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Investigating the origin of Pb pollution in a terrestrial soil–plant–snail food chain by means of Pb isotope ratios

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Abstract

Lead isotope ratios were used to trace the origin of Pb in a soil–plant (*Urtica dioica*)–snail (*Cepaea nemoralis*) food chain in two polluted locations in the floodplains of the rivers Meuse and Rhine (Biesbosch National Park) and one reference location in the Netherlands. Lead isotope ratios and concentrations were determined in soil, litter, plant leaves, snails, rainwater and airborne particulate matter. Anthropogenic Pb in the soils of all locations was found to be derived from deposition of Pb polluted river sediments. Discharging rivers influenced the reference location before being reclaimed from the sea. The river sediment contains anthropogenic Pb from various sources related to industrial activities in the hinterland of the rivers Meuse and Rhine. Lead in the atmosphere contributed substantially to Pb pollution and Pb transfer in plant leaves and snails in all locations. Lead pollution in plant leaves and snails can be explained from a mixture of river sediment-Pb and atmospheric Pb from various transfer routes that involve low concentrations.

1. Introduction

Lead is a trace element occurring naturally in rocks and soils. Due to a low melting point, the metal has been smelted and worked since historic ages, resulting in widespread environmental Pb pollution (Davies, 1990; Nriagu, 1978). Although legislative measures have been taken to decrease Pb emissions to the environment, many places in the world are still polluted with Pb due to the element's

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long residence time, and its tendency to accumulate in soils and sediments (Davies, 1990; Pain, 1995).

In the western part of the Netherlands, the rivers Rhine and Meuse unite. This floodplain area, designated as Biesbosch National Park, has been exposed to chronic and diffuse pollution of Pb, as well as other inorganic and organic pollutants (Dirksz et al., 1990; Otte, 1991; Van der Scheer and Gerritsen, 1998; Winkels and Vink, 1993). Metal pollution in the sediments and sediment-derived soils mainly originates from the 1960s and 1970s, when the metal load in the rivers was very high (Beurskens et al., 1993; Middelkoop and Van Haselen, 1999). In an earlier study, metal concentrations were investigated in a soil–plant (*Urtica dioica*)–snail (*Cepaea nemoralis*) food chain in the Biesbosch and two reference locations outside this area (Notten et al., 2005). This food chain was selected because stinging nettles (*U. dioica*; Urticaceae) and *C. nemoralis* Linnaeus (Pulmonata) are very common in the Biesbosch, and *C. nemoralis* includes nettle leaves in its diet (Grime et al., 1970; Wolda et al., 1971). Besides, terrestrial snails are well known for their metal accumulating capacities (Dallinger et al., 2001). Elevated Pb concentrations were found in all compartments of the food chain in the Biesbosch, as well as positive relationships of Pb concentrations between the snail-leaf and snail-soil compartments (Notten et al., 2005). The results showed that Pb transfers to snails via nettle leaves as well as directly from the soil.

Investigating Pb concentrations, however, does not reveal the origin of Pb pollution in the food chain. This can be studied using ratios of the stable Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb). The isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are the result of the radioactive decay of U and Th (^{238}U, ^{235}U and ^{232}Th, respectively). Lead-204 is the only nonradiogenic Pb isotope (Faure, 1997). The ratios of these isotopes are used to trace the origin of Pb, and to distinguish anthropogenic Pb from naturally occurring Pb (Faure, 1997). Basically, Pb ores have characteristic Pb isotope ratios, which depend on the initial U/Pb and Th/Pb ratios as well as on the geological age of the source rocks from which Pb was removed during the ore formation. In this way, products that originate from specific Pb ore deposits, have characteristic Pb isotope ratios (Faure, 1997). For example, the ^{206}Pb/^{207}Pb ratio of leaded fuel used in the Netherlands (1.10–1.12) clearly differs from the ratio of natural Pb in Dutch clay soils (1.18–1.21) (Walraven and Van Os, 1997).

The use of Pb isotope ratios has proved to be a useful tool for tracing the origin of Pb in soils, sediments and atmospheric compartments such as snow and particulate matter (Haack et al., 2003; Hansmann and Koppel, 2000; Monna et al., 2000; Rosman et al., 1994; Widory et al., 2004). In addition, Pb isotope ratios have been determined in organisms, such as in bird bones and blood, mussels, peat and lichens (Klaminder et al., 2003; Labonne et al., 2001; Meharg et al., 2002; Scheuhammer et al., 2003; Simonetti et al., 2003). In a similar way, Pb isotope ratios in snails and stinging nettles can be used to trace the origin of Pb pollution in the soil–plant–snail food chain in the polluted floodplains of the Biesbosch.

The current study aimed at tracing the origin of Pb pollution in the terrestrial soil–plant (*U. dioica*)–snail (*C. nemoralis*) food chain in the Biesbosch. Similar Pb isotope ratios in different food chain compartments indicate a possible common source of Pb pollution in these compartments, and thus transfer of specific Pb through the food chain. It was expected that Pb in plants and snails in the Biesbosch would be mainly derived from direct or indirect transfer from the soil, and thus mainly originate from the Pb pollution of the 1960s and 1970s that is still present. Other possible Pb origins in the food chain compartments are natural Pb from the soil and Pb in contemporary atmospheric pollution.

Atmospheric Pb concentrations have sharply decreased since the ban on leaded fuel, and concentrations are well below air quality standards (recent atmospheric Pb concentrations are about 15 ng m^{-3}) (Buijsman, 2004). It was expected that the contribution of Pb in the atmosphere to Pb pollution in the soil–plant–snail food chain in the Biesbosch would be low. The situation in the Biesbosch was compared with a reference location outside the Biesbosch in which Pb concentrations in the food chain compartments are low (Notten et al., 2005). This location is not situated in a floodplain area, and a larger contribution of natural and atmospheric Pb was expected in comparison with the situation in the Biesbosch.

