Geochemistry

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The aim of this study is to model downward migration of lead from the plow layer of an experimental site located in Versailles (about 15 km southwest of Paris, France). Since 1928, samples have been collected annually from the topsoil of three control plots maintained in bare fallow. Thirty samples from 10 different years were analyzed for their lead and scandium contents and lead isotopic compositions. The fluxes are simple because of the well-controlled experimental conditions in Versailles: only one output flux, described as a first-order differential function of the anthropogenic lead pool, was taken into account; the inputs were exclusively ascribed to atmospheric deposition. The combination of concentration and isotopic data allows the rate of migration from the plowed topsoil to the underlying horizon and, to a lesser extent, the atmospheric fluxes to be assessed. Both results are in good agreement with the sparse data available. Indeed, the post-depositional migration of lead appears negligible at the human time scale: less than 0.1% of the potentially mobile lead pool migrates downward, out of the first 25 cm of the soil, each year. Assuming future lead inputs equal to 0, at least 700 yr would be required to halve the amount of accumulated lead pollution. Such a low migration rate is compatible with the persistence of a major anthropogenic lead pool deposited before 1928. Knowledge of pollution history seems therefore to be of primary importance.

Introduction

Among heavy metals, lead is probably the most widely emitted by anthropogenic activities throughout the history of mankind. Significant atmospheric Pb pollution started in Europe from Antiquity (*1*, *2*), but the major peak of pollution occurred only recently during the 1970s due to extensive use of lead-based antiknock agents in petrol (*3*, *4*). Since Pb is recognized as toxic for most animals and plants (*5*, *6*), environmental policies in most industrialized countries over the last two decades have resulted in a significant decrease of Pb contents in the atmosphere (*3*, *7*). However, high Pb contents are still frequently reported worldwide in accumulating environments such as soils (*8*, *9*), peat bogs (*10*, *11*), and sediments (*12*, *13*). They are generally ascribed to the persistence of past contaminations originating from automotive traffic; coal ash, ore-mining, and smelting activities; agricultural inputs; waste incineration; or pollution of unknown origin. Lead is predominantly concentrated in the surface horizon and generally considered as being much less mobile than Zn, Cd, or Cu (*14*). Nevertheless, limited downward migration has frequently been demonstrated not only in contaminated soils (*8*, *15*−*17*) but also in soils affected only by diffuse atmospheric deposition (*18*). Environmental risk related to metal mobility after soil contamination has often been studied via chemical partitioning, this latter subordinating bioavailability and long-term migration. As a result, several models of metal speciation have been developed and compared to field data or laboratory experiments (*19*). They yielded important information, but sequential extractions are often criticized for poorly constraining the dissolved chemical phases (*20*). Moreover, such methods do not allow any quantification of migration rate in natural conditions, although they indicate a certain migratory ability. Another approach for assessing the release rate of metals from soils consists of lixiviation experiments operated in batch columns (*21*) or long-term studies using lysimeters in the field (*15*, *16*). Other scientists prefer the study of metal distribution in natural soil profiles or batch columns (*22*) in order to evaluate metal incorporation. Retention can then be determined by using a speciation scheme, by examining the shape of the profile in the soil, or by a combination of both. However, the approach focusing on vertical distribution in soils to estimate downward migration processes is better adapted to elements for which the input function is well-constrained. One of the most widely studied in this context is probably ^{137}Cs, which was deposited in European soils in known quantities after the Chernobyl accident. In undisturbed conditions, the concentration profiles approximately follow an exponential decline with depth, which can be described by various time-dependent diffusion models (*23*, *24*), allowing the rate of change of vertical distribution to be calculated (*25*, *26*). In the case of lead, the situation is greatly complicated, as mentioned above, by the long history of its emission into the atmosphere. Most of the time, its fluxes are not precisely known over time, and it is hazardous to calculate any mass balance or migration rate (*8*) except when assumptions are made as to the history and nature of lead inputs (*27*). Some authors have also

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TABLE 1. Pb and Sc Concentrations and Pb Isotopic Compositions of Samples Collected in Three Control Parcels (T1−T3) in 10 Different Years and Parent Material

yr of collection[a]	control parcel	Pb (μg g^{-1})	Pb$_{\text{Mean}}$ (μg g^{-1})	±	Sc (μg g^{-1})	Sc$_{\text{Mean}}$ (μg g^{-1})	±	^{206}Pb/^{207}Pb	^{206}Pb/^{207}Pb$_{\text{Mean}}$	±
1929	T1	48.5	49.1	3.9	5.7	5.6	0.5	1.1833	1.183	0.001
	T2	47.8			5.4			1.1833		
	T3	50.9			5.8			1.1826		
1934	T1	49.6	51.3	3.8	6.0	5.9	0.3	1.1828	1.183	0.001
	T2	52.6			5.7			1.1827		
	T3	51.6			5.9			1.1835		
1939	T1	54.2	55.3	2.3	5.8	5.7	0.4	1.1824	1.182	0.002
	T2	55.7			5.5			1.1814		
	T3	55.9			5.8			1.1829		
1945	T1	55.6	54.3	6.3	5.8	5.8	0.5	1.1807	1.182	0.003
	T2	51.4			5.6			1.1830		
	T3	56.0			6.0			1.1825		
1954	T1	62.3	61.5	1.7	6.0	5.9	0.9	1.1810	1.182	0.003
	T2	61.1			5.5			1.1824		
	T3	61.1			6.2			1.1832		
1963	T1	61.5	60.6	8.9	5.9	5.9	0.1	1.1816	1.181	0.003
	T2	56.6			5.9			1.1803		
	T3	63.6			5.9			1.1823		
1972	T1	69.4	68.1	3.2	5.9	5.9	0.4	1.1805	1.182	0.003
	T2	67.9			5.7			1.1815		
	T3	66.8			6.0			1.1825		
1981	T1	63.5	60.7	11.6	6.0	5.9	0.2	1.1803	1.181	0.002
	T2	55.3			5.8			1.1812		
	T3	63.3			5.9			1.1817		
1991	T1	69.4	69.0	1.2	5.9	5.7	0.4	1.1787	1.180	0.003
	T2	68.5			5.6			1.1796		
	T3	69.2			5.6			1.1808		
2000	T1	74.1	71.3	14.7	5.9	5.7	0.5	1.1783	1.179	0.002
	T2	75.2			5.5			1.1796		
	T3	64.5			5.7			1.1799		
parent material		15.8			5.6			1.2035		

[a] For each year, the concentration and isotopic average of the three parcels is given as well as the 95%.confidence interval.

proposed interesting combinations of these approaches with the use of lead isotopic geochemistry. Fundamentals of this method applied to soils are based on the isotopic difference existing between anthropogenic lead and endogenous lead derived from rocks and soils and are extensively described elsewhere (*18, 27−34*). Lead isotopic geochemistry is generally more powerful than concentration measurement to identify any minor anthropogenic component.

