Modeling lead input and output in soils by using lead isotopic geochemistry

EGS – AGU – EUG Joint Assembly, Nice, France, April 2003

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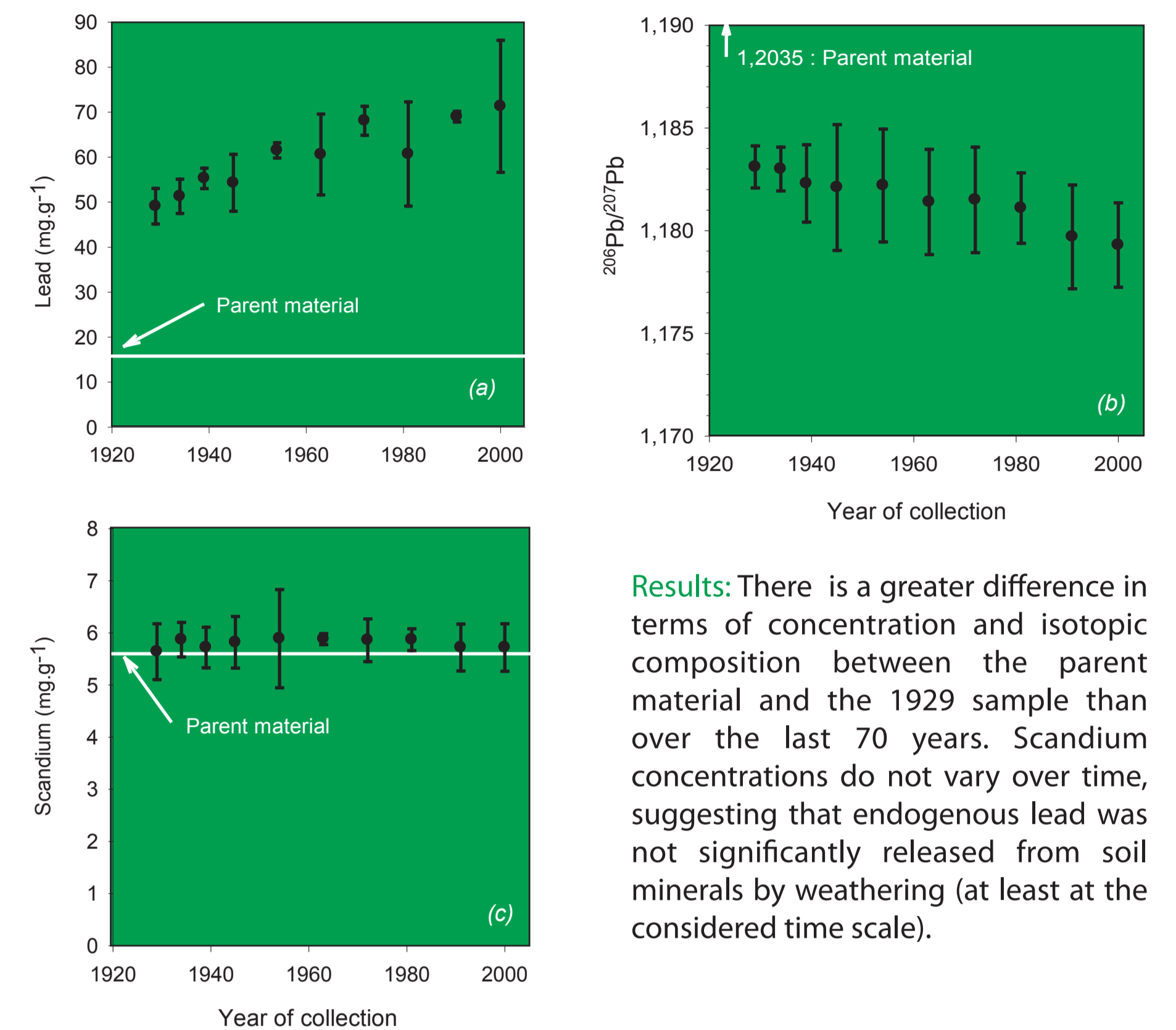F-78026 Versailles Cedex,
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Introduction: High Pb contents are still frequently reported worldwide in accumulating environments such as soils, peat bogs and sediments. In soils, they are generally ascribed to the persistence of past lead contamination from various anthropogenic activities. Lead, generally concentrated in the surface horizon, is considered as being much less mobile than Zn, Cd or Cu. Nevertheless, limited downward migration has frequently been demonstrated in contaminated soils, but also in soils affected only by diffuse atmospheric deposition.

