

## Biogeochemistry of lead in an urban forest in Athens, Greece

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**Abstract.** The distribution and cycling of lead (Pb) was examined in an urban forest of Aleppo pine stand in Athens. Concentrations of the soluble fraction of Pb in bulk and throughfall deposition were low, reflecting the change in petrol form in recent years. However, Pb concentrations in forest floor remain high due to Pb accumulation in previous years. The soil A horizon showed unexpectedly high levels of Pb concentration resulted probably from Pb migration from organic horizons. Pb concentrations in pine needles, litterfall and wood were low, whereas tree bark acted as a sink for Pb and stored high amounts of the metal.

### Introduction

Lead (Pb) poisoning often leads to mental retardation and neurologic disorders through damage to the brain and central nervous system (Matta et al. 1996). One of the largest contributions to Pb pollution was derived from the use of Pb compounds as a petrol additive. Pb is presumed to enter various ecosystems in the particulate form via precipitation and dry deposition. It is well established that soils near roads are more polluted than soils in remote areas (Davies 1995). However, it has been found that forests located far away from major sources of Pb emissions, receive precipitation with a Pb content much higher than might be expected (Schlesinger et al. 1974). The reason for this is that fine particles containing Pb can be transported within air masses on very long distances (Sturges and Barrie 1989).

Forest ecosystems have showed a remarkable capacity of Pb retention in large quantities (Siccama and Smith 1978). Ukonmaanaho et al. (2001), after two years of observation, found that 94–97% of Pb deposition was retained in two forested watersheds in Finland. This capacity is due to a humus layer in forest floors, which is very effective in retaining heavy metals (Tyler 1978; Bergvist et al. 1989; Derome and Nieminen 1998). Since Pb is strongly bound by organic matter, the Pb accumulation rates in forest floors reflect Pb deposition rates (Friedland et al. 1984; Brūmelis et al. 2002). The phasing out of

leaded petrol in Europe and USA has led to a substantial decrease of Pb deposition in forests (Miller and Friedland 1994). Pb concentrations in precipitation in Northeastern USA declined from  $32.7 \mu\text{g l}^{-1}$  to  $1.9 \mu\text{g l}^{-1}$  during the period 1966–1989 (Miller and Friedland 1994). Despite this fact, Pb accumulation in forest floors during the previous years and its long residence time, still pose problems for forest ecosystems.

Urban forests receive much higher pollutant loads than mountainous or rural forests. Parker et al. (1978), examining metal distribution in forested ecosystems in urban and rural areas, found that the levels of Pb were significantly higher in soils and vegetation on the urban than those on the rural sites. Urban soils, which become airborne during dry summers, can act as the source of pollution-derived elements such as Pb (Kaya and Tunkel 1997).

Athens, the capital of Greece, is a large and populous city. Nearly four million people live in an area of  $450 \text{ km}^2$ . Pollutants derived from industrial activity, vehicle traffic and central heating have created serious problems. Chronopoulos et al. (1997) determined Pb concentration in the plant species *Pittosporum sinensis* and *Nerium oleander* and in the soils of two parks in Athens. They found high concentrations of Pb in both plants and soils at the peripheral zones of the parks.

Aleppo pine (*Pinus halepensis*, Miller) is an indigenous species to the dry environment of the Mediterranean zone and is widely used for plant cover in the urban forest parks of Athens. So far, the study of Pb distribution and cycling has been focused on mountainous forests (Smith and Siccama 1981; Friedland and Johnson 1985; Turner et al. 1985). The objectives of this work are to determine Pb concentrations in bulk and throughfall deposition, litter-fall, forest floor, mineral soil, wood and bark tissue and quantify Pb fluxes and loads in a forest stand of Aleppo pine in Athens. The results will help researchers compare Pb biogeochemistry in forest ecosystems in urban and mountainous environments.

## Study site and methods

### Site description

The climate in the city of Athens is typically Mediterranean. The mean annual rainfall is 400 mm and the average temperature  $19^\circ\text{C}$ . Most rain falls in autumn and winter, whereas summers are hot and dry. The study site is an urban forest park situated in the south east of Athens. The distance from the center of the city is approximately 2.8 km. The area the park occupies is approximately 15 ha.