In the present study, we examine the fate of Pb concentrations and isotopic compositions in soils sampled annually from an experimental field managed by the French National Research Institute of Agronomy (INRA) since 1928. This experimental site, originally created for the study of long-term effects of various fertilizing agents on the quality of bare soils (*35*), provides an invaluable and unique (at least for France) set of available samples with a 70-yr topsoil library. To study the behavior of lead in soil from these samples, we took as a basis a previously published model (*36, 37*), which was developed to estimate critical loads of trace metals in soils. However, as it originally applied to a whole soil submitted to constant lead inputs, it was adapted to fit the present experimental conditions. Hence, we attempted to assess downward Pb migration and, to a lesser extent, atmospheric lead fluxes.

Setting

The site, known as "42 plots", is located in a peri-urban area next to the gardens of the Chateau of Versailles, about 15 km from Paris. The soil is an aquic Hapludalf (luvisols), developed in eolian loess deposits, typical of the Paris basin. Ten reference plots did not receive any fertilizing amendments but were maintained in bare fallow, except episodically for potato cultivation during World War II. The others were annually amended with basic slugs, ammonium phosphate, superphosphate, Moroccan rock-phosphate, farmyard manure, and calcium carbonate (*38*). All were plowed twice a year, at a mean depth of 0.25 ± 0.05 m.

Experimental Section

Sampling. From 1929 onward, about 1 kg representing the mixed and plowed 0−0.25-m A horizon was collected annually from each reference plot. The soil samples were dried, crushed, and stored in hermetically closed glass bottles. Because of the exceptional importance of the "42 plots" device for long-term studies, no dig was operated in underlying soils, which means that no such samples were available in the soil library. However, in an adjacent field (200 m away), at more than 0.80 m depth, we collected a sample supposed to be representative of the undisturbed C horizon and, hence, of pristine parent material.

Analysis. Ten years were selected among the 70-yr archive: 1929, 1934, 1939, 1945, 1954, 1963, 1972, 1981, 1991, and 2000. For each year, three samples from three different reference plots were analyzed for their Pb and Sc contents and Pb isotopic compositions (Table 1). Chemical preparation followed the procedure AFNOR NF X31-151 (*39*), which consists of ashing 250 mg of powdered samples at 450 °C for 3 h and total acid dissolution by Merck Suprapur and concentrated HF, $HClO_4$, and HNO_3. Pb concentrations were analyzed by inductively coupled plasma-mass spectrometer (ICP-MS) (relative standard deviation, rsd, $<5\%$), while Sc contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (rsd $< 2\%$). For isotopic measurements, lead contained in an aliquot of the above-mentioned solution was purified twice using AG1X8 (Bio-Rad) anion-exchange resin (*18, 40*). Pb solution was dried down with 10 μL of 0.05 M H_3PO_4 and then loaded on a degassed Re single filament. The whole procedure was performed in a clean room. Lead isotopic compositions were measured on a Finnigan MAT 261 thermoionization-mass spectrometer (TIMS). Results were corrected for mass fractionation by systematic NIST 981 measurements, yielding a value of about 0.14% per atomic mass unit. Blanks were systematically checked and were always found negligible in relation to the amount of material analyzed.

We used scandium as a conservative element because (i) it is not of any significant anthropogenic origin and (ii) it is hosted by the most refractory minerals (*41*). Endogenous lead contribution in soil samples ($\mathrm{Pb_{end}}$) was estimated following the conventional equation:

$$\mathrm{Pb_{end}} = \mathrm{Sc_{bulk}}\left(\frac{\mathrm{Pb}}{\mathrm{Sc}}\right)_{\text{parent material}} \tag{1}$$

where $\mathrm{Sc_{bulk}}$ represents Sc sample concentration and $(\mathrm{Pb/Sc})_{\text{parent material}}$ is the ratio of parent material (*18, 41, 42*). Given that the majority of exogenous lead derives from human activity, anthropogenic lead ($\mathrm{Pb_{anthr}}$) was then obtained by subtracting endogenous contribution ($\mathrm{Pb_{end}}$) from measured total Pb concentration ($\mathrm{Pb_{bulk}}$):

$$\mathrm{Pb}_{\mathrm{anth}r} = \mathrm{Pb_{bulk}} - \mathrm{Pb_{end}} \tag{2}$$

Model. A first natural approach to treat these results would have consisted in considering only one input function, which would have corresponded to atmospheric deposition, and no lead migration from topsoil; this element being viewed as lowly mobile. From the available 70-yr collection of topsoils, it would be tempting to reconstruct the history of atmospheric lead fluxes and hence the evolution of isotopic compositions of anthropogenic deposition over time. However, such a reconstruction yields either uncertain or simply aberrant values for both fluxes and isotopic signatures (see Supporting Information for more details). Anthropogenic lead deposited between two successive samples is very low in comparison with the pool already accumulated so that the propagation of error is huge. In addition to which, there is relatively high dispersion of field data from the three control parcels. The present soil library cannot be treated in such a way, unlike sedimentary or peat archives which are time-resolved. Nonetheless, a previous model elaborated by Pačes to assess critical loads of trace metals in soils can be adapted to fulfill the purpose in view (*36, 37*). In this model, soils were seen as black boxes receiving metal fluxes from atmosphere (F_{atm}), agriculture (F_{agr}), and bedrock weathering (F_{wea}), whereas outputs were considered to be biological uptakes (F_{up}) and runoff (F_{run}). With P, the bioavailable pool, a mass balance equation was formulated by

$$\mathrm{d}P/\mathrm{d}t = F_{\mathrm{atm}} + F_{\mathrm{agr}} + F_{\mathrm{wea}} - F_{\mathrm{up}} - F_{\mathrm{run}} \tag{3}$$

