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A semi-mechanistic aging model of Pb added to soil by a modified stable isotope dilution technique

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The aging of Pb added to soils has not been studied by the isotopic technology because of difficulties in determination of isotopically exchangeable Pb in soil, so that a set of 10 typical agricultural soils in China and a one-year aging experiment with the addition of water-soluble Pb to the soils were carried out. A modified stable isotope dilution technique to determine isotopically exchangeable Pb in soil was developed where 0.2 mM EDTA (ethylenediaminetetraacetic acid) as the extractant. When water-soluble Pb was added to soil, the isotopically exchangeable Pb (E_{add}%, the percentage of isotopically exchangeable Pb to total Pb added to soil) initially decreased rapidly and gradually slowly. A semi-mechanistic aging model of Pb added to soils, including precipitation/nucleation (Y_1), micropore diffusion (Y_2), and organic matter encapsulation processes (Y_3) was developed with the root mean square error 8.3% where Y_1, Y_2, and Y_3 accounted for 0.02~26.9%, 1.4~21.8% and 3.8~11.3%, respectively, when the pH 4.0~8.0 and organic matter 2.0~6.0%. Soil pH was a vital factor affecting the aging rate. When the pH increased by 1 unit, the E_{add} value decreased by approximately 9%. The model could be used to scale ecotoxicological data of Pb in soil generated in different aging times.

Keywords Lead, Stable isotope dilution, E-value, Aging model, Soil

Accurate assessment of the risk of lead (Pb) in soil is a prerequisite to judge whether the soil is suitable for planting crops and to take correct control measures. After water-soluble Pb is added to soils, its availability decreases rapidly due to aging processes, including precipitation/nucleation, micropore diffusion and organic matter encapsulation[1], indicating that its extractability, exchangeability, bioavailability and toxicity decrease with time[2,3]. The aging processes of added Pb in soils directly affect the concentration of available Pb and absorption by crops and therefore are important in risk assessment for metals in soils.

The aging processes of some metals (such as Cu, Ni, Zn, etc.) in soil have been studied, which certified that isotope dilution is better than conventional chemical extraction[4–6]. Nolan[7] first used stable isotopes (^{65}Cu) to study the aging of Cu in soils and compared them with radioactive isotopes (^{64}Cu) and showed that these two results were parallel, and the former had the advantages of being safer and more stable. However, there are few similar studies on Pb because the concentration of Pb in the soil liquid phase is too low to meet the limit of instrument measurement.

On the one hand, although the aging degree and availability of Pb vary in soils with different physical and chemical properties, Pb is apt to be fixed in soils. Conventional chemical extraction agents, which ought to represent the real aging degree of added Pb, have difficulty matching soils with large differences in properties. Some of them have a quite low extraction capacity (such as 0.01 M $CaCl_2$) in alkaline soils will generate partial Pb, which could have been absorbed by plants and was not fully extracted, thus underestimating the damage of Pb. In contrast, high extraction capacity agents (such as 0.5 M EDTA) reach 60~80% or even more than 100%. Its excessive extractable capacity may lead to the release of Pb that has been fixed by soils and will not be absorbed by plants, overestimating the damage of Pb[8].

On the other hand, isotope dilution was the best way to study the aging process to date because the isotopic exchange process occurred only between different nuclides without any interference from other reactions. The nature of it is adding a negligible mass of stable nuclides by spikes (such as ^{208}Pb), which change the abundance of water soluble Pb and measure its changes in abundance after rebalancing. Then, the concentration of soil

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isotopically exchangeable Pb, called the E-value (mg Pb/kg), could be calculated according to the concentration of Pb in the spike. Nevertheless, the low extraction capacity of water-soluble Pb (extracted by water or $CaCl_2$) cannot meet the requirement of the test apparatus for isotope dilution. Meanwhile, the E value will be underestimated or overestimated if more Pb in the spike precipitates or if nonisotopically exchangeable Pb is released[9]. Therefore, it is crucial to find another reagent with a suitable concentration to replace water or $CaCl_2$ to smoothly match the isotope dilution in various soils. In general, its extractable capacity is supposed to reflect the aging trend and meet the detection limits of the apparatus.

The aging process of added Pb in soil can be divided into precipitation/nucleation, micropore diffusion, and organic matter encapsulation processes[1]. Precipitation is mainly a fast reaction, while the latter two are mainly slow reactions. Semi-mechanistic models that combine mathematical laws and mechanisms can take both into account[10]. With studies of stable isotope dilution and semi-mechanistic models, these aging laws and models of some heavy metals have been developed successfully and have been widely applied to estimate the real risk, confirm the ecological threshold or safety threshold of agricultural products and establish relevant standards[6]. The current study aimed to ascertain a reagent with a suitable concentration as a soil Pb extractant to develop a new stable isotope dilution, determining the isotopically exchangeable Pb added to soil (E_{add}-value, mg Pb/kg), revealing the law of aging, exploring the relationship with soil properties, and establishing a semi-mechanism model to better describe the aging process of added Pb in soils.

Materials and methods

Soil samples and properties

A set of 10 topsoil (0~20 cm) samples covering a range of different soil properties were collected from Nov. to Dec. 2016 in China. Soil samples were air-dried and sieved through 2 mm sieves. Soil pH was measured by pH meter (soil/water ratio, 1:2.5); soil electrical conductivity (EC) was measured by EC meter (soil/water ratio, 1:5); soil organic matter (SOM) was measured following the method utilized to Liu[11]; the measurement methods of soil cation exchange capacity (CEC), noncrystalline iron (N-Fe), noncrystalline aluminium (N-Al) and noncrystalline manganese (N-Mn) were following the method utilized to *Analysis of soil physico-chemical properties* (1978)[12] (Oxalate-ammonium oxalate-colorimetric method); the measurement methods of crystalline iron (C-Fe), crystalline aluminium (C-Al) and crystalline manganese (C-Mn) were following the method utilized to Lu[13] (Sodium disulfite-Sodium citrate-sodium bicarbonate extraction (DCB method)-phenanthroline colorimetric method); the measurement method of total Pb was following the method utilized to HJ 766-2015[14] (digested with HCl, HNO_3, HF, H_2O_2, and determined by inductively coupled plasma—mass spectrometry ICP—MS, 7700X, Agilent). The soil properties are listed in Table 1.

Experimental design for Pb aging in soil

Soil samples were subjected to Pb aging experiments, and the concentrations of added Pb in different soils are listed in Table 1. $Pb(NO_3)_2$ solution was added to 100 g air-dried soil and mixed well, keeping the soil moisture content same as 80% field capacity, and the temperature of incubation was 25 °C. The aging incubation times were 1, 9, 30, and 100/360 days (the longest aging times of S1, S3 and S5 were 100 d). All Pb aging experimental samples were collected and air-dried and sieved through a 2 mm sieve again after incubation.