To realize the research aim, the main compartments of the soil–plant–snail food chain were sampled in two polluted locations in the Biesbosch and the reference location. In addition, airborne particulate matter and rainwater were sampled to describe the isotopic composition of contemporary atmospheric Pb pollution. Total Pb concentrations were also determined in all samples, because in many cases the combination of isotope ratios and concentration data provides more specific information on mixing and transfer of potential pollution sources (Faure, 1997; Labonne et al., 2001; Monna et al., 2000). Few other studies have measured Pb isotope ratios in terrestrial snails and vegetation. Newman et al. (1994) measured Pb isotope ratios in terrestrial snails, but they focused on the shells only. In addition, the current study is the first that investigated Pb isotope ratios in the Biesbosch.

2. Materials and methods

2.1. Field locations

Two locations were selected in Biesbosch National Park: BB1 (51°45′ N, 4°46′ E) and BB2 (51°48′ N, 4°45′ E). BB1 is not accessible to the public, while BB2 is situated in a recreational area. Due to human-induced hydrological changes, the locations are currently not flooded (BB1), or only flooded sporadically (BB2). The reference location (REF: 52°28′ N, 5°26′ E) is situated in a forestry area in the northern part of the Netherlands. All locations were studied in a field survey earlier (Notten et al., 2005, the locations BB1, BB2 and REF were named Poll-2, Poll-4 and Ref-1, respectively). *C. nemoralis* and *U. dioica* were abundant in all locations.

2.2. Field sampling procedure

At each location, the following compartments were sampled in July 2003: soil, litter, plant leaves, snails and rainwater. One soil core per location was sampled with a stainless steel soil corer (diameter 10 cm) to a depth of 15 cm. In this way, the entire rooting zone of stinging nettles was included. The core was divided into 5 slices of 3 cm each. Subsoil samples obtained earlier in the Biesbosch ($n = 2$, depth interval 50–80 cm, spring 2003) and in the vicinity of REF ($n = 1$, depth interval 100–120 cm, spring 2002) were included in the dataset. These samples were not taken exactly in the selected locations. It was assumed that Pb concentrations and the Pb isotope composition in these subsoil samples are characteristic for the unpolluted situation in the respective areas. One litter sample was taken per location.

Two *U. dioica* samples were collected per location, each consisting of 7 leaves sampled at random. Two mixed leaf samples per location were also taken. These samples also included possible other food sources and resting places for *C. nemoralis*. Leaves of the most common plant species were sampled in such a way that the quantity was in accordance with the abundance of the plant species. Vegetation composition differed among the locations, and thus the composition of the mixed leaf samples differed accordingly. *U. dioica* and *Galium aparine* were present in all locations. BB1 samples also included leaves of *Phragmites australis*, *Symphytum officinale* and *Calystegia sepium*, whereas BB2 samples also contained leaves of *Rubus fruticosus* and *Humulus lupulus*. REF samples also included *Cirsium arvense*.

Two adult *C. nemoralis* snails were sampled per location by means of hand searching. All snails had a brown-black ‘lip’, indicating adulthood (Williamson, 1976). Rainwater was collected in the Biesbosch and at the reference location during the week preceding the other sampling activities. It was assumed that there is no difference in the Pb isotope composition of rainwater falling on BB1 and BB2, because they are only 5 km apart. Therefore, only one rain gauge was installed close to BB1. The rain gauges consisted of a 500 mL LDPE bottle covered with Al foil, connected to a funnel (area 177 cm^2). The inside of the funnel was covered with a nylon mesh. The gauges were placed at the same height as the vegetation (between 1.50 and 2 m).

During another survey in the Biesbosch, airborne particulate matter (APM) was sampled with quartz-filters (Schleicher & Schuell QF20, diameter 150 mm) by means of a high volume sampler close to BB1. Four of these filters were also used in the current study. The selected filters were derived from 24 h sampling (sampling rate approximately 70 $\text{m}^3\,\text{h}^{-1}$) on four different dates (10 June 2002, 11 February 2003, 4 March 2003 and 5 March 2003) with varying wind directions (W, SE, SE and S, respectively). The sampling dates did not correspond with the sampling period of the other compartments.

2.3. Laboratory procedures

2.3.1. Soil sample preparations

Soil samples were hand sorted to remove roots and debris, and dried (60 °C, 4 days). For Pb and Al_2O_3 analysis by means of X-ray fluorescence (XRF), a subsample (10 g) was ground and subsequently pressed with wax into tablets by means of an automated grinding- and pressing machine (Herzog

HSM-HTP). One sample of ISE 921 reference material (International Soil Exchange Programme; river sediment) was included in the entire procedure.

For Pb isotope analysis by means of ICP-MS, soil subsamples (about 0.125 g) were digested with 16 M HNO_3, 12 M $HClO_4$ and 29 M HF. All acids used were prepared by sub-boiling analytical grade commercial acid (Merck, p.a. quality). One sample of ISE 921 reference material and one blank were included.

2.3.2. Preparation of other sample types

All leaf samples were rinsed in demineralized water, and dried (60 °C, 4 days). Soil particles were removed from the litter samples. The snails were kept for two days without food to evacuate their guts, and subsequently killed by immersion in boiling tap water. Then they were dissected into shell, digestive gland and the remaining soft tissues. All parts were dried (60 °C, 4 days). Lead taken up by snails mostly accumulates in the digestive gland, and therefore only this soft tissue part was taken into consideration (Dallinger et al., 2001). Shells were cleaned in an ultrasonic bath with MilliQ water.

All chemical operations were carried out in a class A100 laminar flowhood. All solutions were made with Teflon distilled acids and MilliQ water. Ground leaf and litter samples, snail digestive glands, snail shells and filter samples were digested with a mixture of 6–7 M HCl, 14 M HNO_3 and 9 M HBr at 100 °C. Rainwater samples were evaporated to dryness, and the residue dissolved in 3 M HNO_3. After two days at 100 °C, all sample types were evaporated to dryness at 120 °C, and dissolved in 0.7 M HBr. Subsamples of this solution, evaporated to dryness and nitrated with 14 M HNO_3, were used to determine total Pb concentrations on ICP-MS. Before concentration measurements, samples were dissolved in 1% HNO_3. Five control blanks and one sample of BCR 062 reference material (Institute for Reference Materials and Measurements; olive leaves) were included during the entire procedure.