Annual input ($F = F_{\mathrm{atm}} + F_{\mathrm{agr}} + F_{\mathrm{wea}}$) was assumed constant in time, whereas outputs were supposed to be proportional (k, positive factor) to the biologically available pool P at time t, $P(t)$:

$$\frac{\mathrm{d}P}{\mathrm{d}t}(t) = F - k\cdot P(t) \tag{4}$$

In the Pačes model, k was a constant (expressed as yr^{-1}), which corresponds to a coefficient of annual lead loss from the whole soil (*36, 37*). By integrating from an initial pool P_0 at t_0, this became

$$P(t) = \frac{F}{k} - \frac{F - k\cdot P_0}{k}\mathrm{e}^{-k(t-t_0)} \tag{5}$$

Pačes determined the bioavailable pool using chemical extraction applied to soils. The k factor and local fluxes used to run the model came from the literature. Future evolution of concentrations was calculated first. The moment at which critical concentrations (established by ecotoxicological studies) were reached enabled critical time to be forecast.

In the present study, due to the information from the Versailles site, we are able to check the validity of this first-order differential model by confronting field values with those predicted by modeling. Adding lead isotopic geochemistry may also produce a better understanding of how lead entered the soil system and how it has migrated through underlying horizons. Interestingly, experimental conditions at the Versailles device allow simplification with respect to the original model, which means that a new degree of complexity can be introduced: the variability of input fluxes. The modifications performed to match our experimental conditions are listed below:

(i) The black box now corresponds to the plowed mixed 0−0.25-m layer instead of the whole soil of the Pačes model.

(ii) The fluxes related to agriculture are simplified because no amendments were operated ($F_{\mathrm{agr}} = 0$) and because there was no harvest ($F_{\mathrm{up}} = 0$).

(iii) Bedrock weathering does not measurably occur during the considered time scale ($F_{\mathrm{wea}} = 0$). This assumption will be discussed later.

(iv) Lateral runoff can reasonably be ignored because plot slope is negligible ($F_{\mathrm{run}} = 0$). Consequently, only one unique output flux is taken into account. It corresponds to downward transfer by lixiviation from the 0−0.25-m layer to the underlying horizons (F_{out}).

(v) It is well-known that past atmospheric lead deposition varied widely during the last century (ref *4* and references therein). Therefore, we do not consider atmospheric lead fluxes (F_{in}) as constant over the period of collection.

(vi) If the above assumptions are verified, in particular the insignificant release of lead by minerals over a 70-yr time scale, the only potentially mobile pool must originate from anthropogenic atmospheric deposition (P_{anthr}). Hence, no further consideration will be given to the biologically available lead pool of the Pačes model, which is here replaced by the anthropogenic pool for computation.

To take into account the fluctuation of input fluxes over time, a natural approach would consist in generalizing the Pačes model directly:

$$\frac{\mathrm{d}P_{\mathrm{anthr}}}{\mathrm{d}t}(t) = F_{\mathrm{in}}(t) - F_{\mathrm{out}}(t) \tag{6}$$

$$F_{\mathrm{out}}(t) = k\cdot P_{\mathrm{anthr}}(t) \tag{7}$$

$$\frac{\mathrm{d}P_{\mathrm{anthr}}}{\mathrm{d}t}(t) + k\cdot P_{\mathrm{anthr}}(t) = F_{\mathrm{in}}(t),\ t \in [1929, 2000] \tag{8}$$

with k now corresponding to the annual lead losses from the 0−0.25-m horizon (expressed as yr^{-1}). As we shall see later, introducing isotopic parameters will decisively improve the efficiency of the model. One of the major drawbacks of the aforementioned equation is that it ignores isotopic variations of the anthropogenic component through time, although it is well-known that such isotopic signatures varied widely during the last century depending on the primary origin of the metal (the fundamentals of these variations are explained elsewhere) (*7, 43−45*). As a consequence, each annual input must be examined individually regarding its pool and isotopic composition (Figure 1).

Modeling Total Lead Concentrations. For each year i, let $P^{i}_{\mathrm{anthr}}(t)$ denote the anthropogenic lead pool deposited at year i per surface unit, observed at time t (Figure 1). If F^{i}_{in} is the anthropogenic flux of year i, the Pačes model states that