The forest vegetation is dominated by *Pinus halepensis*, with occasional codominant species of *Cupressus sempervirens*, *Ceratonia siliqua*, *Cercis siliquastrum*, *Arbutus unedo* and *Morus alba*. The understory vegetation consists of the species *Urtica* sp., *Galium aparine*, *Tirimnus leucographus*, *Oxalis*

*acetossela*, *Anemone coronaria*, *Sonchus oleraceus*, *Geranium* sp. *Alium* sp. and *Bromus* sp. Soils are classified as Eutric Leptosols and Calcic Luvisols depending on horizon depth (FAO-Unesco 1988). The parent material is calcite schist. The plot installed in the park has an area of 0.1 ha.

#### *Bulk and throughfall deposition collection*

Bulk deposition was collected by two collectors placed at the roof of a building 20 m high, very close to the plot. For throughfall measurements, 10 collectors were placed at random under the tree canopies in the plot. Bulk and throughfall deposition collectors were identical and each of them consisted of an 18 cm diameter polyethylene funnel connected through a long hose (1 m) to polyethylene bottle of five-litter capacity. A small plug of tulle was fitted into the neck of the funnel. The assembly was enclosed vertically in a PVC drainage pipe, dug firmly into the ground to keep the collecting bottle underground so as to exclude light from the water samples.

There was no regular water collection as this depended on the amount of rainfall necessary for chemical analysis. On average, two collections per month took place. After water volume was measured, samples were placed in plastic bottles and stored for analysis at 4 °C. In most cases, chemical analysis took place within 2 weeks time. With each water sampling, bulk and throughfall deposition collectors were washed with 20% HNO<sub>3</sub> and deionized water.

#### *Forest floor and litterfall collection*

Forest floor was collected by an iron template 15 cm × 15 cm in a systematic way. There were three forest floor collections in 2002. Each time five samples were taken and formed a composite sample.

Litterfall was collected by five-litter traps, each occupying an area of 0.242 m<sup>2</sup>, placed at random in the stand. In 2002, it was collected twice a year. There was no separation of needles, cones and twigs.

Forest floor and litter samples were oven dried at 80 °C for 48 h and weighed. Sub samples were pulverized by a ball mill prior to chemical analysis. Cones, branches and twigs were cut and crushed before entering the mill chamber.

#### *Pine needle collection*

Current and second year needles were collected from five dominant and codominant trees chosen at random in the plot in December 2002. Samples were cut from the upper part of the tree crowns with pole pruners. Needles were dried at 80 °C for 48 h and equal quantities from each tree sample were

mixed and formed a composite sample. A sub sample was ground in a stainless mill and stored prior to analysis.

#### *Wood and bark biomass determination*

The breast diameter and height of all trees were measured in the plot area of 0.1 ha. In total, 75 trees were found. Allometric equations (Apatsidis and Sifakis 1994), specific for Aleppo pine, were applied to find the bark and trunk wood volumes of each tree. Branch volume was estimated visually, for each tree, as a percentage of the trunk tree volume.

For biomass determination, the wood and bark density were calculated by sampling wood and bark tissue. In order to avoid cutting down trees in the park, wood tissue was extracted by increment borers, at breast height, from three trees having the average tree diameter in the stand. Bark tissue was extracted by means of a special knife from the same three trees, also at breast height. Wood and bark volumes of the extracted samples were measured immediately by immersing the samples into a volumetric cylinder containing deionized water and measuring the change in water volumes before and after immersion. The sample masses were measured after oven drying at 80 °C for 48 h and wood and bark densities were calculated in these samples. The masses of tree wood and bark were calculated taking into account the respective total volumes and densities.