The remaining 0.7 M HBr solutions were separated on 0.17 mL quartz columns with AG X-8 200–400 mesh anion exchanger. The Pb fraction, in 6–7 M HCl, was equally divided in two aliquots. One aliquot was used for isotope analysis, and the other one was used to determine post-column Pb concentrations. These were determined in order to synchronize sample and standard concentrations before isotope measurements. Both aliquots were evaporated to dryness at 120 °C, and nitrated with 14 M HNO_3. Before analysis, the samples were dissolved in 1% HNO_3.

2.4. Pb concentration analyses

2.4.1. Soil samples

Soil tablets were analysed for Pb and Al_2O_3 using an ARL9400 X-ray spectrometer fitted with a Rh tube, with full matrix correction for major elements and Compton scatter method for trace elements. Precision and accuracy of ISE 921 based on the current measurement and many measurements before was 0.5–1% relative standard deviation and 1–5% relative standard deviation, respectively. The accuracy of Pb and Al_2O_3 concentrations of the ISE 921 measurements was within $166 \pm 8.4\ \mathrm{mg\ kg^{-1}}$ (2sd) and $10.6 \pm 0.4\%$ (2sd), respectively.

2.4.2. Other sample types

All samples for Pb concentration analysis (before and after column separation) were measured on an ICP-MS HP 4500+ at standard settings. The result of the measurement of olive leaves reference material (only determined before column separation) was within the certified range for Pb ($25 \pm 1.5\ \mathrm{mg\ kg^{-1}}$). The mean (±se) Pb concentration in the procedural blanks was 90 (20) ng L^{-1}.

2.5. Pb isotope analysis

2.5.1. Soil samples

Pb isotope composition of the soil samples was determined with an Agilent 7500a ICP-MS equipped with low uptake nebulizer. Data were taken in the peak jumping mode with 3 data points acquired across each peak at masses m/z 201, 204, 206, 207 and 208. Ten runs were measured for each sample. For mass bias correction, a sample of NIST SRM 981 standard was measured after each batch of 6 samples. The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the soil samples were determined with a precision of 2sd < 0.14% and 2sd < 0.07%, respectively. The accuracy of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the measured ISE 921 sample was within 1.166 ± 0.002 (2sd) and 2.444 ± 0.003 (2sd), respectively. Reagents used and the procedural blank contained negligible amounts of Pb (<20 ng L^{-1}).

2.5.2. Other sample types

Lead isotope measurements of the other sample types were carried out on a ThermoFinnigan

Neptune MC-ICP-MS using the sample standard bracketing technique. Sample concentrations determined in post-column aliquots were matched with SRM 981 concentrations (National Institute of Standards and Technology; common lead isotopic standard) at 100 or 50 $\mu g\,L^{-1}$. Each sample measurement was incorporated in two measurements of running blanks (1% HNO_3) and SRM 981. Every sample was measured in 3 blocks of 30 runs. The mean value of the sample was corrected for mass bias with an exponential correction, using the data of the previous and the next SRM 981 measurements. One sample of SRM 982 reference material was measured during each series. The accuracy of $^{207}Pb/^{206}Pb$ ratios of SRM 982 measurements was within certified values (0.46707 ± 0.0002) for 6 series. The SRM 982 measurement of one series exceeded the certified value (deviation = 1.7%). Precision of $^{206}Pb/^{207}Pb$ ratios of all samples (total 7 series) was 2sd < 0.013%.

2.6. Calculations

To calculate the natural and anthropogenic Pb concentrations in the soil samples, results of the research of Huisman (1998) were used. He investigated natural variation in heavy metal concentrations in Dutch subsoils, and found a strong relationship between the natural metal concentrations and Al concentrations (expressed as Al_2O_3 (%)). This relationship is based on the joint occurrence of Al_2O_3 and metals in aluminosilicates. His dataset has been expanded, and comprises more than 5000 subsoil samples. For Pb, the following relationship was found (Fig. 1)

$$[Pb]n = 1.308 \times (Al_2O_3) + 3.86 \qquad (1)$$

in which $[Pb]n$ is the natural Pb concentration ($mg\,kg^{-1}$ dw), and Al_2O_3 is the Al_2O_3 concentration (%) of the soil ($n = 5219$; $R^2 = 0.80$; standard error of estimate = 3.13). Because Dutch soils are seldom polluted with Al, the anthropogenic Pb concentration in the soil ([Pb]a) ($mg\,kg^{-1}$ dw) can be calculated from the following equation:

$$[Pb]a = [Pb]t - [Pb]n \qquad (2)$$

where $[Pb]t$ ($mg\,kg^{-1}$ dw) is the measured total Pb concentration in the soil sample, and $[Pb]n$ the natural Pb concentration in the sample calculated from Eq. (1).

If both natural and anthropogenic Pb is present, the total (measured) Pb isotope composition in the soil is a mixture of the isotope composition of natural and anthropogenic Pb. To derive the Pb isotope composition of anthropogenic Pb, it is necessary to adjust for the amount of natural Pb present in the soil. The following equation describes this mass balance principle:

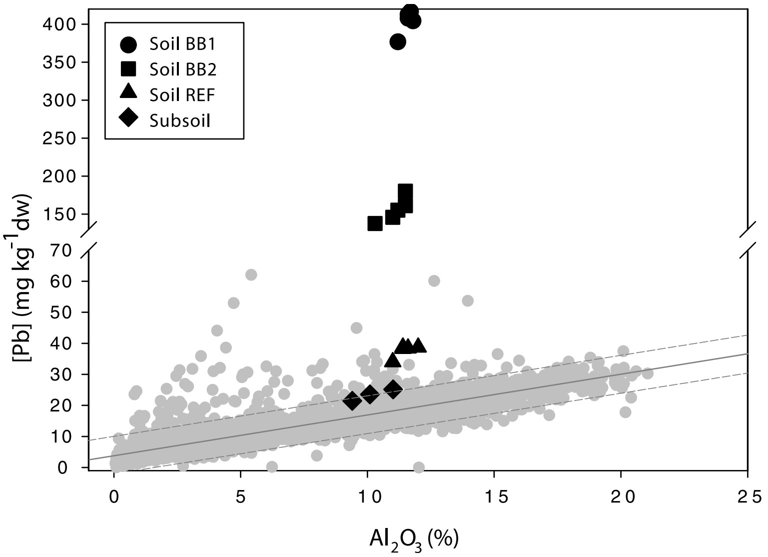


Fig. 1. Pb ($mg\,kg^{-1}$ dw) versus Al_2O_3 (%) concentrations of topsoil cores (divided in 5 samples of 3 cm each) taken in two polluted locations in Biesbosch National Park (BB1 and BB2) and the reference location (REF); and of subsoil samples collected in the Biesbosch area ($n = 2$) and the vicinity of the reference location ($n = 1$). The regression line (±95% confidence level) is formed by Pb ($mg\,kg^{-1}$ dw) and Al_2O_3 (%) concentrations of samples (grey dots) in Dutch subsoils (Huisman, 1998, extended dataset; see text, Eq. (1)).