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) and managed by the French National Research Institute of Agronomy (INRA) since 1928 (Fig. 1). Our basis is a model previously published by Paces (1998, 1999) [1,2].

Fig. 1: The INRA experimental field

Settings: From 1929 onwards, about one kilogram representing the first 0.25 m plowed A-horizon was collected annually from each reference plot. Ten years were selected among the 70-year 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 (ICP-MS) and Sc (INAA) contents, and Pb isotopic compositions (ICP-MS)

Results: There is a greater difference in terms of concentration and isotopic composition between the parent material and the 1929 sample than over the last 70 years. Scandium concentrations do not vary over time, suggesting that endogenous lead was not significantly released from soil minerals by weathering (at least at the considered time scale).

Fig. 2: Evolution of $^{206}Pb/^{207}Pb$ ratios, lead and scandium contents through time
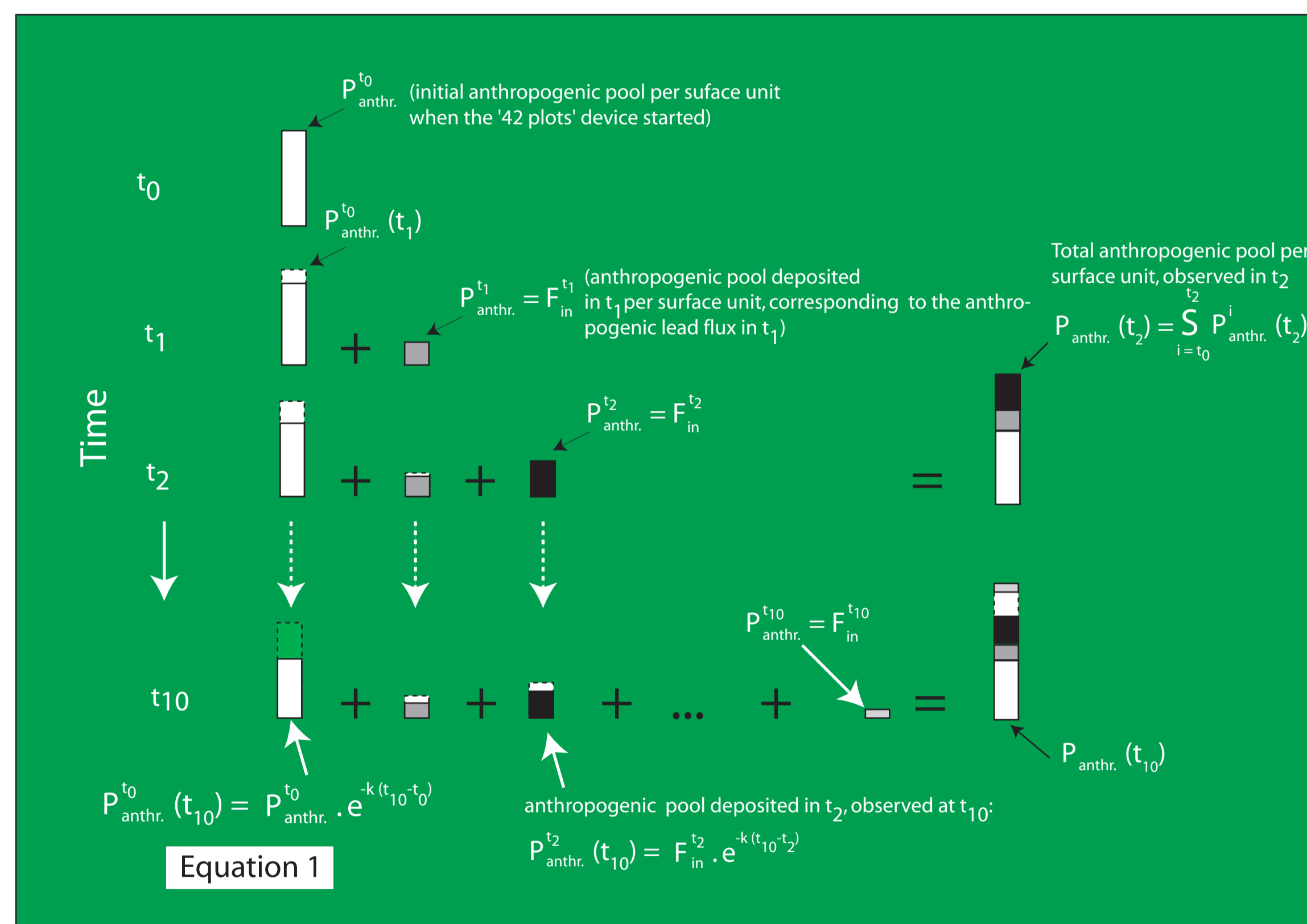