Soils	Sample location	Longitude and latitude	Soil type	pH	Added Pb	SOM	CEC	Total Pb	N-Fe	N-Al	C-Fe	C-Al	N-Mn	C-Mn	Clay (< 2 μm)
					mg/kg	g/kg	cmol/kg	mg/kg	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	%
S1	Jiangxi	28°11′44.30″N 116°56′47.14″E	Red earth	4.91	250	10.11	12.07	27.08	3.45	2.12	23.04	3.77	0.14	0.16	38.56
S2	Heilongjiang	47°25′49.98″N 126°47′33.25″E	Black soil	5.78	250	54.71	33.41	21.83	4.35	1.92	7.42	1.67	0.59	0.52	32.80
S3	Hainan	19°58′44.18″N 109°55′38.15″E	Latosol	6.07	250	14.37	10.58	7.86	1.78	1.33	79.08	4.97	0.55	1.28	36.44
S4	Hunan	27°51′21.70″N 112°36′32.60″E	Paddy soil	6.60	250	27.61	13.90	33.42	5.46	1.29	23.34	2.61	0.54	0.49	33.74
S5	Zhejiang	30°51′41.91″N 120°41′44.49″E	Paddy soil	6.82	250	33.43	20.42	31.35	6.11	0.89	8.07	0.69	0.21	0.13	26.24
S6	Yunnan	25°41′3.00″N 100°16′22.00″E	Yellowish red earth	6.93	300	26.52	16.13	40.80	5.99	0.78	15.18	1.03	0.19	0.09	24.74
S7	Jilin	42°28′12.00″N 124°51′36.00″E	Black soil	7.92	300	33.30	28.26	25.03	1.95	1.56	7.40	1.26	0.66	0.62	36.18
S8	Shandong	36°23′31.00″N 116°6′52.00″E	Fluvo-aquic soil	8.24	350	8.04	5.40	16.64	0.35	0.29	3.18	0.29	0.09	0.04	5.34
S9	Henan	35°00′31.90″N 113°41′25.50″E	Fluvo-aquic soil	8.35	350	12.18	10.10	18.15	0.93	0.47	7.38	0.52	0.28	0.31	11.09
S10	Ningxia	38°7′4.31″N 106°50′59.84″E	Sierozem	8.89	350	3.31	4.87	13.65	0.21	0.21	4.11	0.31	0.07	0.05	12.52

Table 1. Soil properties for the Pb aging experiment. "N" from "N-Fe", "N-Al" and "N-Mn" means noncrystalline, "C" from "C-Fe", "C-Al" and "C-Mn" means crystalline.

Selection of soil Pb extraction methods

Soil Pb extraction is the key to stable isotope dilution. To find a better soil Pb extraction agent, three kinds of typical soil with varying characteristics, including red earth (S1, pH 4.91), fluvo-aquic soil (S9, pH, 8.35), black soil (S7, SOM, 33.3 g/kg), and six extractants, were selected to extract soil Pb. They were 0.01 M $CaCl_2$, 1 M NH_4NO_3 and 0.05/0.5/5/50 mM EDTA-2Na (hereinafter referred to as EDTA), respectively. The extraction results are expressed in the form of extraction rates, which represents the percentage of the concentration of Pb^{2+} extracted by the extraction agents in the concentration of Pb^{2+} added to soils.

After mixing with the mass ratio of soil and extracting agents as 1:10 in 50 mL centrifuge tubes, samples were oscillated (200 rpm, 120 min) and centrifuged (2865 rpm, 10 min) when using $CaCl_2$ and NH_4NO_3. Samples using EDTA (0.05/0.5/5/50 mM) were oscillated (200 rpm, 120 min) and centrifuged (4000 rpm, 10 min) at a ratio of 1:5. Then, the supernatants were filtered through a 0.45 µm pore-size polyether sulfone membrane filter, and the concentration of Pb in the supernatants was tested by ICP—MS.

Measurement and calculation of E_{add}-value

Determination of final abundance of ^{208}Pb (FA_{208}) and ^{206}Pb (FA_{206}) were as follows: 2 g air-dried soil sample (< 2 mm) was placed in a 50 mL centrifuge tube, then 10 mL 0.2 mmol/L EDTA and two drops of toluene were added into tubes and well mixed to reduce microbial activity. After that, 0.2 mL $^{208}Pb\ (NO_3)_2$ (200 mg Pb/L) (prepared with ^{208}Pb particles, ^{208}Pb abundance, 99.36%, ISOFLEX, California) was added into tubes and mixed well again. Tubes were oscillated for 24 h (200 rpm) and centrifuged for 20 min (4225 rpm). Then, the supernatant in the tube was removed and filtered through a 0.45 µm filter membrane. The filter liquor was analysed for the abundance of Pb, such as $\frac{FA_{208}}{FA_{206}}$, by multicollector inductively coupled plasma—mass spectrometry (MC–ICP—MS, NEPTUNE PLUS, Thermo Fisher Scientific). The analysis procedures of soil Pb natural abundance (NA_{208} and $NA_{206)}$ were the same as the above procedure without adding $^{208}Pb\ (NO_3)_2$ solution.

The E-value (mg Pb/kg, hereinafter referred to as E) is the concentration of isotopically exchangeable Pb added to soils determined by the isotope dilution, which could be calculated from the results of MC–ICP—MS determination. Hence, the natural abundance of ^{208}Pb (NA_{208}) and ^{206} Pb (NA_{206}) from initial soil samples (without spike) was determined; the final abundance of ^{208}Pb (FA_{208}) and ^{206}Pb (FA_{206}) from the treated soil samples (with spike) was determined; SA_{208} and SA_{206} were the abundance of ^{208}Pb and ^{206}Pb in the spike, respectively. According to the calculation principle of the isotopic abundance ratio, the following equation is used[15]:

$$\frac{FA_{208}}{FA_{206}} = \frac{SA_{208} \times R + NA_{208} \times E}{SA_{206} \times R + NA_{206} \times E}$$

After extracting the common factor "E", it can be written as:

$$E = \frac{R \times \left(SA_{208} - SA_{206} \times \frac{FA_{208}}{FA_{206}} \right)}{NA_{206} \times \frac{FA_{208}}{FA_{206}} - NA_{208}} \tag{1}$$

where R was the total concentration of Pb added to soil samples through the spike (mg Pb/kg), and the concentration of total Pb added through the spike was 20 mg Pb/kg in this study.

Then, the concentration of isotopically exchangeable Pb from added Pb (E_{add}-value (mg Pb/kg, hereinafter referred to as E_{add})) in soils was defined as:

$$E_{add} = E_{total} - E_{ck} \tag{2}$$

where E_{total} is the E-value from samples with added Pb, which includes the total Pb and added Pb in Table 1, and E_{ck} is the E-value from samples without added Pb.

Establishment of a semi-mechanistic aging model by soil-added Pb

The E_{add}-value (%) (hereinafter referred to as E_{add} (%)) is the percentage of the concentration of isotopically exchangeable Pb added to soil to the concentration of Pb added to soil, which is related to soil available Pb and can be used to construct a semi-mechanistic model for estimating available Pb. Therefore, E_{add} (%) is used to represent the change in added Pb activity in the model. Its calculation is as follows:

$$E_{add}(\%) = \frac{E_{add}}{Pb_{add}} \tag{3}$$

where E_{add} is the E_{add}-value (mg Pb/kg) from Equation (2); Pb_{add} means added Pb in soils during incubations of aging.