#### *Mineral soil collection*

Three soil pits 1 m × 0.5 m, chosen in a random way, were excavated in the plot. Horizon depths were measured and soil samples were collected from each horizon. Soil volume weight (bulk density) was determined by collecting undisturbed soil cores from each horizon in each pit. Mineral soils from each horizon were dried at 80 °C for 48 h and passed a 2 mm sieve. For total Pb determination, soil sub samples were pulverized in a ball mill and stored for analysis at room temperature.

#### *Water chemical analysis*

All water samples from bulk and throughfall deposition passed through a 0.45 µm filter prior to analysis. Sulfate,  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations were determined by ion chromatography using commercially available standard solutions. Bicarbonates were determined colorimetrically by the methyl orange method. For Pb determination separate samples were acidified with ultra pure  $\text{HNO}_3$  so that the final sample volume would contain 1%  $\text{HNO}_3$ . For quality assurance and quality control, three tests were carried out. These tests were the

charge balance between anions and cations, the sodium to chloride ratio and the correlation between measured and calculated conductivity.

Pb was determined by electrothermal atomic absorption spectrometry (ETAAS), using a Perkin–Elmer 5100PC spectrometer equipped with a Zeeman THGA 5100ZL furnace. The selected wavelength was 283.3 nm. A  $\text{Pd}(\text{NO}_3)_2$ – $\text{Mg}(\text{NO}_3)_2$  mixed modifier was used for the determination of Pb. Quantification was performed with matrix-matched calibration. Recovery experiments were used to assess the analytical performance of the procedure. Recoveries were determined by spiking samples with Pb concentrations, at four levels. Recoveries (%) of  $101 \pm 4$  were obtained for eight replicates.

#### *Soil chemical analysis*

The pH of soils (1:1 soil:water ratio) was determined by a glass electrode. Organic C was measured by wet oxidation with  $\text{K}_2\text{Cr}_2\text{O}_7$  (Walkley 1946). Calcium carbonate was measured with a calcimeter (Nelson 1982).

Total Pb concentrations in forest floor samples were determined by dry ashing 2 g of ground dry material at 475 °C for 8 h, followed by digestion in 10 ml of boiling 6 N  $\text{HNO}_3$  (Miller and Friedland 1994).

Total Pb in pulverized mineral soils was extracted by aqua regia (Sastre et al. 2002). Before the aqua regia application, soil samples (2 g) were predigested in 15 ml mixture (2:1) of  $\text{HNO}_3$ – $\text{HClO}_4$  acids to minimize frothing during the aqua regia extraction. The extracts were filtered through a fiberglass filter and stored in polyethylene bottles for analyses at 4 °C. Concentration of Pb was determined on a Perkin–Elmer flame atomic absorption spectrometer (FAAS) at the wavelength of 283.3 nm. Analytical accuracy was verified, using reference solutions of known concentration made of commercially available Pb standards.

#### *Litterfall, needle tissue, wood and bark analysis*

Pb concentrations in ground material of all unwashed vegetation were determined by dry ashing (Miller and Friedland 1994). For this analysis, 4 g of material were dry ashed and eluted with 20 ml of 6 N  $\text{HNO}_3$ . Final determination was carried out by FAAS as described above.

### **Results and discussion**

#### *Bulk and throughfall deposition*

Dissolved Pb is operationally defined as the Pb fraction passing through a 0.45  $\mu\text{m}$  membrane. It contains hydrated and complexed Pb ions as well as Pb