$$({}^{x}\mathrm{Pb}/{}^{y}\mathrm{Pb})a \times [\mathrm{Pb}]a = ({}^{x}\mathrm{Pb}/{}^{y}\mathrm{Pb}) \times [\mathrm{Pb}]t - ({}^{x}\mathrm{Pb}/{}^{y}\mathrm{Pb})n \times [\mathrm{Pb}]n \qquad (3)$$

in which the letters *a*, *t* and *n* indicate the Pb concentration [Pb] and Pb isotope ratio (^{x}Pb/^{y}Pb) of the anthropogenic, total and natural Pb fraction, respectively. It was assumed that the natural Pb isotope ratios (^{x}Pb/^{y}Pb)*n* in the soils of the Biesbosch and the reference location are equal to the measured ratio in the respective subsoil samples. For calculating the anthropogenic isotope ratios in the soils of the Biesbosch locations, the mean ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratio of both Biesbosch subsoil samples was used in Eq. (3).

3. Results

3.1. Soil compartment

Total Pb concentrations in the soil cores of the floodplain locations BB1 and BB2 were on average 11 and 4 times higher than the mean concentration in the reference core, respectively (Table 1). The Pb concentrations within each core did not vary considerably with depth. Total Pb concentrations in the topsoil of both Biesbosch locations as well as in the reference location were higher than the concentrations in the subsoil samples (Table 1). The concentrations in the subsoil samples were near the upper confidence level of the relationship between Pb and Al_2O_3 concentrations in the samples of Huisman (1998) (Fig. 1). This confirms the assumption that the subsoil samples were not influenced by anthropogenic Pb.

The ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the 3 subsoil samples (Table 1) were similar to the ratios known to be typical for Dutch clay soils (^{206}Pb/^{207}Pb = 1.18–1.20, ^{208}Pb/^{207}Pb = 2.46–2.48) (Walraven et al., 1997).

The calculated contribution of anthropogenic Pb to the total Pb concentration in the topsoil samples

Table 1
Measured total soil Pb (mg kg^{-1} dw) and Al_2O_3 (%) concentrations; calculated natural and anthropogenic Pb concentrations (mg kg^{-1} dw); and measured total and calculated anthropogenic ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in soil cores from two polluted locations (Loc.) in Biesbosch National Park (BB1 and BB2); two Biesbosch (BB) subsoil samples (subsoil 1 and 2); one soil core in the reference location (REF); and a subsoil sample in the vicinity of the reference location (subsoil 3)

Loc.	Sample	[Pb]*t*	Al_2O_3	[Pb]*n*	[Pb]*a*	Perc [Pb]*a*	$\left(\frac{^{206}Pb}{^{207}Pb}\right)_t$	$\left(\frac{^{206}Pb}{^{207}Pb}\right)_a$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)_t$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)_a$
BB	Subsoil 1	23.5[a]	10.1	–[a]	–	–	1.196[b]	–	2.457[b]	–
	Subsoil 2	21.5[a]	9.4	–[a]	–	–	1.201[b]	–	2.461[b]	–
BB1	0–3 cm	377	11.2	18.5	358	95.1	1.164	1.162	2.447	2.442
	3–6 cm	404	11.8	19.3	385	95.2	1.164	1.162	2.445	2.440
	6–9 cm	408	11.6	19.0	389	95.3	1.163	1.162	2.444	2.436
	9–12 cm	413	11.6	19.0	394	95.4	1.163	1.161	2.443	2.435
	12–15 cm	417	11.7	19.1	397	95.4	1.163	1.161	2.441	2.435
BB2	0–3 cm	146	11.0	18.2	128	87.5	1.165	1.160	2.439	2.443
	3–6 cm	138	10.3	17.3	120	87.5	1.164	1.159	2.438	2.442
	6–9 cm	155	11.2	18.6	137	88.0	1.164	1.160	2.438	2.440
	9–12 cm	161	11.5	19.0	142	88.2	1.166	1.162	2.444	2.439
	12–15 cm	180	11.5	18.9	161	89.5	1.165	1.161	2.444	2.440
REF	Subsoil 3	25.1[a]	11.0	–[a]	–	–	1.195[c]	–	2.467[c]	–
REF	0–3 cm	34.0	11.0	18.3	15.7	46.2	1.177	1.155	2.455	2.440
	3–6 cm	38.4	11.6	19.0	19.4	50.5	1.177	1.158	2.453	2.439
	6–9 cm	38.3	11.4	18.7	19.5	51.0	1.176	1.158	2.454	2.440
	9–12 cm	38.7	11.4	18.8	19.9	51.4	1.175	1.156	2.454	2.440
	12–15 cm	38.7	12.0	19.6	19.1	49.4	1.175	1.154	2.453	2.438

t = total; *n* = natural; *a* = anthropogenic. Perc [Pb]*a* = percentage anthropogenic Pb. The soil cores of BB1, BB2 and REF were divided into 5 samples of 3 cm each (sample codes indicate depth below ground level). Natural and anthropogenic Pb concentrations, and anthropogenic Pb isotope ratios were calculated with Eqs. (1)–(3) (see text).

[a] The measured total soil Pb concentrations ([Pb]*t*) in the subsoil samples (see also Fig. 1) were assumed to equal the natural Pb concentrations ([Pb]*n*) in these samples.