According to the studies of Cu, Zn, Ni, Co, and Cr, when the heavy metal ions M^{2+} are added to soils, there might be a flowing reaction immediately during the precipitation/nucleation process.

$$[M(H_2O)_n]^{2+} = \left[M(OH)(H_2O)_{n-x-1}\right]^{+} + xH_2O + H^{+}$$

Pb is similar, and Pb^{2+} will sharply decrease with a relatively higher pH. Its chemical equilibrium constant equation is as follows:

$$\mathrm{K} = \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{Pb(OH)}^{+}\right]}{\left[\mathrm{Pb}^{2+}\right]} \tag{4}$$

Hence, the proportion of Pb $(OH)^+$ to the sum of Pb $(OH)^+$ and Pb^{2+} can be represented as:

$$\frac{\left[\mathrm{Pb(OH)}^{+}\right]}{\left[\mathrm{Pb(OH)}^{+}\right] + \left[\mathrm{Pb}^{2+}\right]} = \frac{1}{10^{(\mathrm{pK}^{0} - \mathrm{pH})} + 1} \tag{5}$$

In view of Ma[4,5], assuming these processes are linear with the abovementioned proportion, the rapid aging reaction process of the soil added Pb can be expressed as the following equation:

$$\mathrm{Y}_1 = \frac{\mathrm{B}}{10^{(\mathrm{pK}^{0} - \mathrm{pH})} + 1} \times \mathrm{t}^{\frac{\mathrm{c}}{\mathrm{t}}} \tag{6}$$

where Y_1 represents the ratio of Pb decreased due to precipitation/nucleation to the total added Pb, B is the constant coefficient related to the precipitation/nucleation process, t is the aging time (d), pK^0 is the first-order hydration constant of Pb, and $t^{\frac{c}{t}}$ is a parameter used to describe the relationship between the surface precipitation process and time.

According to Crank[16] and Sparks[17], Ma[4,5] proposed the short-term aging semi-mechanism model (Sqrt-model, ≤ 6 months) and long-term aging semi-mechanism model (Ln-model, > 6 months), and the process of micropore diffusion in both models could be combined and simplified into the following formula by a complementary error function[10]:

$$\mathrm{Y}_2 = \left[1 - \exp\,(\mathrm{Ft}) \times \mathrm{erfc}\sqrt{\mathrm{Ft}}\right] \times 100\% \tag{7}$$

where F is the constant coefficient, erfc represents the complementary error function, and t is the aging time (d).

According to Zeng[10], the process Y_3 of soil with added Pb encapsulated by organic matter was as follows:

$$\mathrm{Y}_3 = \mathrm{G} \times \mathrm{C}_{\mathrm{org}} \times \mathrm{t}^{\frac{\mathrm{H}}{\mathrm{t}}} \tag{8}$$

where Y_3 is the ratio of the added Pb that decreased due to organic matter entrapment and the total added Pb, G is the constant coefficient related to organic matter entrapment, C_{org} is the content of SOM (g/kg), and $t^{\frac{H}{t}}$ is the parameter of the relationship between the organic matter entrapment process and time.

In summary, the aging semi-mechanism model based on the precipitation/nucleation, micropore diffusion process and organic matter wrapping process, which can be used to estimate both short- and long-term aging processes, can be combined as follows:

$$\mathrm{E}_{\mathrm{add}}(\%) = \mathrm{A} - \mathrm{Y}_1 - \mathrm{Y}_2 - \mathrm{Y}_3 \tag{9}$$

i.e.

$$\mathrm{E}_{\mathrm{add}}(\%) = \mathrm{A} - \frac{\mathrm{B}}{10^{\mathrm{pK}^{0} - \mathrm{pH}} + 1} \times \mathrm{t}^{\frac{\mathrm{C}}{\mathrm{t}}} - \left\{1 - \exp\,[\mathrm{Ft}] \times \mathrm{erfc}\left[\sqrt{\mathrm{Ft}}\right]\right\} \times 100\% - \mathrm{GC}_{\mathrm{org}} \times \mathrm{t}^{\frac{\mathrm{H}}{\mathrm{t}}} \tag{10}$$

where E_{add} (%) is the ratio of the isotopically exchangeable Pb to the added Pb from Eq. (2), pH is the soil pH value, t is the soil aging culture time (d), and C_{org} is the soil organic matter (SOM, g/kg). F and G are model fitting constants, and pK^0 is the first-order hydration constant of Pb^{2+}.

According to the results and indicators of isotope dilution, with an accuracy of 0.000001, allowable error of 5%, and convergence degree of 0.0001, the value of each parameter in the semi-mechanism aging model was deduced by the program solving function of Excel.

Data analysis

Data analysis, correlation analysis, figure drawing, and parameter fitting of the semi-mechanism aging model and programming solution were performed in Microsoft Excel 2021, Origin Pro 2017 and IBM SPSS Statistics 22, respectively.

Results and discussion

Optimization of the extraction method for isotopically exchangeable Pb in soil

The critical step of isotope dilution is extracting Pb in soils. Precipitation of Pb in systems or incorrect extraction of exchangeable Pb will lead to the incorrect estimation of E_{add} (%). There are many soil types in China with large differences in properties, which greatly affect the extraction of Pb. Conventional extraction methods cannot meet the detection limit of MC–ICP—MS (≥ 0.5 mg/L) well. Therefore, the key is to select an extractant with a suitable extraction capacity that can meet the detection limit and avoid the release of nonisotopically exchanged Pb. To select the extraction method suitable for acidic, alkaline and high organic matter soils, 0.01 M $CaCl_2$ and 1 M HN_4NO_3 were used to extract Pb from red earth (pH, 4.91), fluvo-aquic soil (pH, 8.35) and black soil (pH, 7.92; SOM, 33.3 g/kg). The results are shown in Fig. 1. The extraction rates of the $CaCl_2$ solution were 11.3~13.5% in red earth, 0.008~0.038% in fluvo-aquic soil, and 0.002~0.014% in black soil. The extraction rates of NH_4NO_3 were 15.9~42.4% in red earth, 0.014~0.052% in fluvo-aquic soil and 0.003~0.047% in black soil. They all showed