Fig. 3: Scheme of the model. Each anthropogenic pool is represented by a grey tone which symbolizes its isotopic signature.

The model: On the site, there was no amendment or cultivation, and negligible lateral runoff. Output, corresponding to the downward transfer by lixiviation is described as a first-order differential function of the anthropogenic lead pool (Fig. 3, eq. 1; k unknown). The inputs were exclusively ascribed to atmospheric fluxes (Fig. 3).

Obviously there was no monitoring of atmospheric fluxes in 1929 around Paris. A curve describing the shape of the evolution of anthropogenic atmospheric lead fluxes was however rebuilt from different sources (Fig. 4a). Hence, the fluxes for Versailles can be estimated by multiplying this curve by an a factor (unknown).

The evolution of anthropogenic lead isotopic ratios, necessary to run the model, is obtained by compiling the sparse set of published data [3-6] (Fig. 4b).
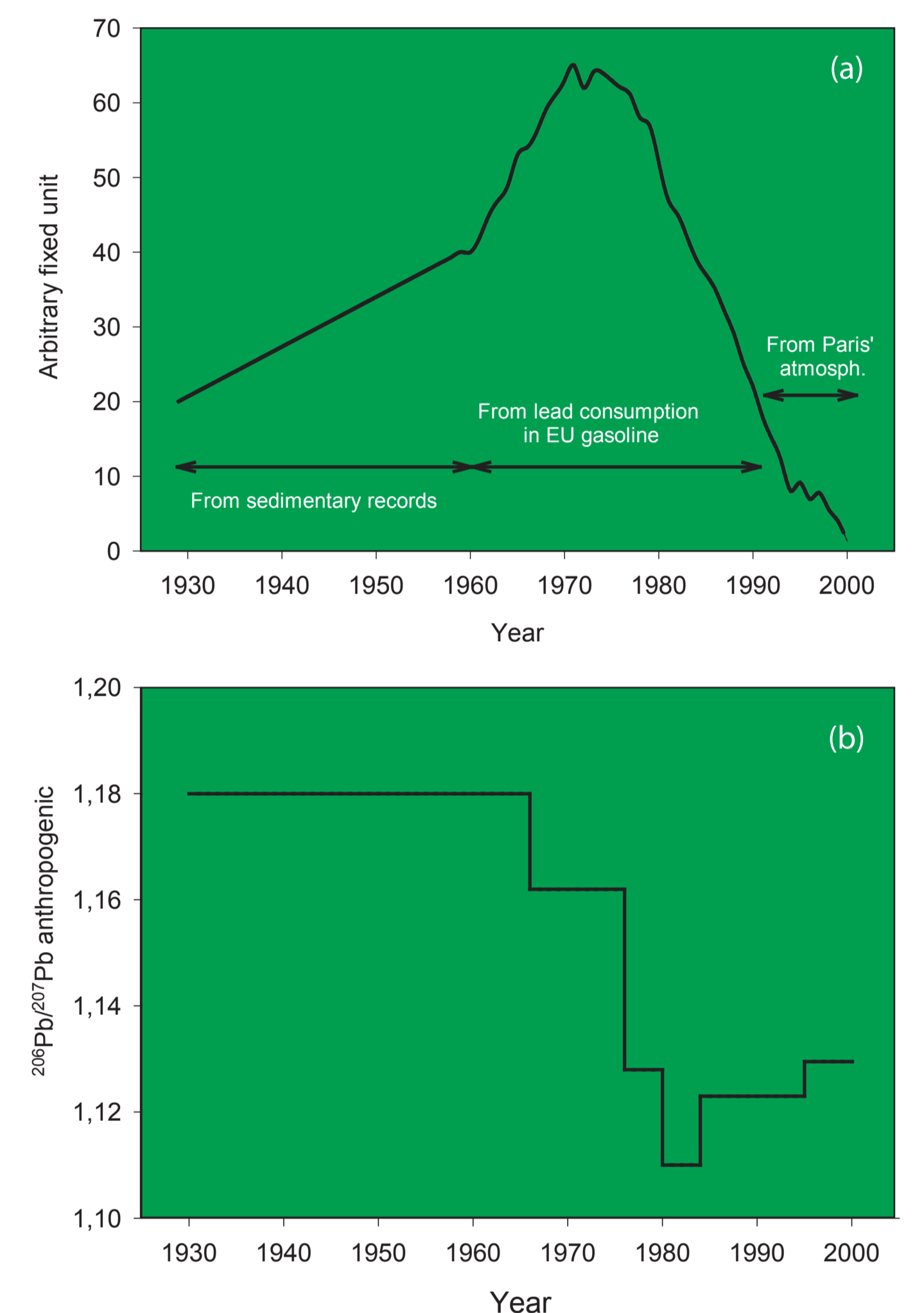

Fig. 4. (a): Composite curve used as a surrogate of lead input fluxes at the INRA site, within a factor a. (b): $^{206}Pb/^{207}Pb$ ratios of anthropogenic deposition.

Model testing procedure:

For each pair $(a; k)$, where a within $[0; 2]$ and k within $[10^{-5}; 10^{-1}]$, theoretical lead concentrations and lead isotopic compositions are calculated through time. They are compared to those observed in the field. Fit errors are plotted in Figure 5a-b using a color code which allows the best pair values to be distinguished.

Figure 5a shows a linear-shaped reddish 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 to be considerably restrained (Fig. 5b): where a within $[0.2; 0.3]$ and $k < 10^{-3}$, the simulation produces approximately the expected concentration and isotopic results (Fig. 6a-b).

Implications on atmospheric fluxes and behavior of lead in soil:

Our flux values are in very good agreement with the rare data available in the literature: 4.5 g cm^{-2} y^{-1} against 3.6 g cm^{-2} y^{-1} for 1991[7], 2.0 g cm^{-2} y^{-1} against 2.31 for 1994 [8], and 0.22 g cm^{-2} y^{-1} against 0.33 g cm^{-2} y^{-1} determined directly at the INRA site in 2002 [9].

A value of $k < 10^{-3}$ corresponds to very low mobility: annual downward migration of less than 0.1% of the potentially mobile lead pool. Although the calculation and parameters used are valid only for the Versailles site, similar values for lead have been reported using independent approaches for other soils: $k = 3.6 \cdot 10^{-4}$ [1,2]. For future lead inputs assumed equal to 0, more than 700 years would be required to halve the anthropogenic pool!