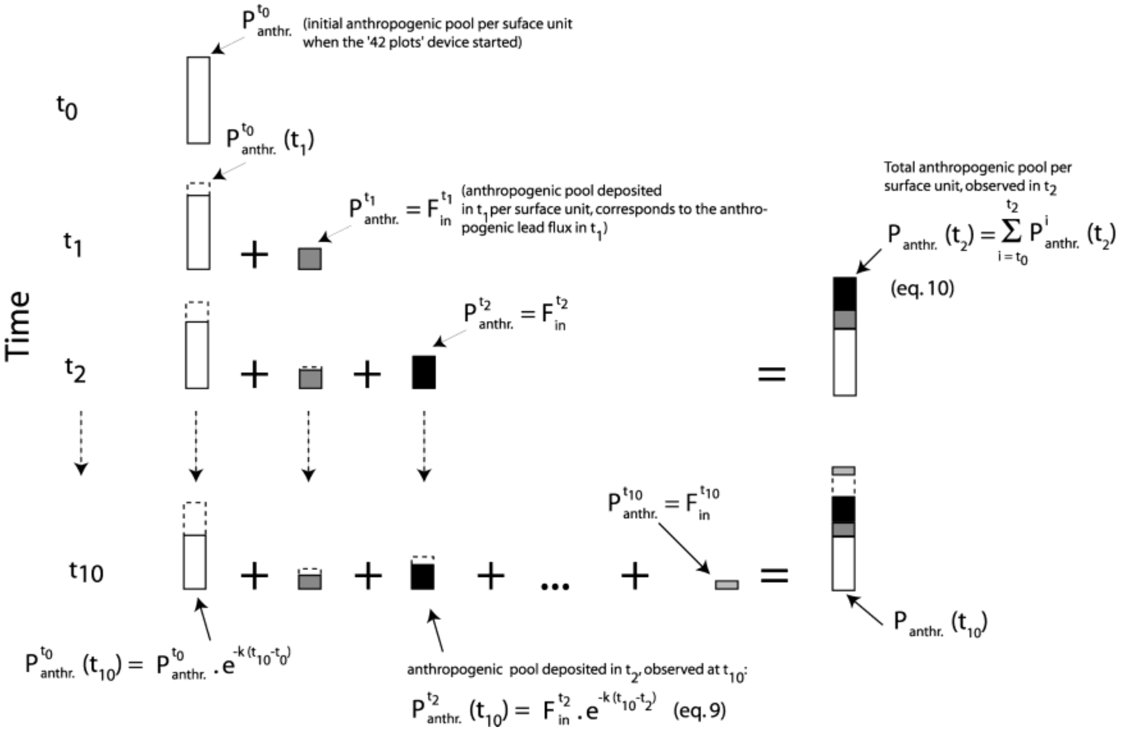

FIGURE 1. Scheme of the model. Each anthropogenic pool is represented by a gray tone, which symbolizes its own isotopic signature.

P^i_{anthr} evolves according to the following differential equation:

$$\frac{\mathrm{d}P^i_{\mathrm{anthr}}(t)}{\mathrm{d}t} + k\cdot P^i_{\mathrm{anthr}}(t) = 0, \text{ for all } t \geq i$$

$$P^i_{\mathrm{anthr}}(i) = F^i_{\mathrm{in}}$$

$$P^i_{\mathrm{anthr}}(t) = 0 \text{ if } t < i$$

A straightforward integration gives this:

$$P^i_{\mathrm{anthr}}(t) = F^i_{\mathrm{in}} \mathrm{e}^{-k(t-i)}, \text{ for all } t \geq i \tag{9}$$

At year t, the total pool, $P_{\mathrm{anthr}}(t)$, is the sum of all remaining annual contributions:

$$P_{\mathrm{anthr}}(t) = \sum_{i=t_0}^{t} P^i_{\mathrm{anthr}}(t) \tag{10}$$

where t_0 is the first sampling year (1929 in our case); $P^{t_0}_{\mathrm{anthr}}$ being the initial anthropogenic lead pool.

Instead of expressing this equation in terms of pool, it can be reformulated in terms of concentration of potentially mobile lead, $\mathrm{Pb}_{\mathrm{anthr}}(t)$:

$$\mathrm{Pb}_{\mathrm{anthr}}(t) = \frac{P_{\mathrm{anthr}}(t)}{h\cdot d_{\mathrm{A}}} \tag{11}$$

with h as thickness of plowed horizon and d_{A} as bulk density. Finally, the total lead concentration observed at year t becomes

$$\mathrm{Pb}_{\mathrm{bulk}}(t) = \mathrm{Pb}_{\mathrm{anthr}}(t) + \mathrm{Pb}_{\mathrm{end}} \tag{12}$$

Modeling Lead Isotopic Compositions. Considering a conventional mixing model (*46*), the ^{206}Pb/^{207}Pb ratio of the sample theoretically becomes

$$\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_{\mathrm{bulk}}(t) \approx \frac{1}{\mathrm{Pb}_{\mathrm{bulk}}(t)}\left[\mathrm{Pb}_{\mathrm{end}}\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)_{\mathrm{end}} + \sum_{i=t_0}^{t}\left(\mathrm{Pb}^i_{\mathrm{anthr}}(t)\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}}\right)^i_{\mathrm{anthr}}\right)\right] \tag{13}$$

where $(^{206}\mathrm{Pb}/^{207}\mathrm{Pb})_{\mathrm{bulk}}(t)$, $(^{206}\mathrm{Pb}/^{207}\mathrm{Pb})^i_{\mathrm{anthr}}$, and $(^{206}\mathrm{Pb}/^{207}\mathrm{Pb})_{\mathrm{end}}$ are the isotopic compositions of bulk soil collected in year t, anthropogenic lead deposition in year i, and endogenous lead, respectively. To sum up, the present model basically aims to calculate theoretical $\mathrm{Pb}_{\mathrm{bulk}}(t)$ and $(^{206}\mathrm{Pb}/^{207}\mathrm{Pb})_{\mathrm{bulk}}(t)$ and to compare them to that measured in the field in order to assess the value of the k factor.

Results and Discussion

Sample Integrity. Little information is available about sampling and handling procedures in the past because different workers were involved in this long-term experiment. It is noteworthy that there was no environmental objective when monitoring started. Consequently, despite precautions taken by successive technicians and researchers, potential contamination may have occurred throughout the entire process from sampling to storage. Table 1 and Figure 2a,b report mean lead concentrations and lead isotopic composition of the three reference plots. Lead contents increase from about 49 to 71 μg g^{-1} from 1929 to 2000; whereas ^{206}Pb/^{207}Pb ratios decrease slightly from 1.183 to 1.179. Such an isotopic shift is much lower than that observed between parent material ($^{206}\mathrm{Pb}/^{207}\mathrm{Pb} = 1.2035$) and the first sample of the set (1929: $^{206}\mathrm{Pb}/^{207}\mathrm{Pb} = 1.183$). Similarly, there is a larger difference in terms of concentrations between parent material and the 1929 sample than over the last 70 yr. The results are coherent and the absence of any sudden shift or disruption strongly favors sample integrity (cf. Figure 2).