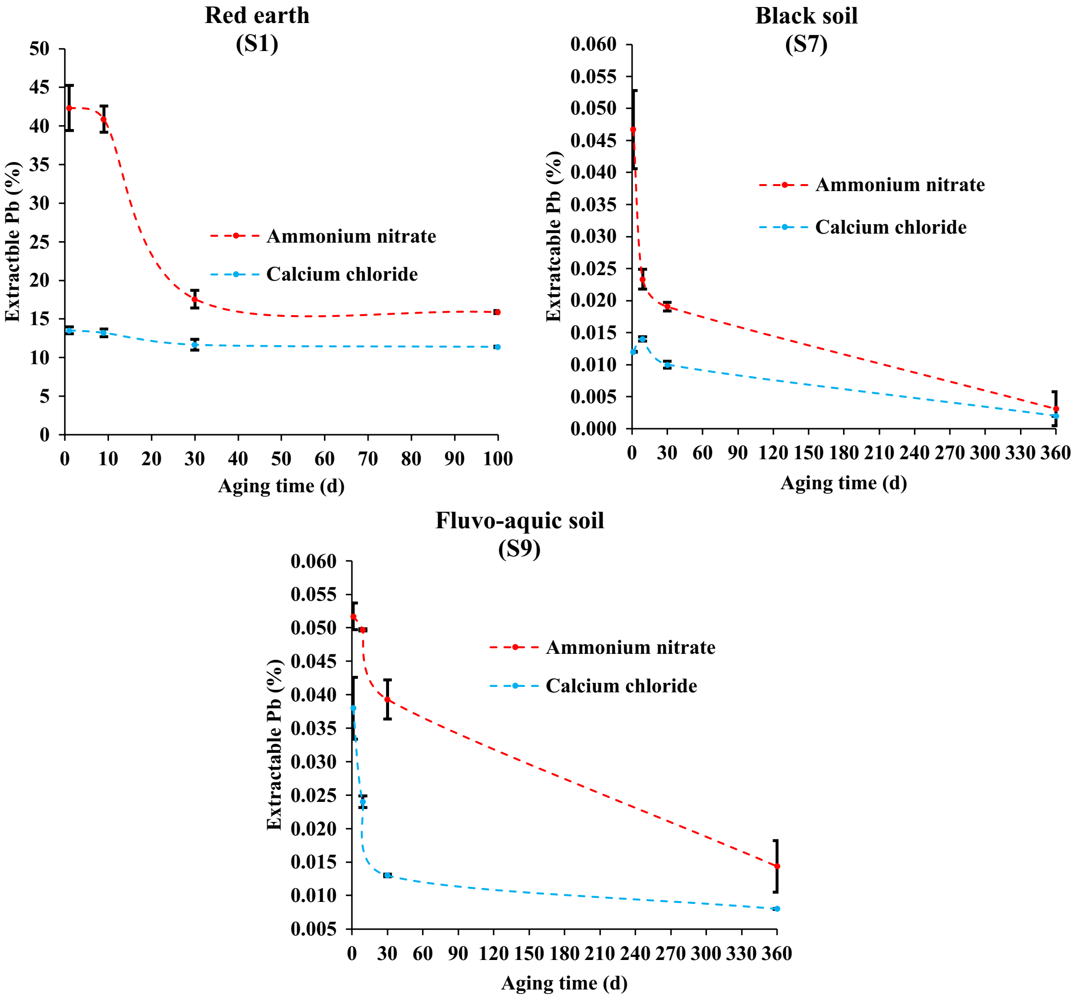

Figure 1. The dynamics of soil extractable Pb at different aging times.

aging trends of added Pb; however, extraction rates of 0.01 M $CaCl_2$ and 1 M NH_4NO_3 are not enough to meet the detection limit for the determination of the abundance of ^{208}Pb and ^{206}Pb as well as the E value of Pb in soil.

EDTA is a strong ion-exchange extraction agent, and the extraction rates are shown in Fig. 2. The extraction rate of 50 mM EDTA was 85~100%, which was too high and could not reflect the aging trend. Therefore, 50 mM EDTA was not suitable. The extraction rates of 0.05/0.5/5 mM EDTA were 0.8~7.1%, 15.6~45.6% and 60.1~88.1%, respectively, and decreased clearly with decreasing concentration. The extraction rate of 0.05 mM in red earth was low (0.8~1.3%), and the extraction rate of 5 mM in the three soils was higher than 60%. Both of them had a risk of over 100% or below the detection limit for soils with more extreme properties. Hence, 0.5 mM EDTA was more rational. During the growth of plants, many organic acids are secreted into the rhizosphere, which could increase the mobility of Pb by generating complexes and entering plants[18,19], and EDTA might play a similar role. Atkinson[20] carried out isotope dilution with 0.337~50 mM EDTA and showed that 0.5 mM EDTA was relatively more suitable. Considering these large differences in soil properties, the concentration of EDTA was tentatively set as 0.2 mM according to the average change in the extraction rate of EDTA on the 1st and 360th d (Fig. 3).

Evaluation of 0.2 mM EDTA as an extractant for Pb isotope dilution

The tendency of the extraction rate of 0.2 mM EDTA decreased with aging time, which decreased from 6.1% to 4.1% in red earth (S1), from 30.7% to 19.6% in fluvo-aquic soil (S9), and from 38.0% to 22.3% in black soil (S7). The results of correlation analysis from those agents show that 0.2 mM EDTA is extremely significantly correlated with 0.05 mM EDTA (S1, 0.924**; S9, 0.917**; S7, 0.939**) and better than 0.5 mM EDTA (S1, 0.959**; S9, 0.863*; S7, 0.942**). Meanwhile, it is also significantly correlated with CaCl2 in S1 (0.814*) and S7 (0.917**). Therefore, 0.2 mM EDTA could reflect the aging processes of Pb in soils and have a good correlation with $CaCl_2$ and 0.05/0.5 mM EDTA on the condition of meeting the detection limit (MC–ICP—MS) well.

In terms of changes in isotopic abundance, 0.2 mM EDTA was evaluated again (Fig. 4). "Max" was the abundance of ^{208}Pb assuming that Pb^{2+} from spikes could remain soluble and no isotopic exchange occurred; hence, the abundance could increase to the max. "Measured" was the measured abundance of ^{208}Pb when the system equilibrated after spiking and isotopic exchange. "CK" was the abundance of ^{208}Pb in the soil solutions without spikes (i.e., natural abundance, NA). If the Pb in the spike was strongly fixed immediately after spiking and no

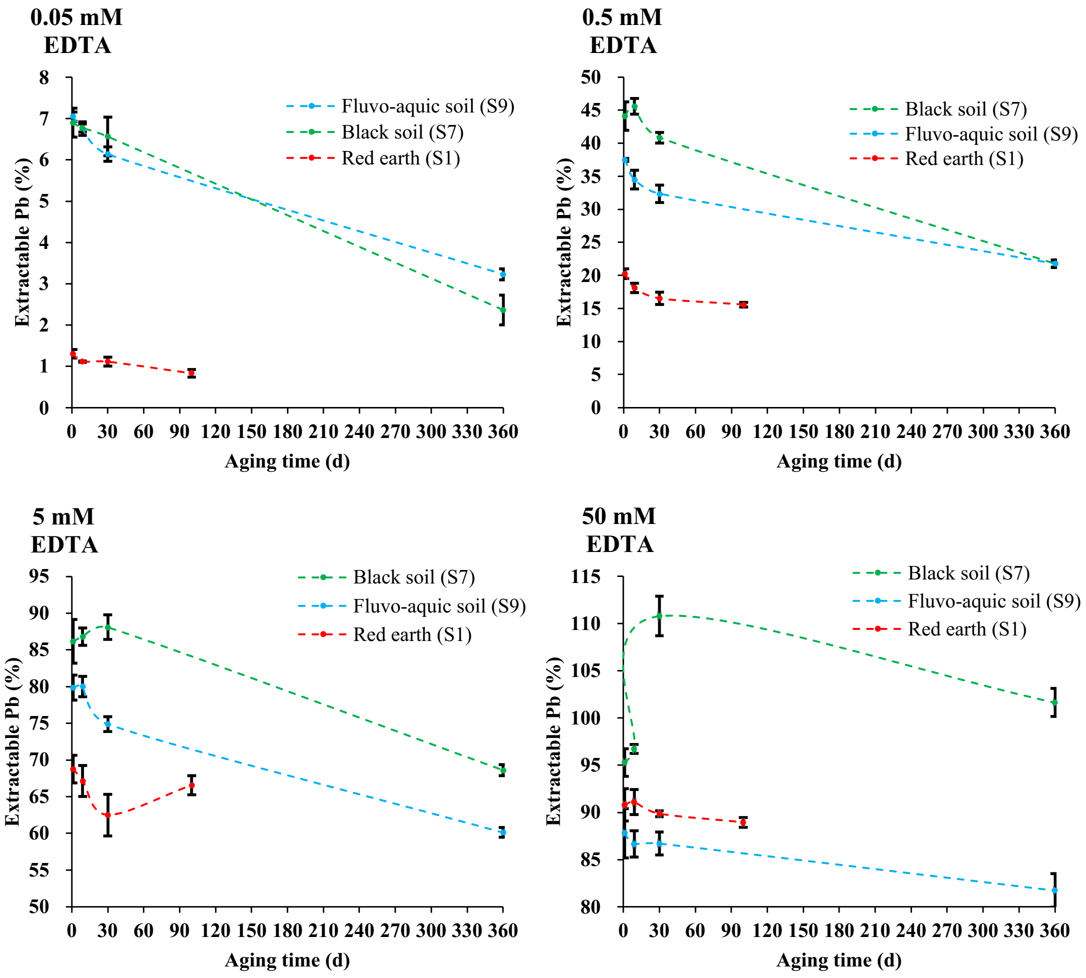

Figure 2. Extraction rate of different EDTA concentrations in soils at different aging times.