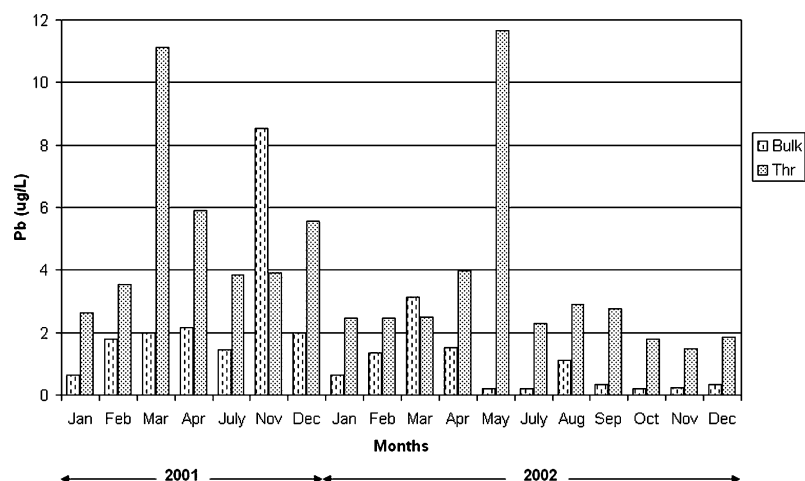


Figure 1. Monthly volume weighted means of Pb concentrations in the period 2001–2002. Months with no water sampling are not included.

adsorbed on organic and inorganic colloids. This fraction has been derived from wet deposition but also from dry deposition that can be dissolved in rain. The insoluble fraction is undissolved particulate matter, which is retained by filters. Figure 1 shows the monthly volume weighted means of Pb concentrations in bulk and throughfall deposition in 2001 and 2002. The concentrations found are considered low.

Analysis of wet only deposition in the center of Athens during the period 1989 to 1991 showed a mean Pb concentration of  $103 \mu\text{g l}^{-1}$  (Smirnioudi et al. 1998). Of course, the center of Athens bears heavier vehicle traffic than the area around the experimental plot and these measures were taken more than 10 years ago. The results obtained in this study are similar to those found in remote forests. In an unpolluted area in Japan, (Yelpatyevsky et al. 1995) measured average concentration of  $15 \mu\text{g l}^{-1}$  in the soluble fraction of Pb in bulk deposition. In a forested watershed of *Pinus rigida* and *Pinus echinata* Turner et al. (1985) measured average volume weighted Pb concentrations  $13 \mu\text{g l}^{-1}$  and  $10 \mu\text{g l}^{-1}$  in bulk deposition and throughfall, respectively in the period 1978–1981. These low concentrations found in the experimental plot reflect the change in rate of Pb pollution due to the disappearance of leaded petrol. However, one cannot underestimate the contribution of undissolved dry deposition in urban environments. Morselli et al. (2003) found that less than 25% of Pb content in dry deposition was in soluble form in the city of Bologna. Apart from two cases, Pb concentrations in throughfall was higher than bulk deposition in the 2 years of measurement (Figure 1). Similar results for forested areas have been found by other researchers (Linberg and Harris 1981). This finding compounds to the fact that the prevalent deposition type for Pb is dry deposition.

Table 1. Spearman correlation coefficients between monthly volume weighted means of Pb and anion concentrations in bulk and throughfall deposition for the period 2001–2002

	Cl <sup>−</sup>	NO <sub>3</sub> <sup>−</sup>	HCO <sub>3</sub> <sup>−</sup>	SO <sub>4</sub> <sup>2−</sup>
Pb (bulk)	0.542*	0.150	0.112	0.345
Pb (throughfall)	−0.013	−0.337	0.478*	0.084

\*Denotes statistical significance at 0.05 probability level.

In 2001, no seasonal pattern was observed in terms of Pb concentration in deposition but in 2002, there was an increase in Pb concentrations in throughfall deposition during the spring months. This increase can be attributed to the intense building activities for the Olympic Games.

In order to find the accompanying anions for Pb salts in bulk and throughfall deposition, a Spearman correlation was applied between Pb and the anions Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup> and HCO<sub>3</sub><sup>−</sup> (Table 1). In bulk deposition Pb concentration was significantly correlated with Cl<sup>−</sup>. The urban forest under study is situated approximately 7 km from the sea, so some quantity of marine aerosols is transported over the experimental plot.

Chloride is a marine derived anion and its concentrations are high in bulk deposition near coastal areas. If Pb is transported in fine particles in long distances, it is possible that PbCl<sub>2</sub> salts are formed, which later on can be scavenged by rain.