[b] Total ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the Biesbosch subsoil samples were assumed to equal the natural Pb isotope ratios in the Biesbosch locations, and the means (1.199 and 2.459, respectively) were used as (^{x}Pb/^{y}Pb)*n* in Eq. (3) (see text).

[c] The total ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratio of the REF subsoil sample were assumed to equal the natural Pb isotope ratios in the reference location, and these ratios were used as (^{x}Pb/^{y}Pb)*n* in Eq. (3) (see text).

(Eqs. (1) and (2)) of BB1 and BB2 was on average 95% and 88%, respectively (Table 1). Total ^{206}Pb/^{207}Pb ratios in the Biesbosch cores were similar and ranged between 1.163 and 1.166 (Table 1). The ^{208}Pb/^{207}Pb ratios were also similar within the two Biesbosch cores, although the range was somewhat larger (range 2.438–2.447) (Table 1). There were no consistent differences across the soil profile for both ratios. Calculated anthropogenic ^{206}Pb/^{207}Pb ratios in both Biesbosch cores varied between 1.159 and 1.162, and the anthropogenic ^{208}Pb/^{207}Pb ratios ranged between 2.435 and 2.443.

The percentage anthropogenic Pb in the soil samples of the reference location was lower than in the Biesbosch cores, and was on average 50% of the total Pb concentration. Total ^{206}Pb/^{207}Pb ratios in the samples of the REF core were higher than in the samples of the Biesbosch cores, and ranged between 1.175 and 1.177 (Table 1). ^{208}Pb/^{207}Pb ratios were also higher (range 2.453–2.455) than in the Biesbosch. No remarkable variation with depth was observed for both ratios. The anthropogenic ^{206}Pb/^{207}Pb ratios in the REF core (range 1.154–1.158) were only slightly lower than in the Biesbosch. The ^{208}Pb/^{207}Pb ratios (range 2.438–2.440) were similar to the values found in the Biesbosch soil cores.

3.2. Biotic sample types

The highest Pb concentrations of all food chain compartments in all locations were found in the snails' digestive glands and the litter samples (Table 2). The other food chain compartments showed the same sequence of concentrations in all locations: *U. dioica* leaf > mixed leaf > snail shells. There was a rather large difference between the Pb concentrations of the two digestive gland and shell measurements of both Biesbosch locations.

^{206}Pb/^{207}Pb ratios in all biotic sample types of BB1 ranged between 1.156 and 1.163 (Table 2). ^{206}Pb/^{207}Pb ratios in most of the samples of BB2 and REF fell within this range also. ^{208}Pb/^{207}Pb ratios in the biotic samples of BB1 ranged between 2.425 and 2.435. For BB2 (range 2.414–2.441), these ratios were mostly somewhat lower, although the values of two samples (litter and digestive gland) were higher than the BB1 range. The ^{208}Pb/^{207}Pb ratios in the biotic samples of the reference location (range 2.417–2.430) fitted within the range of BB1, or were somewhat lower.

3.3. Rainwater and airborne particulate matter

Lead concentrations in the rainwater samples were low: 2.43 and 0.38 μg L^{-1} for the Biesbosch area and the reference location, respectively (Table 3). Isotope ratios did not differ between the two sample areas (Table 3). ^{206}Pb/^{207}Pb ratios in the rainwater (1.151–1.152) were generally lower than the ratios measured in most other compartments. The ^{208}Pb/^{207}Pb ratios (2.425 for both areas) were similar to the ^{208}Pb/^{207}Pb ratios in the biotic samples.

Lead concentrations in airborne particulate matter (APM), determined from the concentrations in the filters, ranged between 9.73 and 21.0 ng m^{-3} (Table 3). These concentrations are well below the Dutch air quality standard ([Pb] < 0.5 μg m^{-3}) (VROM, 2001). ^{206}Pb/^{207}Pb ratios in APM samples covered a large range: 1.155–1.172. This range was smaller for the ^{208}Pb/^{207}Pb ratios (range 2.421–2.431). The Pb isotope ratios of two of the four

Table 2
Total Pb concentrations (μg g^{-1} dw), ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios in litter ($n = 1$), plant leaves (*Urtica dioica* and mixed leaf, see text ($n = 2$)) and snail (*Cepaea nemoralis*) parts (digestive gland and shell ($n = 2$)) sampled in two polluted locations in Biesbosch National Park (BB1 and BB2) and the reference location (REF)

Sample type	Nr.	BB1			BB2			REF		
		[Pb]	$\left(\frac{^{206}Pb}{^{207}Pb}\right)$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)$	[Pb]	$\left(\frac{^{206}Pb}{^{207}Pb}\right)$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)$	[Pb]	$\left(\frac{^{206}Pb}{^{207}Pb}\right)$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)$
Litter	1	5.14	1.160	2.433	4.22	1.163	2.437	1.85	1.163	2.430
Mixed leaf	1	0.41	1.159	2.427	1.13	1.157	2.422	0.44	1.158	2.424
	2	0.48	1.162	2.427	1.27	1.148	2.414	0.65	1.160	2.425
U. dioica leaf	1	1.61	1.156	2.426	2.20	1.152	2.423	0.70	1.158	2.424
	2	1.99	1.156	2.425	2.20	1.155	2.423	1.01	1.157	2.423
Snail digestive gland	1	2.20	1.162	2.430	12.73	1.166	2.441	1.22	1.162	2.430
	2	5.05	1.163	2.435	2.48	1.161	2.422	1.39	1.160	2.425
Snail shell	1	0.07	1.156	2.425	0.28	1.158	2.431	0.22	1.144	2.417
	2	0.19	1.157	2.429	0.17	1.161	2.434	0.44	1.150	2.422

Table 3
Pb concentrations, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios in rainwater collected in Biesbosch National Park (near BB1) and in the reference location (REF), and in airborne particulate matter (APM) sampled near BB1

Sample type	Collection date	BB1			REF		
		[Pb]	$\left(\frac{^{206}Pb}{^{207}Pb}\right)$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)$	[Pb]	$\left(\frac{^{206}Pb}{^{207}Pb}\right)$	$\left(\frac{^{208}Pb}{^{207}Pb}\right)$
Rainwater	1–10 July 2003	2.43[a]	1.152	2.425	0.38[a]	1.151	2.425
APM	10 June 2002	9.73[b]	1.164	2.421	–	–	
	11 November 2002	11.5[b]	1.172	2.426	–	–	–
	4 March 2003	14.3[b]	1.159	2.431	–	–	–
	5 March 2003	21.0[b]	1.155	2.426	–	–	–

[a] $\mu g\ L^{-1}$.
[b] $ng\ m^{-3}$.