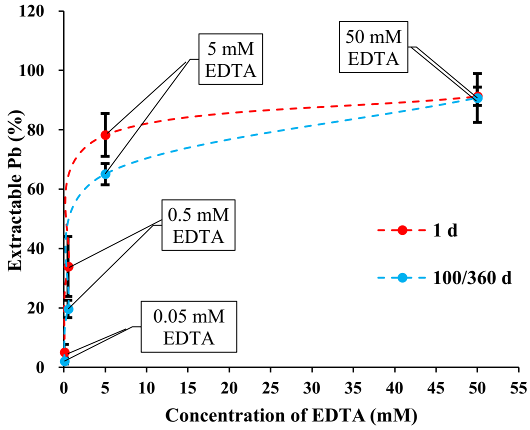

Figure 3. Average extraction rate of different EDTA concentrations on the 1st and 360th d.

isotopic exchange occurred, the abundance of ^{208}Pb would remain, which was the abundance represented by "CK". The actual abundance of ^{208}Pb is always between these two, indicating that isotopic exchange and equilibrium had occurred after spiking; hence, 0.2 mM EDTA could provide an environment for isotopic exchange and rebalancing in the system. It was suitable for isotope dilution to study the aging law of added Pb.

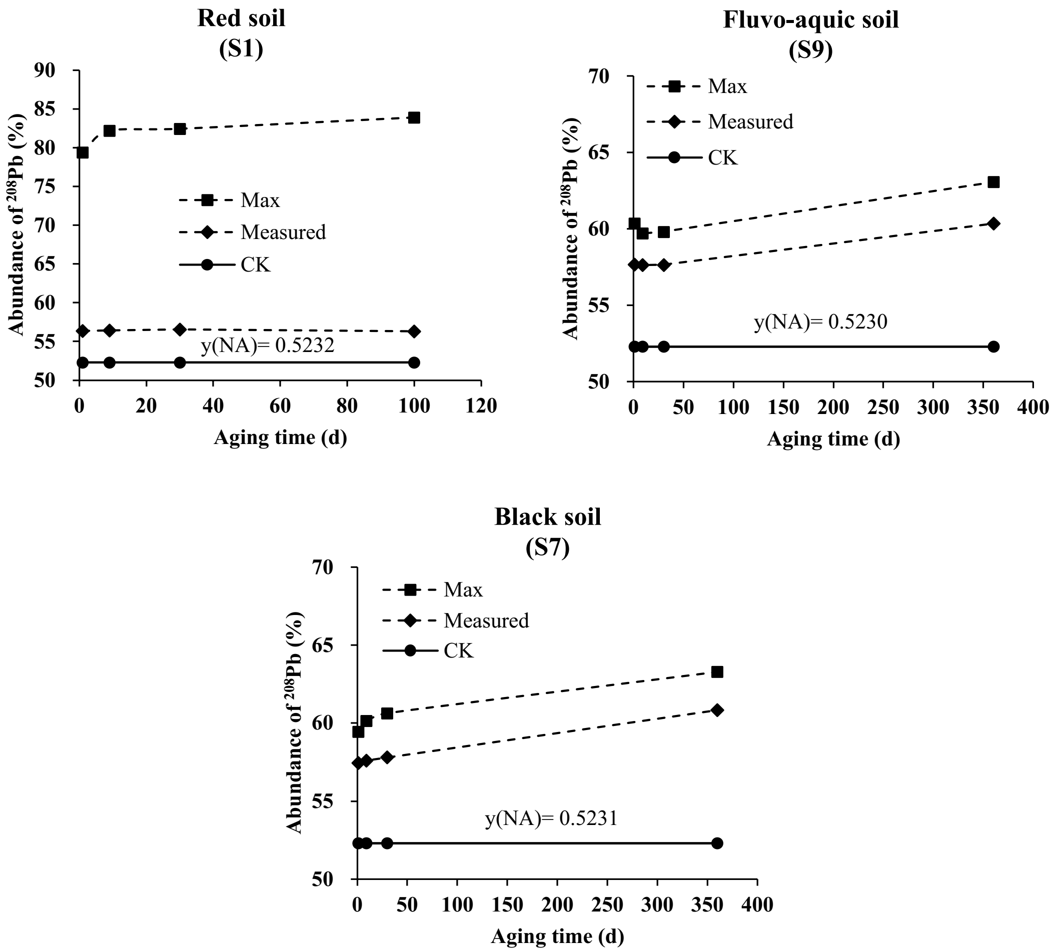

Figure 4. Abundance of ^{208}Pb at different aging times (the standard errors were less than 0.41%, 0.12% for average).

Revealing the aging of added Pb in soils by E_{add} (%)

The isotopically exchangeable Pb, i.e., E_{add} (%), for ten soils at different aging times or intervals is shown in Table 2. The dynamics of E_{add} (%) indicated a decreasing trend with aging time, except for red earth (S1) (Fig. 5). E_{add} (%) decreased sharply on the 1st d, and the descend range of E_{add} (%) ranged from 14.7 to 55.3%, with an average of 35.2%, which indicated a quick-aging stage on the 1st d after Pb entered the soil. However, the dynamics of E_{add} (%) were different with different soil properties. E_{add} (%) decreased in the order of fluvo-aquic

	E (%)	Descend range (%)	E (%)	Descend range (%)		E (%)	Descend range (%)		E (%)	Descend range (%)	
Soils	1 d	0~1 d	9 d	0~9 d	2~9 d	30 d	0~30 d	2~30 d	360 d	0~360 d	2~360 d
S1*	85.4	14.7	84.4	15.6	1.0	82.0	18.0	3.4	86.4	13.6	-1.1
S2	71.9	28.1	69.4	30.6	2.5	66.0	34.0	5.9	48.1	52.0	23.8
S3*	74.2	25.8	66.8	33.2	7.4	69.5	30.5	4.7	65.0	35.1	9.3
S4	66.0	34.0	58.1	41.9	7.8	65.7	34.3	0.3	52.4	47.6	13.6
S5*	76.4	23.6	83.3	16.7	-6.9	78.9	21.1	-2.5	75.0	25.0	1.4
S6	70.3	29.8	71.7	28.3	-1.5	65.2	34.9	5.1	30.3	69.7	40.0
S7	55.0	45.0	53.0	47.0	2.0	50.8	49.2	4.1	30.9	69.1	24.0
S8	46.7	53.3	42.4	57.6	4.3	40.7	59.3	6.0	26.9	73.1	19.8
S9	44.7	55.3	45.2	54.8	-0.5	45.0	55.0	-0.3	28.6	71.5	16.1
S10	58.0	42.1	57.6	42.4	0.4	54.8	45.2	3.1	51.0	49.0	7.0

Table 2. E_{add} (%) and descent range of 10 soils at different aging times. The longest aging time of soils with "*" was 100 d, and the two columns on the right are "0~100 d" and "2~100 d".