Our field results demonstrate that the major part of the anthropogenic lead pool was integrated into the soil before 1928, which is a long time before the pollution peak of the mid-1970s. Such historical accumulation of lead strongly underlines its limited downward migration. 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 at certain sites [Monna et al. this poster session].
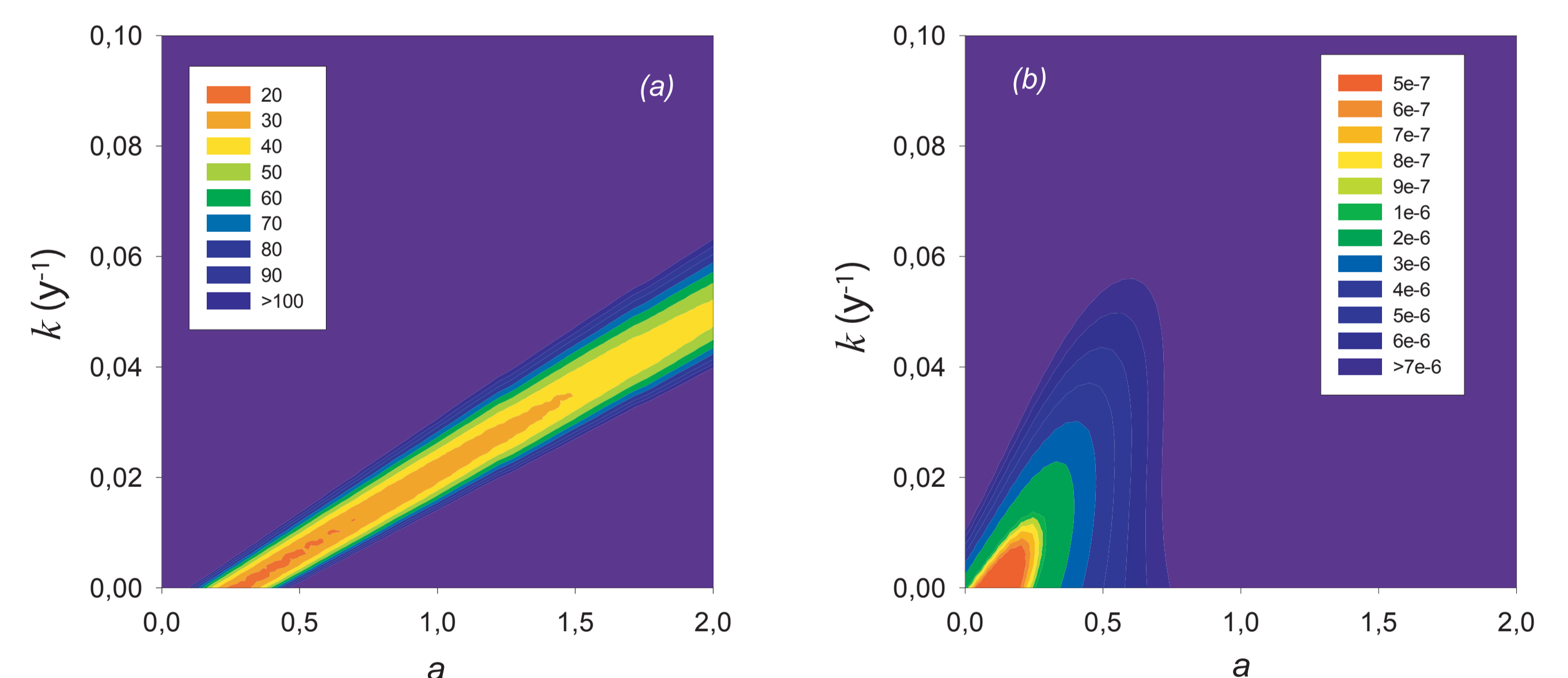