In throughfall, the Pb sources can be different. Suspended soil dust is captured by pine canopies and subsequently washed off by rain. The soils in the experimental plot contain large quantities of CaCO<sub>3</sub> (Table 5). A significant correlation between Pb and HCO<sub>3</sub><sup>−</sup> concentrations in throughfall was established (Table 1). A similar correlation was observed between Pb and Ca<sup>2+</sup> concentrations in PM<sub>2.5</sub> particles in the atmosphere of Athens (Thomaidis et al. 2003) indicating that re-suspended dust contributes to the total Pb concentration in wet and dry deposition.

Although the annual volume weighted means of Pb concentrations were higher in 2001 than 2002, in both bulk and throughfall deposition (Table 2), the annual Pb fluxes in 2002 were higher than 2001 due to rainfall amounts. In 2002, the annual rain height was 854 mm and in 2001 it was 355 mm.

Table 2. Annual volume weighted means (μg l<sup>−1</sup>) and fluxes (g ha<sup>−1</sup>) of Pb in deposition

	Annual weighted means	
	2001	2002
Bulk	4.42	0.67
Throughfall	4.49	2.79
	Annual fluxes	
	2001	2002
Bulk	15.7	5.77
Throughfall	12.0	19.8

Generally speaking, the Pb fluxes are not high considering the high values (more than  $300 \text{ g ha}^{-1}$ ) in bulk and throughfall deposition found in forested areas in central Germany (Heinrichs and Mayer 1980) or USA ( $10\text{--}1000 \text{ g ha}^{-1}$ ) (Lazrus et al. 1970) in the past. The fluxes values of Pb found in bulk deposition in this study are close to the fluxes found by Ukonmaanaho et al. (2001) in remote Finish forests ( $9.5 \text{ g ha}^{-1}$ ). This decline in Pb fluxes in Europe, even in urban forests, due to change in petrol type is good news for society and forest ecosystems. Of course, in these calculations the insoluble Pb fraction was not included. However, from an ecotoxicity point of view the soluble fraction is the most important.

#### *Pb concentrations and amounts in vegetation*

The average Pb concentration followed the order bark > needles > wood (Table 3), consistent with the results quoted by Smith and Siccama (1981) for a hardwood forest in USA. Bark is exposed to Pb deposition and acts as a sink for this metal.

Table 3. Pb concentrations in vegetation and amounts stored in some vegetation compartments

Concentration ( $\text{mg kg}^{-1}$ )		Amounts ( $\text{g ha}^{-1}$ )	
Trunk wood	1.25	Trunk wood	108
Trunk bark	15.1	Trunk bark	253
Needles	5.33	Branch wood	12.0
		Branch bark	87.5
		Total amount	460.5

The  $5.33 \text{ mg kg}^{-1}$  of Pb content found in needle tissues (current plus second year) is not considered high. The mean content of Pb in needle tissue of all ages in a large number of pine trees in Europe was found  $5.5 \text{ mg kg}^{-1}$  (Rademacher 2001). This amount of concentration cannot cause problems for the Aleppo pine trees. Rolfe and Bazzaz (1975) found that below a tissue concentration of  $60 \text{ mg kg}^{-1}$  there was no effect on photosynthesis and transpiration rates of *Pinus taeda*.

The Pb concentration in wood tissue of Aleppo pine (Table 3) is higher than those found in wood tissues of *Pinus rigida* and *Pinus echinata* ( $0.2\text{--}0.7 \text{ mg kg}^{-1}$ ) but similar to concentrations in bark ( $13\text{--}18 \text{ mg kg}^{-1}$ ) (Turner et al. 1985). It is worth pointing that Pb concentrations in the wood of the Aleppo pine is higher than the Pb concentrations in the wood of a variety of forest species ( $0.35\text{--}1.1 \text{ mg kg}^{-1}$ ) in a forested watershed receiving high amounts of Pb in precipitation (Smith and Siccama 1981). It can be assumed that some Pb uptake from soil has taken place.

The total Pb amount ( $460.5 \text{ g ha}^{-1}$ ) in wood and bark is not high in comparison with a full-grown forest. In a mixed forest, Smith and Siccama (1981), for the same tree parts, found a total Pb amount of  $620 \text{ g ha}^{-1}$ . In general, the



amount of an element stored in forest biomass largely depends on the magnitude of biomass, which in turn is influenced by tree species, site quality, and the stages of forest development.