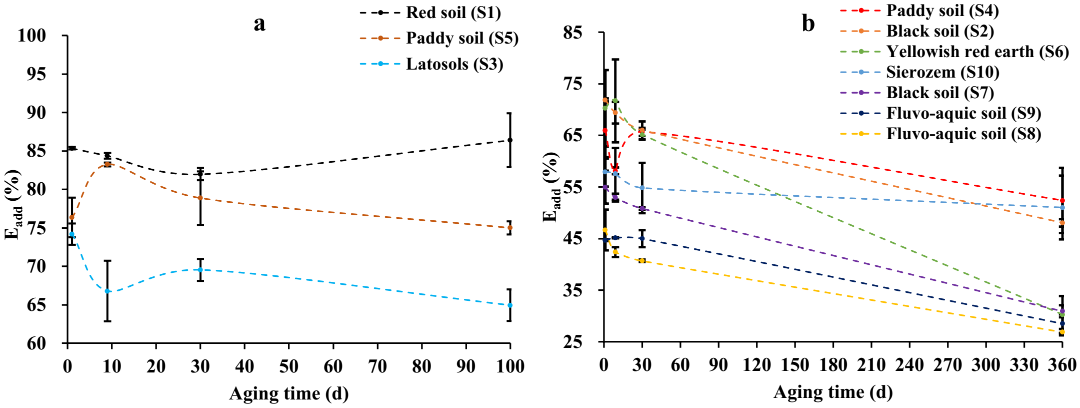

Figure 5. The dynamics of E_{add} (%) in different soils (**a** 0~100 d; **b** 0~360 d).

soil (55.3%, S9) > fluvo-aquic soil (53.3%, S8) > black soil (45.0%, S7) > sierozem (42.1%, S10) > paddy soil (34.0%, S4). For the other five soils, the decreased range of E_{add} (%) was relatively smaller. The decreased range of E_{add} (%) in paddy soil (S5), black soil (S2), yellowish red earth (S6) and latosol (S3) was 23.6~29.8%, with a pH covering the range of 5.78~6.93. The lowest decrease in E_{add} (%) was 14.7%, which occurred in red earth (S1) with the lowest pH (4.91). This result clearly indicated the influence of pH on E_{add} (%) change, and there was a relationship between soil pH and E_{add} (%),

$$E_{add}(\%) = 0.7048\ \mathrm{pH}^{1.9811}, \quad R^2 = 0.817**\tag{11}$$

$$E_{add}(\%) = 9.1971\ \mathrm{pH} - 29.678, R^2 = 0.774*\tag{12}$$

After 1 d of aging with added Pb, the change in E_{add} (%) tended to slow (Fig. 5), which was a slow-aging stage. However, the trend of E_{add} (%) in soils with different properties varied. E_{add} (%) decreased by – 1.1~40.0% up to the end and 15.4% on average, indicating that most of the soils were able to gradually decrease the isotopic exchangeability of added Pb. The E_{add} (%) of red earth (S1) increased, and paddy soil (S5) decreased by only 1.4%, indicating that there is a greater risk of Pb^{2+} compared with the others. The descending ranges of E_{add} (%) in the two black soils (S2 and S7) and in the two fluvo-aquic soils (S8 and S9) are both parallel, indicating that the similar slow-aging stages of both soils may be influenced by their similar soil properties. The E_{add} (%) of latosol (S3) decreased less than that of paddy soil (S4) as the pH increased. The E_{add} (%) of yellowish red earth (S6) decreased the most, and even more than the descending range in 0~1 d, inferring that its aging capacity was in the slow-aging stage. The E_{add} (%) of sierozem (S10) decreased by 7%, showing that aging of added Pb occurred more in 0~1 d. It can be concluded that added Pb is affected not only by pH but also by other properties in the slow aging stage.

Kerndorff[21] showed that Pb could be adsorbed by humic acid at a lower pH range than Cu, Cr, Cd, Zn, Ni, Co and Mn, which may be the reason that the aging degree of S3 was much more obvious than that of S1. According to Tessier[22], the adsorption law of soil oxides and humus was the same, and both increased with increasing pH. In the present study, the degree and speed of aging in S7 were higher than those in S2, and the main difference between the two may be that the pH of S2 was lower. Degryse[15] used isotope dilution, 0.01 M $CaCl_2$ was used as the extractant to compare contaminated field soils (pH, 6.6~7.5) and lab amendment soils (269~14436 mg Pb/kg) with the same total Pb concentration, and it was found that in soils with added Pb $(NO_3)_2$, E_{add} (%) was over 84% (average 89%), which was much higher than that in polluted soils with 48~78% (average 58%). Meanwhile, with the increase in Pb added to the soil, the $CaCO_3$ added to maintain a similar pH also increased, resulting in a sharp increase in the Ca^{2+} concentration in the soil solution of the treatment groups. In the soil with 5457 mg Pb/kg, when Ca^{2+} was 16 times that of the field soil, the pH (4.6) was much lower than that of the corresponding field soils (8.1). According to the study of Christina[23], Ca^{2+} competition can inhibit the adsorption of the heavy metal ion M^{2+} by Fe_xO_y in soil. A large concentration of $CaCO_3$ was applied to unify the pH of lab and field soil, in which Ca^{2+} and low pH may jointly lead to an increase in Pb availability. In summary, a high concentration of Ca^{2+}, high ionic strength, and low pH may affect the results of the abovementioned laboratory amendment soils (89%), which far exceeded field soils, including interactions of Ca^{2+} from $CaCO_3$ and extractant.

In addition, E_{add} (%) measured by $Ca(NO_3)_2$ was close to 0.5 mM EDTA (even lower), and later, it is more appropriate to obtain results without the influences of low Pb^{+2} concentrations and detection limits[24]. Obviously, 0.2 mM EDTA as the extractant rather than $CaCl_2$ could be more feasible to study the aging of added Pb in these ten test soils of China.

The difference in aging described by E_{add} (%) and chemical extractable Pb

By comparison, E_{add} (%) varies from the percentage of Pb in the other six extracts in this study (Fig. 6). S1 (red earth) is a typical strongly acidic soil in southern China (pH, 4.91), and the SOM is low (10.1 g/kg). Pb could maintain strong availability for a long time. The sequence was 50 mM EDTA > E_{add} (%) > 5 mM EDTA > 1 M NH_4NO_3 > 0.5 mM EDTA > 0.01 M $CaCl_2$ > 0.05 mM EDTA. Therefore, its concentration would be overestimated