Potentially Mobile Lead Pool. As indicated by Figure 2c, scandium concentrations do not significantly vary in time (Table 1). The mean scandium concentration of the 30 samples composing the set is 5.7 $\pm$ 0.1 μg g^{-1}, which is the

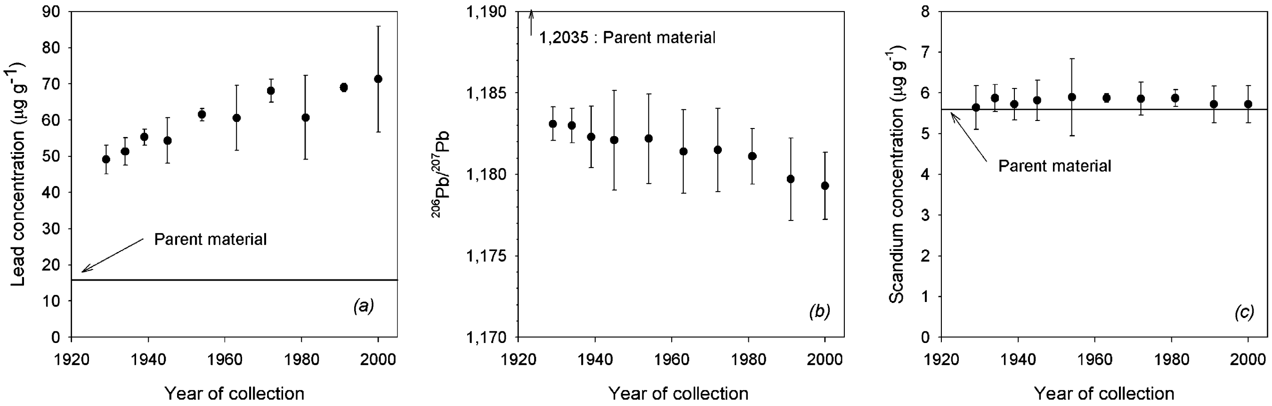

FIGURE 2. Lead concentrations (a), ^{206}Pb/^{207}Pb ratios (b), and scandium contents (c) vs year of collection. The values correspond to the mean of the three control parcels, and the error bar is the confidence interval at a level of 95%.

same as that of parent material (5.6 μg g^{-1}), suggesting the absence of significant selective weathering of minerals at least at the considered time scale. Even if some natural lead also enters the soil system by dust deposition, atmospheric lead input is widely dominated by anthropogenic (*47*, *48*) sources as demonstrated by the high enrichment factors reported even in remote areas (*2*). Thus, the potentially mobile lead pool almost exclusively derives from anthropogenic inputs and can be attributed to atmospheric input. This is in good agreement with other works that have demonstrated that petrol lead in roadside soils is associated with the most labile fractions of the soil, whereas natural lead is mainly hosted in the most stable minerals (*27*, *29*, *30*).

Atmospheric Fluxes. Unfortunately, no continuous values of atmospheric fluxes since 1929 (F^i_{in}) are available around Paris, although such a database would be required to run the model (cf. eq 9, Figure 1). Nonetheless, from knowledge of pollution history, it is possible to propose a curve ($t \rightarrow f(t)$) describing the shape of the evolution of anthropogenic atmospheric lead fluxes in the Paris region. Hence, the specific fluxes for Versailles can be estimated by multiplying this curve by an a factor:

$$F^i_{\text{in}} = a \cdot f(i) \qquad (14)$$

From the 1960s to the late 1980s, anthropogenic emissions were probably dominated by gasoline-derived lead, as there were no heavy industrial point sources close to the INRA site. There is a strong correlation between Pb consumption for gasoline in the EU (white squares in Figure 3) and atmospheric lead content in Paris during the period for which both statistics exist: the linear correlation of data from 1972 to 1993 is featured by $R^2 = 0.9312$ for the Champs Elysées (black circles in Figure 3) and $R^2 = 0.9381$ for Avenue Victor Basch (not shown here) (Paris Police Central Laboratory, personal communication). These trends are comparable to others previously published, such as lead concentrations in the blood of adults in Germany (black squares) (*4*), total lead emission from traffic and industry in Switzerland (white triangles) (*49*), and lead deposition rate at a peat bog in Denmark (white circles) (*50*); the latter two allowing the extension to the 1920s to be performed. At this period, lead from industrial activities and coal combustion, used as heat sources, were the major contributors. Figure 3 was thus drawn by combining all these data. Although rough, the evolution domain of anthropogenic lead fluxes so determined is certainly more realistic than assuming constant lead fluxes over time. The error estimate, shown by dashed curves in Figure 3, will be integrated into further calculations in order to evaluate the uncertainties of the modeled results.

Mean annual precipitations within each sampling interval were also checked because rainfall intensity plays an important role in the deposition and behavior of metals in soils (*28*). The variations within each sampling interval do not exceed ± 14%, so that it is not necessary to take the rainfall parameter into account.

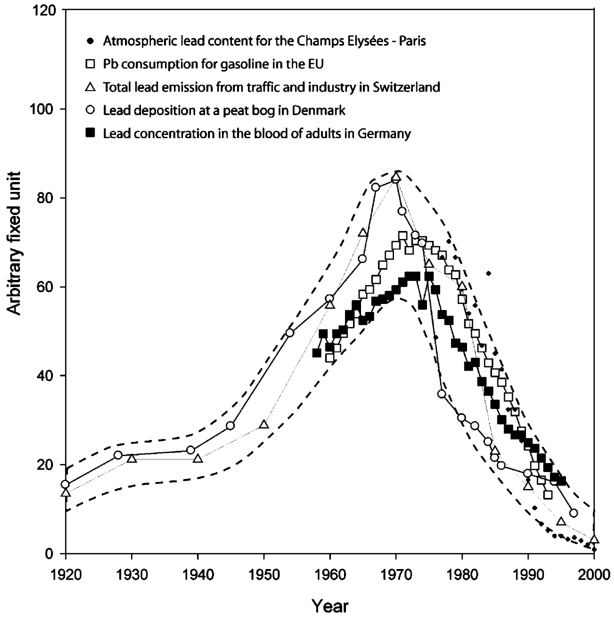

FIGURE 3. Composite curve and uncertainties (see text for construction and references) used as a surrogate of lead input fluxes at the INRA site from 1920 to 2000, within a factor *a*. The *y*-axis unit was arbitrarily fixed.