APM samples were in the same range as the Pb isotope ratios of the biotic samples.

4. Discussion

4.1. Origin of Pb pollution in the soils

The calculations (Eqs. (1) and (2)) showed that the topsoils of all locations are polluted with Pb of anthropogenic origin (Table 1). The Pb concentrations in the Biesbosch soil cores are high, and almost all Pb (88–95%) has an anthropogenic origin (Table 1). This causes the similarity between the total Pb isotope ratios and the anthropogenic Pb isotope ratios (Table 1). The contribution of natural Pb is thus only 5–12%. The Pb concentrations in the soil core from the reference location are low. Only half of the Pb in the reference soil samples has an anthropogenic origin, and thus the other half is natural (Table 1). Therefore, total isotope ratios are higher, and are more similar to the range characteristic of natural Pb in Dutch clay soils (Walraven and Van Os, 1997). The difference between total and anthropogenic Pb isotope ratios is thus larger than in the case of the Biesbosch soil cores.

To trace the origin of anthropogenic Pb in the soil, the anthropogenic $^{208}Pb/^{207}Pb$ ratios of all soil samples were plotted versus the $^{206}Pb/^{207}Pb$ ratios in a so-called 3-isotope plot. This plot also includes data of Pb origins that may be responsible for anthropogenic Pb in the studied soils (Fig. 2). The ellipses in this figure include the majority of samples of a specific origin (e.g., roadside soil, subsoil samples) or group of sources (e.g., galena and charcoal). Generally, Pb sources plotted in this 3-isotope plot form more or less a straight line, in which the geological old sources plot in the lower left corner of the graph, and the young sources in the upper right corner. The old sources were withdrawn from their source regions when the amount of radiogenic Pb was low. This results in low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios. The shape of the relationship between both isotope ratios corresponds with a part of the Pb growth curve (Faure, 1986).

The anthropogenic Pb isotope ratios of the soil cores of all locations form a distinct group, indicating that the anthropogenic Pb is derived from the same source or mixing of sources. This group overlaps with the majority of anthropogenic Pb isotope ratios in Meuse floodplain samples collected 200 km upstream (in: Van den Berg and Van Wijngaarden, 2000, locations and methods are described, but isotope ratios are not shown). The similarity between the ratios of Biesbosch soils and Meuse floodplains is obvious, because both are highly influenced by sedimentation, and thus sediment composition, of the Meuse. The River Rhine also deposits sediments in the Biesbosch area (Van den Berg, 1998), but isotope composition data of Dutch Rhine sediments is not available. Most of the samples in the Meuse dataset that have higher Pb isotope ratios, and are not included in the ellipse, are influenced by another river as well. This river crosses Zn and Pb ores in Belgium. This explains the similarity of these samples with galena and charcoal samples from Belgium.

No rivers are situated in the vicinity of the reference location, yet the anthropogenic Pb isotope ratios of the reference soil samples are similar to Biesbosch and Meuse floodplain ratios. The reference location is part of an area that was reclaimed from the sea between 1950 and 1970. Before this time, polluted sediments from river outlets influenced the current soil. For example, river IJssel, a branch of the river Rhine, discharged in the area. The results suggest that, in the past, deposited river sediments in this area were polluted with Pb from a similar mixture of sources as the Biesbosch floodplains. The contribution of anthropogenic Pb to

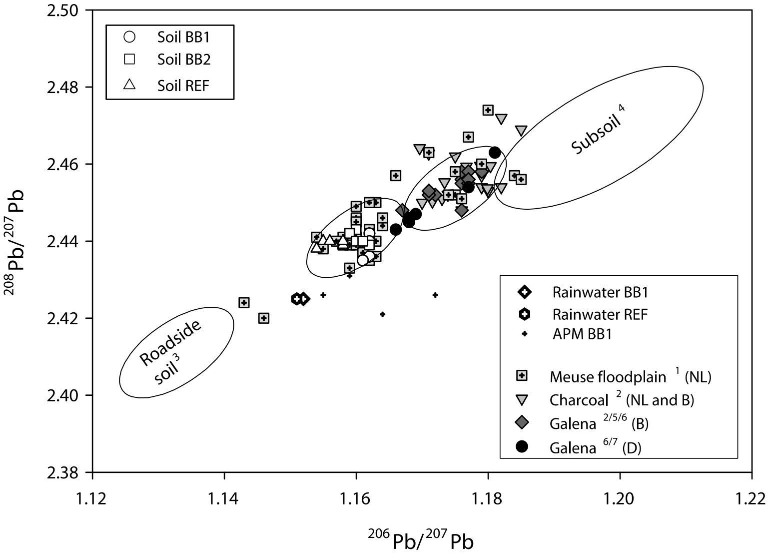


Fig. 2. Calculated (see text, Eq. (3)) anthropogenic ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb ratios of topsoil cores (divided in 5 samples of 3 cm each) collected in two locations in Biesbosch National Park (BB1 and BB2; $n = 1$) and the reference location (REF; $n = 1$); ^{208}Pb/^{207}Pb–^{206}Pb/^{207}Pb ratios in rainwater sampled near BB1 ($n = 1$) and in REF ($n = 1$), and in airborne particulate matter (APM) collected near BB1 ($n = 4$). Ellipses include ^{208}Pb/^{207}Pb–^{206}Pb/^{207}Pb ratios of (groups) of possible Pb origins: Meuse (NL) floodplain samples ($n = 43$; the majority of the samples is included in the second ellipse from the left) ([1]see Van den Berg and Van Wijngaarden, 2000, for sampling description, isotope data not shown); Dutch ($n = 10$) and Belgian ($n = 10$) charcoal samples, and galena samples from Belgium (Plombières, $n = 14$, and Dinant, $n = 2$) and Germany (Rhine-Westphalian district, $n = 2$, Maubach, $n = 1$, and Harz Mountains, $n = 4$) ([2]Walraven et al., in preparation-c; [5]Cauet et al., 1982; [6]Pasteels et al., 1980; [7]Wedepohl et al., 1978) (the majority of the charcoal and galena samples is included in the third ellipse from the left); roadside soil (NL) samples ($n = 16$) ([3]Walraven et al., in preparation-b); and subsoil (NL) samples ($n = 78$) ([4]Walraven et al., in preparation-a).

the soils in the reference location (Table 1), however, is much lower than in the Biesbosch soils.