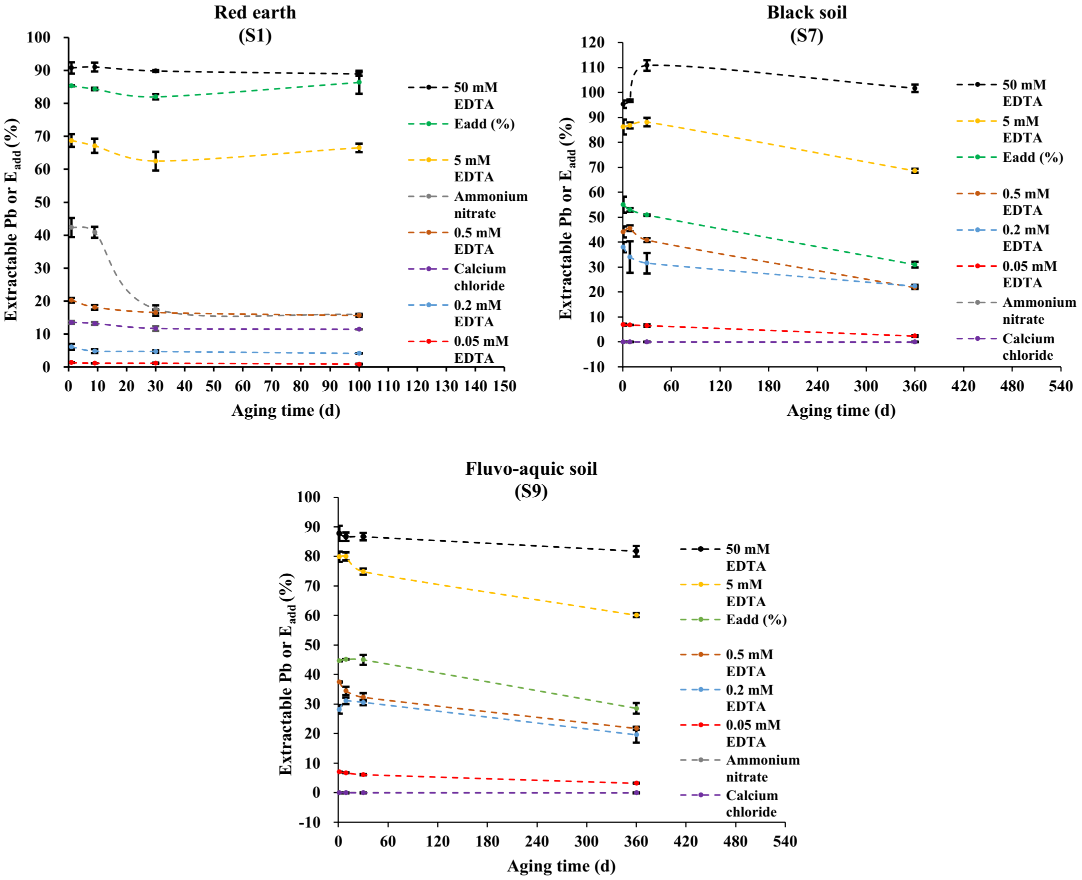

Figure 6. Comparison of the extraction rates of the extractants and E_{add} (%).

when 50 mM EDTA was used to study the aging of added Pb. However, when using the other five extractants, the concentration would be underestimated.

In S7 and S9, the sequence was the same: 50 mM EDTA > 5 mM EDTA > E_{add} (%) > 0.5 mM EDTA > 0.05 mM EDTA> 1 M NH_4NO_3>0.01 M $CaCl_2$. EDTA concentrations of 50 and 5 mM would overestimate the availability of Pb, while the other four solutions would underestimate it. The two soils mentioned above are black soil (SOM, 33.3 mg/kg) in Northeast China and fluvo-aquic soil in the North China Plain (pH, 7.92 and 8.35), which are alkaline soils. Due to the high pH, it is difficult to extract a sufficient concentration by conventional extractants. By comparison, the aging degree of Pb in the fluvo-aquic soil (S9) was higher than that in the black soil (S7) at each aging time, indicating that pH may be an important factor affecting the aging degree of added Pb in soils.

Semi-mechanistic modelling of soil with added Pb aging

Before the semi-mechanism aging modelling, partial correlative analyses were carried out to consider the interference of Al and Fe with pH in soils because some H^+ might be provided from Al. The results showed that pH (R, – 0.637^{***}) and aging time (R, – 0.567^{***}) were still the main factors affecting E_{add} (%) when the effects of Al and Fe were controlled. According to the results and indicators of isotope dilution (Table 3), with an accuracy of 0.000001, allowable error of 5%, and convergence degree of 0.0001, the value of each parameter in the semi-mechanism aging model was deduced by the program solving function of Excel (Table 4).

The final model equation is as follows:

$$E_{add}(\%) = 86.2 - \frac{31.9}{10^{7.27-pH} + 1} - \left\{1 - \exp\left[0.000152t\right] \times \mathrm{erfc}\left[\sqrt{0.000152t}\right]\right\} \times 100\% - 0.189C_{org} \tag{13}$$

In the semi-mechanism model, the first-order hydration constant pK^0 was 7.27, which is near but slightly lower than the result of Lindsay (7.70)[25]. Similarly, the pK^0 of Cu^{2+}, which ranged from 6.89~7.14, in the same rapid reaction stage of the aging process (Y_1) was either lower than the fixed coefficient (7.70) on the basis of Ma[4,5]. This result for Pb2+ in this study may be analogous to the mechanism by which solid soil surfaces could promote the hydrolysis of Cu^{2+}.[26–28]

In addition, the RMSE between the estimated value and the measured value in the fitting results of this model is 8.3%, which theoretically has better prediction accuracy than the RMSE (10.7%, 13.6% and 10.6%) of the three semi-mechanism models developed by Zhang[6] for Zn.

Soils	Aging time (d)	Measured E_{add} (%), mean and range	Estimated E_{add} (%)	Residual
S1	1	85.35 (85.18~85.51)	82.78	− 2.57
	9	84.38 (84.02~84.75)	80.11	− 4.27
	30	81.98 (81.17~82.79)	76.97	− 5.01
	100	86.40 (82.91~89.89)	71.63	− 14.77
S2	1	71.89 (71.59~72.19)	73.48	1.59
	9	69.39 (67.32~71.46)	70.82	1.43
	30	66.00 (64.29~67.70)	67.68	1.68
	360	48.05 (47.35~48.76)	53.11	5.05
S3	1	74.20 (72.97~75.43)	80.23	6.03
	9	66.78 (62.61~70.96)	77.57	10.78
	30	69.54 (68.12~70.95)	74.42	4.88
	100	64.95 (62.90~67.00)	69.08	4.14
S4	1	65.98 (60.81~71.14)	73.97	7.99
	9	58.13 (57.49~58.78)	71.3	13.17
	30	65.68 (64.90~66.47)	68.16	2.47
	360	52.39 (46.37~58.41)	53.59	1.2
S5	1	76.36 (73.79~78.92)	70.2	− 6.16
	9	83.26 (83.00~83.52)	67.53	− 15.72
	30	78.88 (75.40~82.36)	64.39	− 14.49
	100	75.01 (74.14~75.87)	59.05	− 15.95
S6	1	70.25 (70.25) *	69.78	− 0.48
	9	71.71 (71.71) *	67.11	− 4.59
	30	65.15 (64.17~66.14)	63.97	− 1.18
	360	30.29 (26.53~34.05)	49.4	19.11
S7	1	54.96 (51.77~58.15)	52.45	− 2.52
	9	52.97 (52.22~53.72)	49.78	− 3.19
	30	50.84 (50.54~51.13)	46.64	− 4.2
	360	30.93 (29.79~32.07)	32.07	1.14
S8	1	46.67 (38.71~46.67)	54.48	7.81
	9	42.41 (41.45~43.38)	51.81	9.4
	30	40.70 (40.46~40.95)	48.67	7.97
	360	26.91 (26.29~27.53)	34.1	7.19
S9	1	44.68 (44.51~44.85)	53.09	8.41
	9	45.17 (45.17~45.27)	50.42	5.25
	30	45.00 (43.34~46.67)	47.28	2.27
	360	28.55 (26.77~30.33)	32.71	4.16
S10	1	57.95 (55.10~60.80)	53.04	− 4.91
	9	57.26 (51.45~63.67)	50.38	− 7.18
	30	54.82 (50.32~59.31)	47.23	− 7.58
	360	51.00 (45.12~56.89)	32.66	− 18.34

Table 3. Measured E_{add} (%) and estimated E_{add} (%) of the semi-mechanism aging model. Where "*" in S6 indicates that samples with logical results were single.