Isotopic Compositions of Anthropogenic Lead Deposition. The evolution of anthropogenic lead isotopic ratios is only partially known in France, unlike the U.K. where studies have been performed on herbage samples and sphagnum mosses collected since the mid-19th century (*51*, *52*). Here, we have attempted to overcome this by compiling and combining previously published isotopic data obtained from both urban and rural areas. In 1966, ^{206}Pb/^{207}Pb ratio of French gasoline, the dominant source of lead in the environment at that time, was about 1.162–1.163 (*53*) (cf. Figure 4). Later, in the 1980s, the lead added as antiknock compound was much less radiogenic because of the increasing use of metal from old and remote ore deposits, such as those of Australia, so that airborne particulate matter collected in Paris and Montpellier gave low ^{206}Pb/^{207}Pb ratios of 1.09–1.11 (*43*–*45*). During the 1990s, there was a turning point in the ^{206}Pb/^{207}Pb ratios measured in the atmosphere of major French urban centers, which tended to increase, even close to highways (*44*, *45*, *54*, *55*). The gasoline end-member was still dominant, but due to the progressive use of unleaded gasoline

TABLE 2. Summary of Known Data, Initial Values, and Unknowns Used to Run the Model

parameter	name	value(s)
	Known (Measured or Calculated)	
plowed depth	h	0.25 ± 0.05 m, known
bulk density	d_a	1.25 Mg m^{-3}, determined in field
endogenous Pb concn	Pb_{end}	15.8 μg g^{-1}, measured[a]
bulk Pb concn in year t	$Pb_{bulk}(t)$	measured (cf. Table 1)
shape of temporal evolution of anthropogenic inputs	$f(i)$	function rebuilt for present study in arbitrary fixed unit (cf. Figure 3)
isotopic composition of endogenous Pb	$\left(\frac{^{206}Pb}{^{207}Pb}\right)_{end}$	1.2035, measured (corresponds to C horizon of an adjacent field)
anthropogenic Pb isotopic composition deposited in year i	$\left(\frac{^{206}Pb}{^{207}Pb}\right)^{i}_{anthr}$	function rebuilt for the present study (cf. Figure 4)
isotopic composition of bulk soils in year t	$\left(\frac{^{206}Pb}{^{207}Pb}\right)_{bulk}(t)$	measured (cf. Table 1)
	Initial Values	
initial anthropogenic Pb concentration	Pb^{1929}_{anthr}	35 ± 2 μg g^{-1}, calculated (using eq 2; data from Table 1)
initial anthropogenic Pb isotopic composition	$\left(\frac{^{206}Pb}{^{207}Pb}\right)^{1929}_{anthr}$	1.175 ± 0.002, calculated (using eq 13; data from Table 1)
	Unknown	
coeff applied to $f(i)$ to obtain annual fluxes	a	sought value (cf. eq 14)
coeff of annual loss from 0−25-cm plow horizon	k	sought value (cf. eq 9)

[a] Corresponds to C horizon of an adjacent field; supposed constant through time, as Sc concentrations in soils do not vary in time.

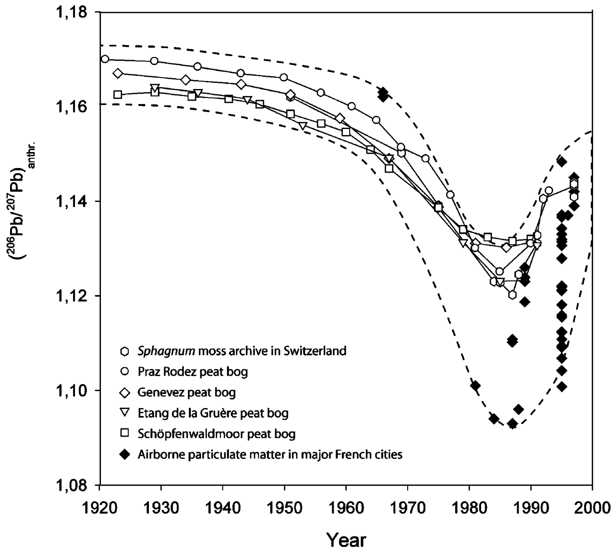

FIGURE 4. ^{206}Pb/^{207}Pb ratios and uncertainties of anthropogenic deposition from 1920 to 2000 (cf. text for details of construction and references).

after more strict environmental policies, lead derived from other more radiogenic sources (natural and industrial) started to rise in relative terms (*44*). Although sparse and limited to the mid-1960s, this whole set of isotopic compositions gives an insight into the evolution of lead isotopic compositions in areas highly affected by automotive traffic. On the other hand, the ^{206}Pb/^{207}Pb ratios of lead recorded in Swiss peat bogs (*56*) and *Sphagnum* moss archives (*57*) constantly decreased from the 20s (^{206}Pb/^{207}Pb ∼ 1.160−1.170) to the 1960s (^{206}Pb/^{207}Pb ∼ 1.155−1.165) because of the progressive replacement of coal by oil after the 20s (Figure 4). Later during the 1960s−1980s, the incorporation of nonradiogenic Australian lead in gasoline also led to a pronounced decline of ^{206}Pb/^{207}Pb ratios, while a return to more radiogenic values was detected following the introduction on the market of unleaded gasoline in 1985 (*56*, *57*). At sites that correspond to rural areas, the proportion of gasoline-derived lead has never reached that observed in major French cites, so that lead isotopic compositions have always been significantly more radiogenic. The Versailles site is located in a peri-urban area. We can therefore reasonably assume that the ^{206}Pb/^{207}Pb ratios of anthropogenic lead accumulated in these soils were comprised between those measured in rural and urban areas. The uncertainty of ^{206}Pb/^{207}Pb signatures, as represented in Figure 4 between the dashed curves, will be taken into account when running the model.