Fig. 5: Fit errors for lead concentrations (a), and lead isotopic compositions (b) reported on diagrams k versus a using a code code.
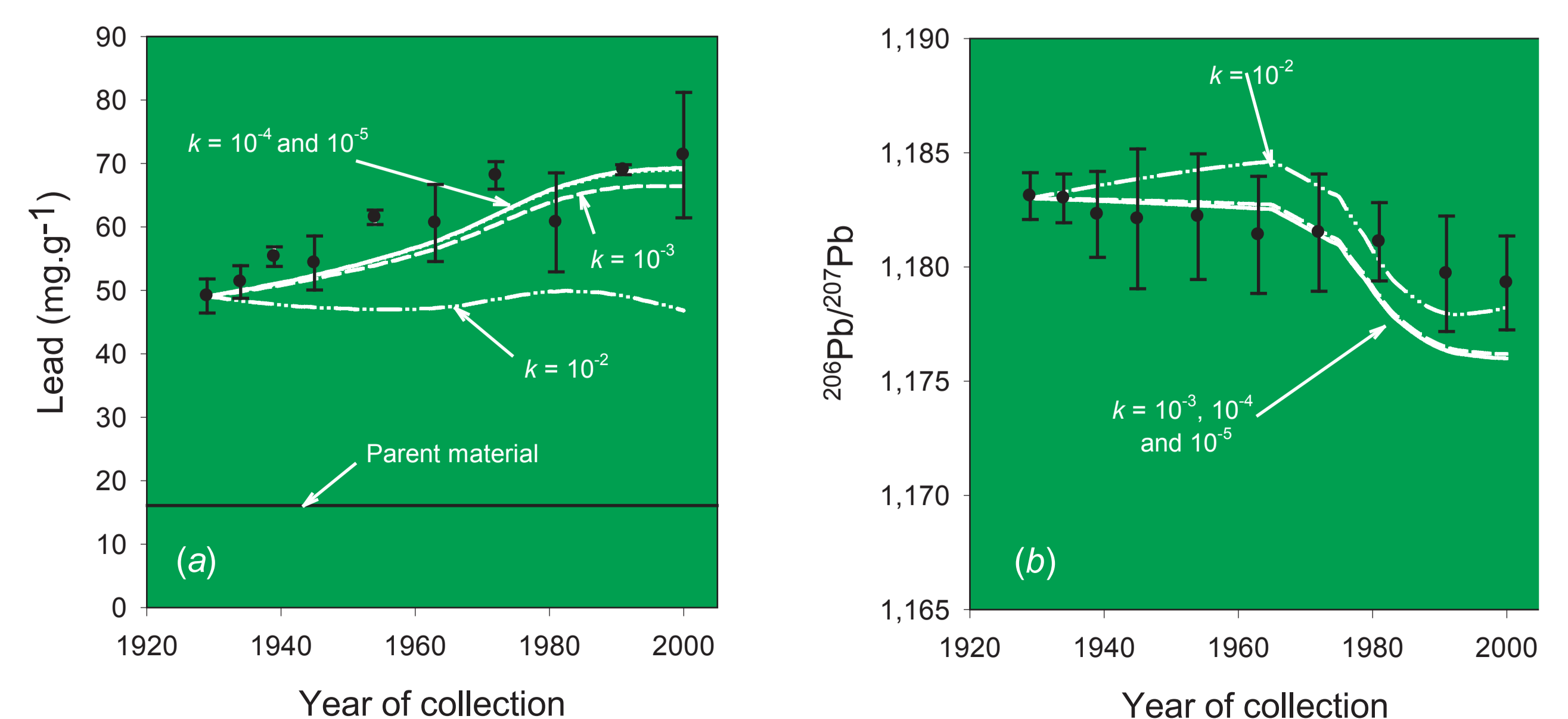

Fig. 6: Simulation of evolution of lead concentrations (a) and lead isotopic compositions (b) vs. time. For $a = 0.25$ and k varying: 2.10^{-2}, 10^{-2}, 10^{-3} and 10^{-4}.

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