A	B	pK^0	C	F	G	H	RMSE
86.2	31.9	7.27	0	0.000152	− 0.189	0	8.32%

Table 4. Parameters of the semi-mechanism aging model and root-mean-square error (RMSE).

By comparing the predicted and measured E_{add} (%) in ten soils (Fig. 7), R^2=0.739**, indicating that this model could accurately predict the change in Pb concentration in the isotopic exchange state in soil with aging time and then evaluate the risk of heavy metal Pb in soil. Moreover, this model can be used to normalize the heavy metal data in the deduction of the safety threshold of soil Pb agricultural products.

In this model, according to Equation (9), aging time (Y_2) or SOM (Y_3) could be grouped together with pH and E_{add} (%), when another was fixed, to obtain 3D surface graphs such as Fig. 8 and Fig. 9 showing relationships between E_{add} (%) and pH, aging time or SOM. Fig. 8 is plotted by 154 groups fitting data of E_{add} (%), pH and aging

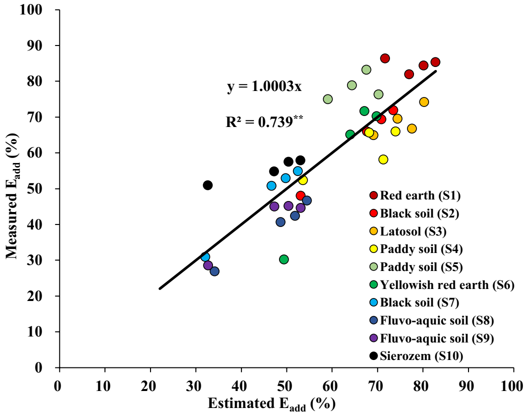

Figure 7. The comparison of measured E_{add} (%) and estimated E_{add} (%).

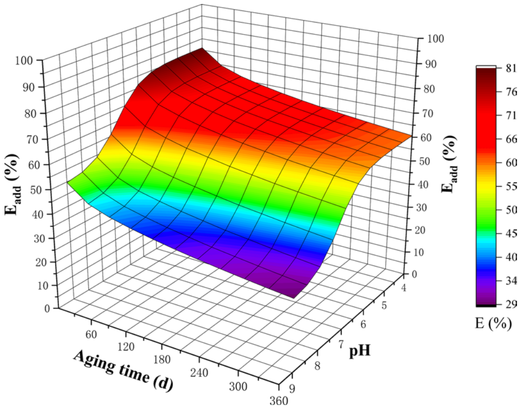

Figure 8. The combined effects of soil pH and aging time on E_{add} (%) when the SOM was set at 25 g/kg.

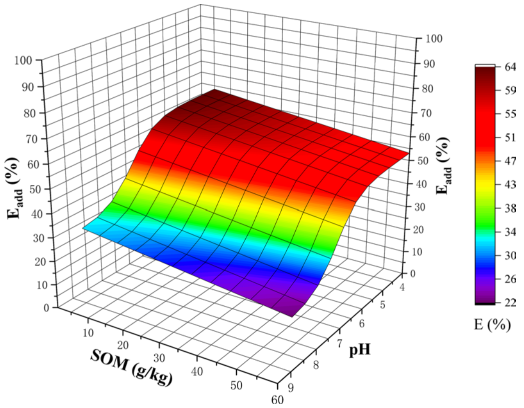

Figure 9. The combined effects of soil pH and SOM on E_{add} (%) when the aging time was set at 360 d.

time, with SOM approximately set at the mean value of China (25 g/kg, Yang[29]). Under these conditions, E_{add} (%) accounted from 80.1~29.1% with increasing pH (4.0~9.0) and aging time (0~360 d). Fig. 9 is plotted by 132 groups fitting data of E_{add} (%) pH and SOM at the longest aging time (360 d). E_{add} (%) ranges from 63.5~21.8% with increases in pH (4.0~9.0) and SOM (0~60 g/kg). Obviously, it can be observed that pH influences E_{add} (%) much more than others, and especially, E_{add} (%) tended to decrease sharply when the pH was over 6.0.

Moreover, Fig. 10 shows that Y_1 (0.02%, pH, 4.0) is close to zero, and Y_1 (26.9% pH, 8.0) is much larger than Y_1 (1.63%, pH, 6.0); Y_2 increases with aging time from 1.4% to 21.8%; Y_3 increases with SOM (2~6%) from

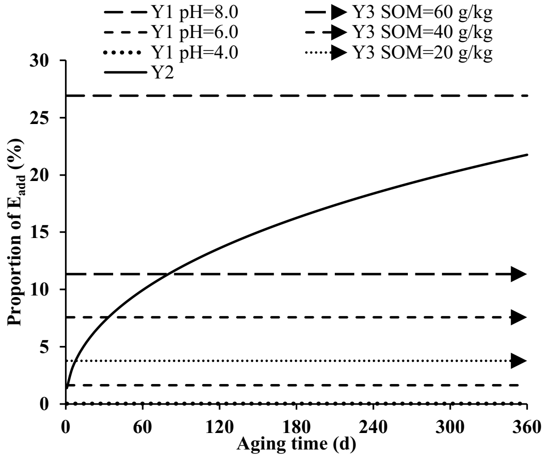

Figure 10. The distribution of E_{add} (%) changed with aging time (d) and pH and SOM (g/kg) in soil. From Eq. (9), Y_1 represents the pH-dependent portion, Y_2 represents the aging time-dependent portion, and Y_3 represents the SOM-dependent portion.

3.8% to 11.3%. Then, E_{add} (%) would constantly change under these three aging processes and eventually reach equilibrium.

Conclusion

The solution of 0.2 mM EDTA can be selected to replace the conventional extractants ($CaCl_2$, NH_4NO_3) for the measurement of the abundance of ^{208}Pb and ^{206}Pb in the soil liquid phase, as well as the isotopic exchangeability of Pb in soil, to characterize the aging of Pb added to soils. The semi-mechanism aging model of Pb added to soils based on precipitation/nucleation, micropore diffusion and organic matter encapsulation has been constructed by E_{add} (%), which can well estimate the aging of added Pb in an isotopically exchangeable state at different aging times and reflect the risk of absorption by crops. Soil pH is the principal factor affecting the aging degree of Pb added to soils, and micropore diffusion is the main process leading to aging after the initial stage. The model can be used to predict the isotopic exchangeability of Pb added to soils based on three parameters: soil pH, SOM, and aging time.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

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Author contributions

Xuezhi Ji finished the mostly experiments and wrote the main manuscript text; Yibing Ma offered the idea of this study and the keys of isotope dilution; Jumei Li solved the problems of experiments to ensure the methods are reasonable and assisted in data analysis; Ying Zhong finished the determinations of the isotope dilution by MC-ICP-MS; Shuo Sun finished the sampling; aging incubates of soils and extraction by calcium chloride; All authors reviewed the manuscript.

Competing Interests

The authors declare no competing interests.

Additional information

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