The anthropogenic Pb in the river sediment of the soils in all locations most likely consists of a mixture of different anthropogenic Pb sources, emitted largely during the 1960s and 1970s (Beurskens et al., 1993; Middelkoop and Van Haselen, 1999). The Pb isotope composition of the river sediment resembles Pb isotope ratios of Dutch and Belgian charcoal samples, and galena samples from Belgium (Plombières and Dinant) and Germany (Rhine-Westphalian district, Maubach and Harz Mountains) (Cauet et al., 1982; Pasteels et al., 1980; Walraven et al., in preparation-c; Wedepohl et al., 1978) (Fig. 2). These sources are related to industrial activities in the hinterland of the rivers Meuse and Rhine, and material is present in the sediment of both rivers. It is likely that other industrial Pb sources also contributed to the mixture of Pb pollution in the river sediment. Walraven and Van Os (1997) indicated a range of ^{206}Pb/^{207}Pb ratios between 1.15 and 1.18 for industrial Pb in the Netherlands, and the isotope ratios of the current soil samples fit in this range.

Current deposition of river sediment is not contributing greatly to Pb pollution in the selected Biesbosch locations. Only in BB2 does some sporadic flooding take place, leaving a new layer of sediment. But because current Pb concentrations in water and suspended matter in the Dutch rivers have improved considerably (VWS, 2004), the newly deposited sediment will not highly influence Pb isotope ratios in the soil.

The Pb isotope ratios of APM and rainwater clearly differ from the anthropogenic soil ratios (Fig. 2). This suggests that the contribution of current atmospheric Pb deposition to Pb pollution in soils and sediments of the Biesbosch is low. This was expected because of the current low Pb concentrations in the air (Buijsman, 2004). Lead concentrations and the Pb isotope composition of APM at the reference location were not determined. Possibly, Pb concentrations in the air in this location are lower than in the Biesbosch, because the location is situated in a less densely populated and less industrialized part of the Netherlands. It is assumed that the Pb isotope ratios of APM in the reference location are comparable with the ratios in the Biesbosch samples, due to the long-range transport of fine Pb particles (Pain, 1995). It is thus concluded that in the soils of the reference location the contribution of Pb from the atmosphere is low also.

Deposition of atmospheric Pb from the use of leaded fuel in the past could also have contributed to Pb pollution in the soils of the studied research locations. The anthropogenic Pb isotope ratios in the soils, however, clearly differ from the isotope composition of highly gasoline-influenced roadside soils (Fig. 2). This suggests that leaded fuel did not contribute greatly to Pb pollution in the soils of the 3 research locations. Large Pb particles in exhaust fumes are deposited close to the emission source, such as in road verges (Pain, 1995). None of the 3 locations is situated close to major roads, and a clear contribution of Pb from the use of leaded fuel was thus not expected. Fine particles derived from leaded fuel, however, can be carried by winds, and are deposited over very large areas (Pain, 1995). The results show that the contribution of this deposition is also negligible in the soils of the research locations.

4.2. Origin and transfer of Pb in plant leaves and snails

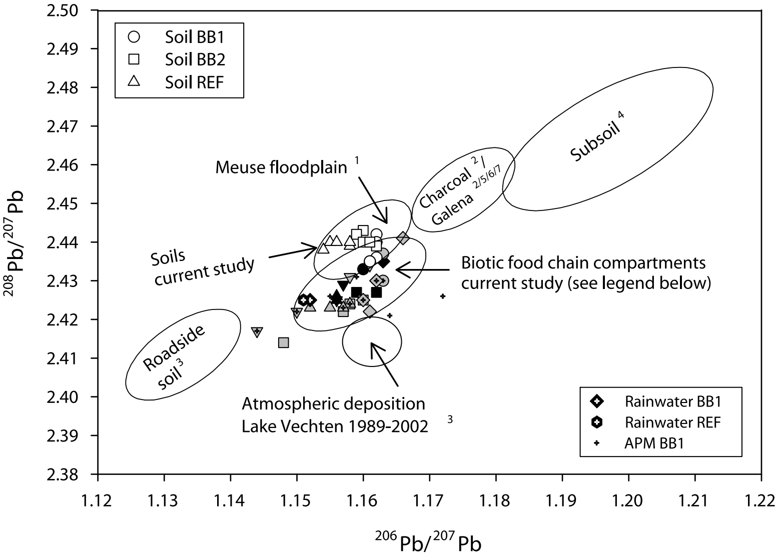
All ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb ratios in the biotic samples of the 3 locations form a distinct cluster if plotted in a 3-isotope plot (Fig. 3). Only two samples (mixed leaf BB2 and shell REF) have lower ratios. The ^{206}Pb/^{207}Pb ratios of the biotic cluster are similar to the range of ^{206}Pb/^{207}Pb ratios in the soil, and this implies that Pb in the soil is transferred to plant leaves and snails. However, the ^{208}Pb/^{207}Pb ratios of the biotic cluster (range 2.414–2.441) are lower than the ^{208}Pb/^{207}Pb ratios of the soil samples (range 2.435–2.443). This suggests the contribution of another Pb origin. From the data it can be inferred that the contribution of natural Pb to the Pb in plant leaves and snails is negligible. Otherwise, the Pb isotope ratios of plant leaves and snails should have been higher. This is also the case for the reference location in which half of the Pb in the soil is natural Pb. Thus, the suggested other Pb source should have an anthropogenic origin.