### *Litterfall*

The Pb concentration in litterfall, for both collection periods (Table 4), is much higher than the  $5.33 \text{ mg kg}^{-1}$  found in pine needles. Pine needles before the abscission stage are exposed to Pb deposition for longer periods than younger needles. The pine canopies are very effective at capturing dust particles, which are abundant in big cities (Beckett et al. 1998). Higher Pb concentrations ( $30$  and  $27 \text{ mg kg}^{-1}$ ) were found in litterfall of *Fagus sylvatica* and *Picea abies* in central Germany in the beginning of the eighties (Heinrichs and Mayer 1980). At that time, the use of leaded petrol was at its height and even non urban forests accumulated high amounts of Pb. In a recent publication, Kapusta et al. (2003) found that the maximum Pb concentration in litterfall in an urban deciduous forest in polluted areas in Poland was  $12.3 \text{ mg kg}^{-1}$ . This finding illustrates the difference between conifers and deciduous trees, the former being more effective as pollutant sinks.

The flux of Pb in litterfall in 2002 (Table 4) is not high taking into account that litterfall fluxes of Pb for the species *Fagus sylvatica* and *Picea abies* were  $120$  and  $256 \text{ g ha}^{-1} \text{ year}^{-1}$ , respectively (Heinrichs and Mayer 1980).

Table 4. Pb concentrations and amounts in litterfall

Collection period	Concentration ( $\text{mg kg}^{-1}$ )	Amounts ( $\text{g ha}^{-1}$ )
1/1/02–15/7/02	22.5	33.4
15/7/02–1/1/03	17.8	20.5
Total litterfall flux		53.9

However, these large differences are mostly due to the low amounts of litterfall that characterize the Aleppo pine trees in comparison with the above-mentioned species. In 2002, the total amount of aboveground litterfall for the Aleppo pine stand was  $2647 \text{ kg ha}^{-1}$ . Litterfall amounts are high in fertile and productive soils (Kimmins 1996), whereas in the dry Mediterranean environment the opposite is always true, especially for pine trees.

### *Forest floor and mineral soil*

Selected chemical properties of forest floor and mineral horizons are showed in Table 5. Pb concentrations in forest floor and mineral soil (Table 6) are much higher than the value of  $20 \text{ mg kg}^{-1}$  characterizing unpolluted soils (Davies 1995).

Table 5. Selected chemical parameters of the soils in the experimental plot

	Depth (cm)	pH	Org-C (g kg <sup>-1</sup> )	CaCO <sub>3</sub> (g kg <sup>-1</sup> )
Forest floor	4–0	7.47 (2)*	400 (23)	45.1 (72)
A horizon	0–6.83	7.92 (3.5)	39.9 (16.2)	207 (1)
B/C horizon	6.83–26.3	8.24 (0.4)	6.33 (45)	222 (3)

Means are based on three replicates.

\*Coefficient of variation (%).

Table 6. Pb concentrations and amounts in forest floor and mineral soil

	Concentration (mg kg <sup>-1</sup> )	Amounts (kg ha <sup>-1</sup> )
Forest floor	92.1 (54.3–133)*	4.45
A horizon	81.8 (69.9–93.1)	31.3
B/C horizon	37.7 (33.0–43.5)	42.2
	Total	78.0

\*Range.

The Pb concentrations in forest floor are considerably lower than those found in organic soil horizons by Chronopoulos et al. (1997) in the perimeters of Athenian parks (172–592 mg kg<sup>-1</sup>) close to heavy traffic. The plot under study is located approximately 270 m from the major traffic roads. Sutherland and Tolosa (2001) found that at a distance of 50 m from highways Pb concentration decreased substantially. However, there is Pb pollution in this park. The mean Pb concentration in humus layer in European forest soils has been found 74.9 mg kg<sup>-1</sup> (Rademacher 2001).