Model Testing Procedure. The model was computed using Matlab 5.02 software with data summarized in Table 2, carefully transformed in order to make the units compatible. For each pair (a; k), with $a \in [0; 2]$ and $k \in [0; 10^{-1}]$, theoretical lead concentrations and lead isotopic compositions were calculated through time. However, the input data [(i) the composite curve used as a surrogate of lead input fluxes (Figure 3), (ii) the evolution of ^{206}Pb/^{207}Pb ratios of anthropogenic deposition over time (Figure 4), (iii) the depth of the plowed horizon, (iv) initial anthropogenic lead concentrations, and (v) initial isotopic compositions (cf Table 2)] present significant uncertainties. The model was therefore computed 1000 times using random sampling within the estimate range of each parameter. The first two are supposed to be uniformly distributed and the others normally distributed. Hence 1000 theoretical output curves of lead concentrations and lead isotopic compositions were obtained for each pair (a; k). Mean curves and associated envelopes, corresponding to a confidence level of 95%, were also calculated. The error appears to be mainly propagated by the depth of the plowed horizon and by the values of the initial parameters: Pb^{1929}_{anthr} and $(^{206}Pb/^{207}Pb)^{1929}_{anthr}$. This is probably due to the fact that (i) more than half the anthropogenic lead present nowadays in the topsoil was deposited before the start of the experiment in 1928 and (ii) the depth h of plowing acts strongly on the lead pool considered in the model. These theoretical flux and isotopic curves were then compared to those observed in the field in order to define a domain of compatible (a; k) values. The quality of the adjustment was evaluated by calculating fit errors for concentrations (FE_{conc}) and isotopic compositions (FE_{ic}) as follows:

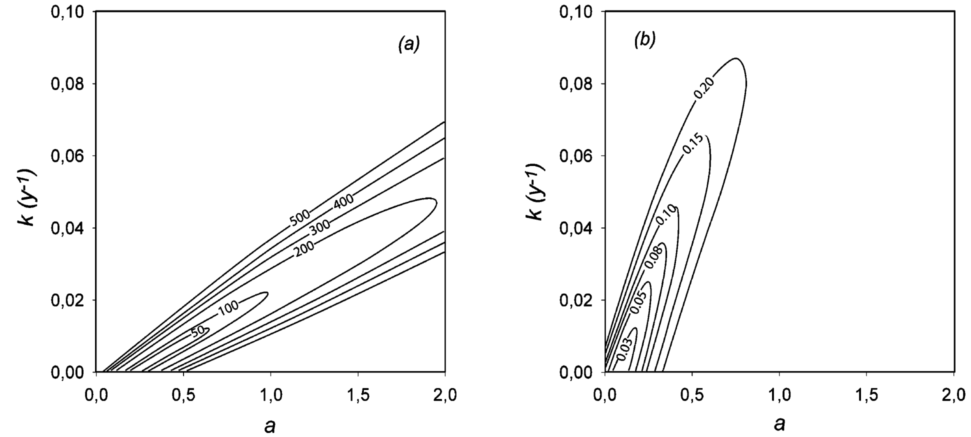

FIGURE 5. Fit errors for lead concentrations (a) and lead isotopic compositions (b) reported on diagrams *k* versus *a* using a gray-scale code. The lower the value, the better the concordance between modeled and field data.

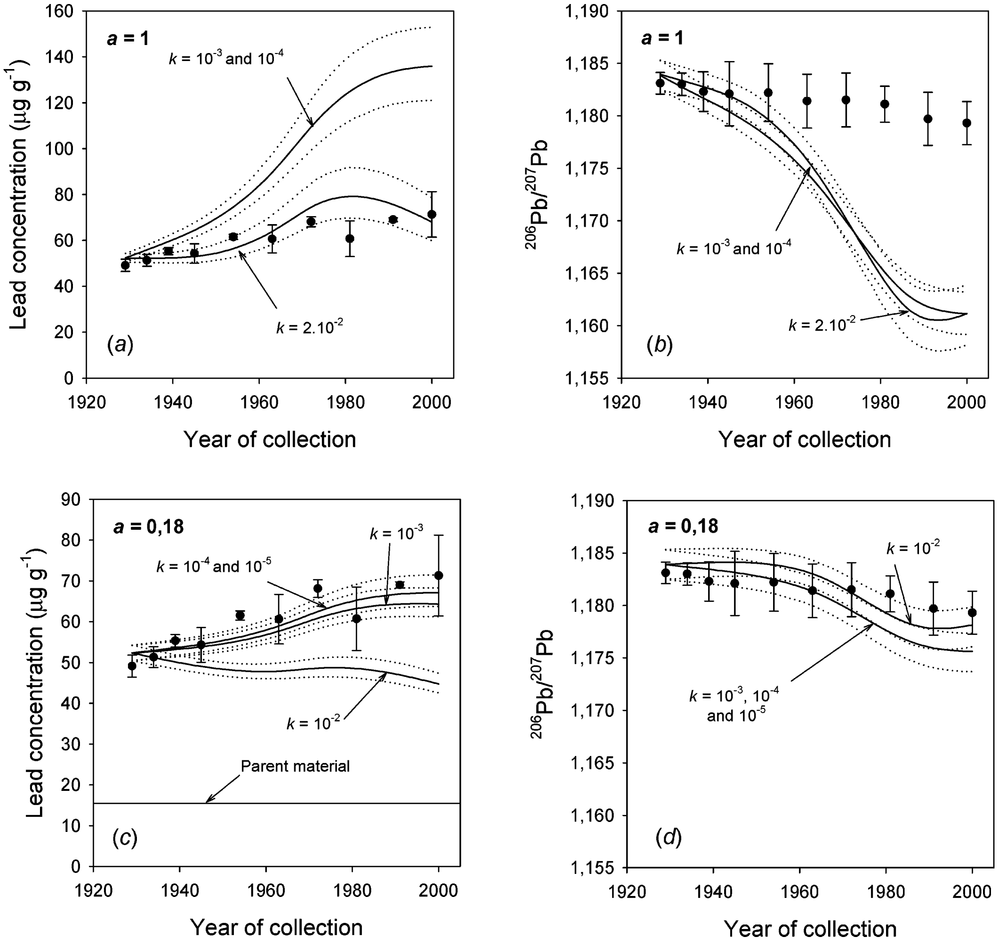

FIGURE 6. Simulation of evolution of lead concentrations and lead isotopic compositions vs time (solid line). For *a* = 1 and *k* varying: 2 × 10^{-2}, 10^{-3}, and 10^{-4} (panels a and b, respectively); and for *a* = 0.18 and *k* varying: 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} (panels c and d, respectively). The envelopes (dotted lines) represent the propagation of input parameter errors and correspond to a confidence level of 95%. For purposes of comparison, the field data are reported as bold circles with error bars corresponding to a confidence level of 95%.