The Pb isotopic signature of the biotic cluster (both ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios) is similar to the Pb isotope ratios in rainwater and 2 out of 4 APM samples (Fig. 3). The Pb isotopic signature of the biotic cluster is also close to Pb isotope ratios measured in sediments in Lake Vechten in the Netherlands (Fig. 3). These sediments are only influenced by atmospheric deposition. In contrast to the data for rainwater and APM, the data from Lake Vechten give an integrated signal of atmospheric pollution between 1989 and 2002 (Walraven et al., in preparation-b). The variation in Pb isotope composition of these sediments is therefore smaller than those of the APM samples, which are prone to large temporal variations (Flament et al., 2002).

The results show that, despite low atmospheric Pb concentrations, contemporary atmospheric Pb pollution contributes substantially to Pb pollution levels in plant leaves and snails in all 3 locations. From the similarity of the Pb isotope ratios in leaves and snails to the Pb isotope ratios of the cluster of APM samples and in rainwater, it could be inferred that Pb from the atmosphere is the only contributor to Pb pollution in plant leaves and snails in all locations. It is more plausible, however, that the Pb pollution in plant leaves and snails is due to a mixture of atmospheric Pb and soil (i.e. river sediment) Pb. The integrated Pb isotopic signature found in the sediments of Lake Vechten is a more suitable measure for contemporary atmospheric Pb pollution than the small number of variable measurements in rainwater and APM in the current study.

Transfer of atmospheric Pb to plant leaves and snails can occur by a number of routes. Pb deposition on plant leaves sticks to the surface, and especially nettle leaves are expected to retain more Pb on their leaves due to their hairy, rough surface (Pain, 1995). Although the plant leaves were rinsed with demineralized water before analysis in the present study, the results suggest that atmospheric Pb was not removed completely, most probably due to the hairy surface. Otherwise, Pb isotope ratios of the plant leaves should have been more comparable to the Pb isotope ratios of the soils. Lead could also transfer through the leaf surface, but experimental studies have shown that only extremely small amounts of Pb penetrate the cuticle (Arvik and Zimdahl, 1974). Plants can also take up atmospheric Pb deposition via the soil. Snails can take up atmospheric Pb pollution directly by inhalation, or while feeding and moving on vegetation with a layer of atmospheric deposition on top of it (Gomot de Vaufleury and Pihan, 2000).

The suggested mixture of atmospheric and sediment-derived Pb in plant leaves and snails is caused by the transfer of Pb from several routes that



Location	Litter (n=1)	Mixed leaf (n=2)	Nettle leaf (n=2)	Snail digestive gland (n=2)	Snail shell (n=2)
BB1	●	■	▲	◆	▼
BB2	○	□	△	◇	▽
REF	⊙	⊡	⟁	◈	⩢

Fig. 3. ^{208}Pb/^{207}Pb versus ^{206}Pb/^{207}Pb ratios in the biotic compartments of a terrestrial soil–plant (*Urtica dioica*)–snail (*Cepaea nemoralis*) food chain in two locations in Biesbosch National Park (BB1 and BB2) and the reference location (REF) (for number of samples: see figure legend); in rainwater sampled near BB1 and in REF ($n = 1$); and in airborne particulate matter (APM) collected near BB1 ($n = 4$). Anthropogenic isotope ratios of soil samples from the 3 locations are also displayed (see also Fig. 2). Ellipses include ^{208}Pb/^{207}Pb–^{206}Pb/^{207}Pb ratios of (groups) of possible Pb origins (see Fig. 2 for more detail): Meuse (NL) floodplain samples ($n = 43$) ([1]see Van den Berg and Van Wijngaarden, 2000; for sampling description, isotope data not shown); Dutch ($n = 10$) and Belgian ($n = 10$) charcoal samples, and galena samples from Belgium (Plombières, $n = 14$, and Dinant, $n = 2$) and Germany (Rhine-Westphalian district, $n = 2$, Maubach, $n = 1$, and Harz Mountains, $n = 4$) ([2]Walraven et al., in preparation-c; [5]Cauet et al., 1982; [6]Pasteels et al., 1980; [7]Wedepohl et al., 1978); sediment samples in Lake Vechten (NL) between 1989 and 2002 ($n = 11$) ([3]Walraven et al., in preparation-b); roadside soil (NL) samples ($n = 16$) ([3]Walraven et al., in preparation-b); and subsoil (NL) samples ($n = 78$) ([4]Walraven et al., in preparation-a).

involve low concentrations. Lead in plant leaves taken up from the soil will mostly be the Pb from the polluted river sediment, because current atmospheric Pb deposition does not greatly influence Pb pollution in the studied soils due to the low Pb concentrations in the atmosphere. The uptake and translocation of soil Pb to plant leaves in the Biesbosch is, however, low, due to low bioavailability of metals in the soil (Hobbelen et al., 2004; Notten et al., 2005). Also in the reference location, the transfer of soil Pb to plants is low due to the low Pb concentrations and high soil pH (Notten et al., 2005). Snails ingest the Pb *in* plant leaves (i.e. from the soil) and *on* plant leaves (i.e. from the atmosphere) via feeding. The uptake route of Pb via feeding on plants is more important than the uptake of Pb directly from the soil while moving or soil-feeding (Notten et al., 2005; Cœurdassier et al., 2002). This latter route, however, contributes to the uptake of soil Pb, thus sediment-derived Pb.

The results of this study show that atmospheric Pb pollution contributes substantially to Pb pollution and Pb transfer in plant leaves and snails in both the polluted Biesbosch locations as well as in the reference location. The occurrence of possible effects on snails due to the pollution of Pb and other metals in the soil–plant–snail food chain in the Biesbosch is investigated in another study (Notten et al., 2006).

5. Conclusions

The soils in the Biesbosch floodplains and the reference location contain 88–95% and 50% anthropogenic Pb, respectively. The anthropogenic Pb isotope compositions in the soils of the 3 locations are similar. A comparison with information on several Pb origins shows that anthropogenic Pb is derived from sedimentation of the rivers Rhine and Meuse during flooding. This river sediment contains a mixture of Pb from various sources related to industrial activities in the hinterland of both rivers. Lead pollution in plant leaves and snails results from a mixture of river sediment-Pb and Pb in the atmosphere. The contribution of atmospheric pollution is substantial, despite the current low concentrations of Pb in the atmosphere. The different Pb origins mix via several transfer routes that involve low concentrations.

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