Although the humus layer in coniferous forests is considered an effective sink for Pb, high Pb concentrations were found in A and B horizon despite the low levels of organic C in these horizons (Tables 5 and 6). Two mechanisms have been suggested for this. The first is the migration of Pb down the soil profiles in colloidal form complexed with organic matter proposed by Friedland et al. (1992). These researchers found an unexpected decrease in Pb concentration levels in forest floors of forests in northeastern United States in various sampling periods. The second mechanism is the dissolution of organic compounds in the humus layer and the promotion of organic Pb complexes due to the high pH values (Table 5) in the forest floor in the experimental plot. This explanation was suggested by Haapala et al. (2001) who found that Pb was less strongly complexed with organic matter than expected in the humus layer of podzolic soils undergoing alkalization.

Pb migrated from the forest floor can be bound by Al and Fe sesquioxides or CaCO<sub>3</sub>. The latter has a high concentration in the mineral soil of the Aleppo pine stand (Table 5). These chemical processes can further enhance Pb concentrations in the mineral horizons. It is not clear how much Pb in mineral horizon comes from the parent material or Pb atmospheric deposition. The full clarification of this matter can be made only by Pb isotope studies.

The Pb content in the forest floor and mineral soil should not have an effect on soil microorganisms but surely affects the population of invertebrates. High Pb concentrations ( $> 940 \text{ mg kg}^{-1}$ ) are required to affect soil microorganisms but lower concentrations (approximately  $36 \text{ mg kg}^{-1}$ ) can adversely affect soil invertebrates (Tyler et al. 1989).

The amount of Pb,  $4.45 \text{ kg ha}^{-1}$ , stored in the forest floor is not high. Andresen et al. (1980) compiled an extensive list of Pb amounts stored in the forest floors of Northeastern United States forests. The average amount was found  $12.3 \text{ kg ha}^{-1}$ . However, the forest floor depth in the Aleppo pine stand is only 4 cm. Assuming that Pb is homogenized along a forest floor depth gradient, the Pb amount can be twice or three times as much at depths of 8 and 12 cm, respectively.

The bulk of Pb pools in the experimental plot are located in mineral soil reaching a total amount of  $73.5 \text{ kg ha}^{-1}$  at a total depth of 33.1 cm (Table 6). This amount is larger than the total Pb amount found in the mineral soil of the Hubbard Brook forest (50 cm depth), which was  $35.6 \text{ kg ha}^{-1}$  (Smith and Siccama 1981) and Northern Vermont Forest (40 cm depth) with a total Pb amount of  $63 \text{ kg ha}^{-1}$  (Friedland and Johnson 1985).

#### *Pb residence time in the forest floor and A horizon*

The mean residence time of Pb in the forest floor can be found by dividing the total Pb load in the forest floor by the total Pb input (Gosz et al. 1976). The presupposition for applying this equation is that the ecosystem is at a steady state. In forests, this stage can be more or less accomplished when the canopy closure is complete. In the experimental plot, this ecological stage has been achieved. Miller and Friedland (1994) added a further presupposition for the application of the mean residence time equation. They argued that the Pb amount in the forest floor should not change with time. Unfortunately, there is no previous data on Pb concentration in the forest floor of the experimental plot. Furthermore, Pb levels in atmospheric deposition may keep dropping. For these reasons, results concerning residence time should be accepted with reservation.

The total input is the sum of throughfall and litterfall Pb fluxes. Since litterfall collection took place in 2002, the mean residence time of Pb will be calculated for this year. The total Pb input, in 2002 was  $73.7 \text{ g ha}^{-1}$  (Tables 2 and 4) and the total Pb load in the forest floor was  $4450 \text{ g ha}^{-1}$  (Table 6). The calculated mean residence time for Pb in the forest floor is 60.4 years. If the same equation is applied for the A horizon with a total Pb load of  $31.3 \text{ kg ha}^{-1}$ , the mean residence time of Pb is found to be 425 years. If the insoluble Pb particles in throughfall deposition entered the equation as an additional input, the Pb residence time in both horizons could be further reduced.

It can be concluded that forest floor is not as efficient sink for Pb as the underlying A horizon.

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