$$\mathrm{FE}_{\mathrm{conc}} = \sum_{i=0}^{9} w_i [\mathrm{Pb}_{\mathrm{model}}(t_i) - \mathrm{Pb}_{\mathrm{measured}}(t_i)]^2 \quad (15)$$

$$\mathrm{FE}_{\mathrm{ic}} = \sum_{i=0}^{9} z_i \left[\left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}} \right)_{\mathrm{model}} (t_i) - \left(\frac{^{206}\mathrm{Pb}}{^{207}\mathrm{Pb}} \right)_{\mathrm{measured}} (t_i) \right]^2 \quad (16)$$

where t_0, ..., t_9 correspond to times at which samples have been collected. Results from the three different reference plots were sometimes scattered (cf. Table 1) and produce uncertainties in the concentration and isotopic composition averages. As mentioned above, errors are also associated with the modeled curves, so that weights inversely proportional to the square root of the sum of the variances of both field and modeled data were used in eqs 15 and 16: w_i and z_i, respectively. Fit errors are plotted in Figure 5a,b allowing the best pair values within $a \in [0; 2]$ and $k \in [0; 10^{-1}]$ to be distinguished, despite the introduction and propagation of uncertainties in the parameters feeding the model. Figure 5a shows a linear-shaped domain, indicating a good correspondence between simulation and field data. If a increases, k has to increase simultaneously; in other words, high inputs have to be compensated by high losses. However, the use of lead isotopic compositions allows the range of possible pairs (a; k) to be restrained (Figure 5b).

Computing for $a = 1$. This example is presented in Figure 6a,b, where $a = 1$ and k varies between 10^{-4} and 2×10^{-2}. There is a k value around 2×10^{-2} for which the model matches measured concentrations well (Figure 6a), but no k will produce predicted isotopic compositions comparable with those measured, in particular for the 1950−2000 period (Figure 6b). If fluxes had been that high, isotopic compositions would have been much less radiogenic than those measured because of the wide use of nonradiogenic lead as antiknock compounds from the 1980s (Figure 4). As a result, $a = 1$ is not realistic.

Computing for $a = 0.18$. There is a range of [a; k] values in which the simulation produces approximately the expected concentration and isotopic results: $a \in [0.15; 0.2]$ for $k < 10^{-3}$. Figure 6c,d presents the computation with $a = 0.18$ where k varies from 10^{-5} to 10^{-2}. A minor divergence is still observed for lead isotopic compositions from the 1980s. A slight underestimation of ^{206}Pb/^{207}Pb ratios of the anthropogenic end-member may have occurred. In that case, the relative contribution of gasoline may have been overestimated in comparison to an industrial component, generally found to be more radiogenic (*32*, *58*).

Implications for Atmospheric Fluxes and Behavior of Lead in Soil. It is important to recall that the main purpose of this study was not to reconstruct lead atmospheric flux history. However, our flux values are in relatively good agreement with the rare data available in the literature. For 1991, we calculate an atmospheric lead flux of $2.9 \pm 1.4\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ (data for $a = 0.18$), which is compatible with the value of $3.6\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ measured around Paris the same year (*59*). Likewise, the model produces a flux of $1.9 \pm 1.2\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ for 1994 (data for $a = 0.18$), comparable to $2.31\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ measured at Rueil-Malmaison, about 10 km from Versailles (*60*). Finally, atmospheric lead deposition flux, determined directly at the INRA site in 2002, was $0.22\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ (S. Azimi, unpublished data), while the model yields $0.45 \pm 0.44\ \mu\text{g cm}^{-2}\ \text{yr}^{-1}$ for 2000.

Although the value of the k factor is valid only for the Versailles site, such Hapludalf soils (luvisols) are frequent throughout Western Europe. These soils were continuously disturbed and homogenized in the 0−0.25-m horizon because they were plowed twice a year. Moreover, as they were maintained in bare fallow for more than 70 yr, the plowed layers today show remarkably low quantities of organic compounds (approximately $6\ \mu\text{g g}^{-1}$) (*61*); organic matter being generally supposed to favor lead retention in topsoil. All these conditions should have promoted the mobility of lead, in part because of greater leaching from a more exposed surface area in turned soil, so that the post-depositional migration rates calculated here are probably overestimated in comparison with natural unaltered soil systems. Even if the model does not enable the k factor to be calculated more precisely, a value of $k < 10^{-3}$ corresponds to very low mobility: in other words, more than 99.9% of the potentially mobile lead pool remains in the topsoil each year Similar values for lead have been reported using independent approaches for other soils: $k = 3.6 \times 10^{-4}$ (*37*). Hence, the evolution of the lead stock can easily be simulated with a decay equation for future lead inputs assumed equal to 0: more than 700 yr would be required to halve the anthropogenic pool. It might also be interesting to apply the present model to the data obtained from the experimental farm of Rothamsted (U.K.), where a similar experimental device, but under pasture land, has been conducted since 1860 and where lead concentration and isotopic signatures are available (*51*). This model could also be adapted to the study of ^{137}Cs migration for which flux history is well-constrained, with a worldwide peak of deposition in 1963/1964 because of nuclear weapon tests in the atmosphere and the Chernobyl accident in 1986.

Our field results demonstrate that the major part of the anthropogenic lead pool was integrated into the soil before 1928, which is long before the pollution peak of the mid-1970s. This historical accumulation of lead also strongly underlines its limited downward migration. The question of pollution history seems therefore to be of primary importance. Many recent studies focusing on sedimentary records, ice cores, or peat bogs have pointed out early metallurgical activities that strongly impacted the global environment (*1*, *2*). In all likelihood, a significant fraction of exogenous lead detected nowadays in soils was integrated before the 20th century and probably well before the Industrial Revolution, as demonstrated in certain sites (*9*).

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Supporting Information Available

Another approach to the reconstruction of the history of lead fluxes and isotopic compositions of the anthropogenic end-member through time, assuming $k = 0$. This material is available free of charge via the Internet at http://pubs.acs.org.

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