

Anthropogenic Pb accumulation in forest soils from Lake Clair watershed: Duchesnay experimental forest (Québec, Canada)

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Received 9 November 2005; accepted 9 June 2006

Editorial handling by G. Filippelli

Available online 7 September 2006

Abstract

Mineral soil horizons (Ae, Bhf1, Bhf2, Bf, BC and C) were carefully collected from two podzolic soil profiles in the Lake Clair watershed (Québec) in order to assess anthropogenic trace metal accumulation. Petrographic and selective analyses were performed to establish the soil mineralogy and properties. Furthermore, a complete sequential extraction procedure has been applied to help understanding the complex chemical speciation of Pb in forest soils. Chemical speciation of Pb showed a strong vertical gradient: 85% of this metal is mainly partitioned in refractory minerals in the C-horizon whereas in the upper Bhf1 and Ae-horizons, less than 50% of Pb is associated with this fraction. In the Ae-horizon, for example, 35%, 30% and 12% of total Pb, respectively, is associated with the exchangeable, labile organic matter and amorphous Fe-Mn oxides fractions. The distribution of Pb and Cr in the studied forest soils mainly reflects progressive contamination of the watershed by anthropogenic atmospheric sources. The anthropogenic source is indicated by elevated Cr and Pb concentrations in the topsoil (Bhf and Ae) horizons and by strong negative correlation between ²⁰⁶Pb/²⁰⁷Pb ratios and total Pb concentrations. According to these isotopic values, penetration of anthropogenic Pb does not exceed 10 cm in both soil profiles. Below this depth, both Pb concentrations and isotopic ratios remain nearly constant and similar to values observed in pre-anthropogenic sediments from Lake Clair. These values are interpreted as the natural geochemical backgrounds of the watershed. Based on that behaviour, calculated anthropogenic Pb net inputs amounted to between 1.24 and 1.8 g/m².

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1. Introduction

Over the past 150a in North America, human activities such as metal refining, incineration of refuse, coal, and wood, and combustion of alkyl-leaded gasoline have greatly increased the fluxes of trace metals to the environment (Shirahata et al.,

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1980; Patterson and Settle, 1987; Sturges and Barrie, 1987; Nriagu and Pacyna, 1988; Carignan and Gariépy, 1995; Simonetti et al., 1999). Because of their presence in fine aerosols, atmospheric trace metals can be transported over long distances and

deposited in various earth ecosystems, sometimes remote from source areas. In the last two decades, widespread concern has arisen over the effects of increasing amount of heavy metals into the environment (e.g. 330,000 tons/a of Pb worldwide in 1983;

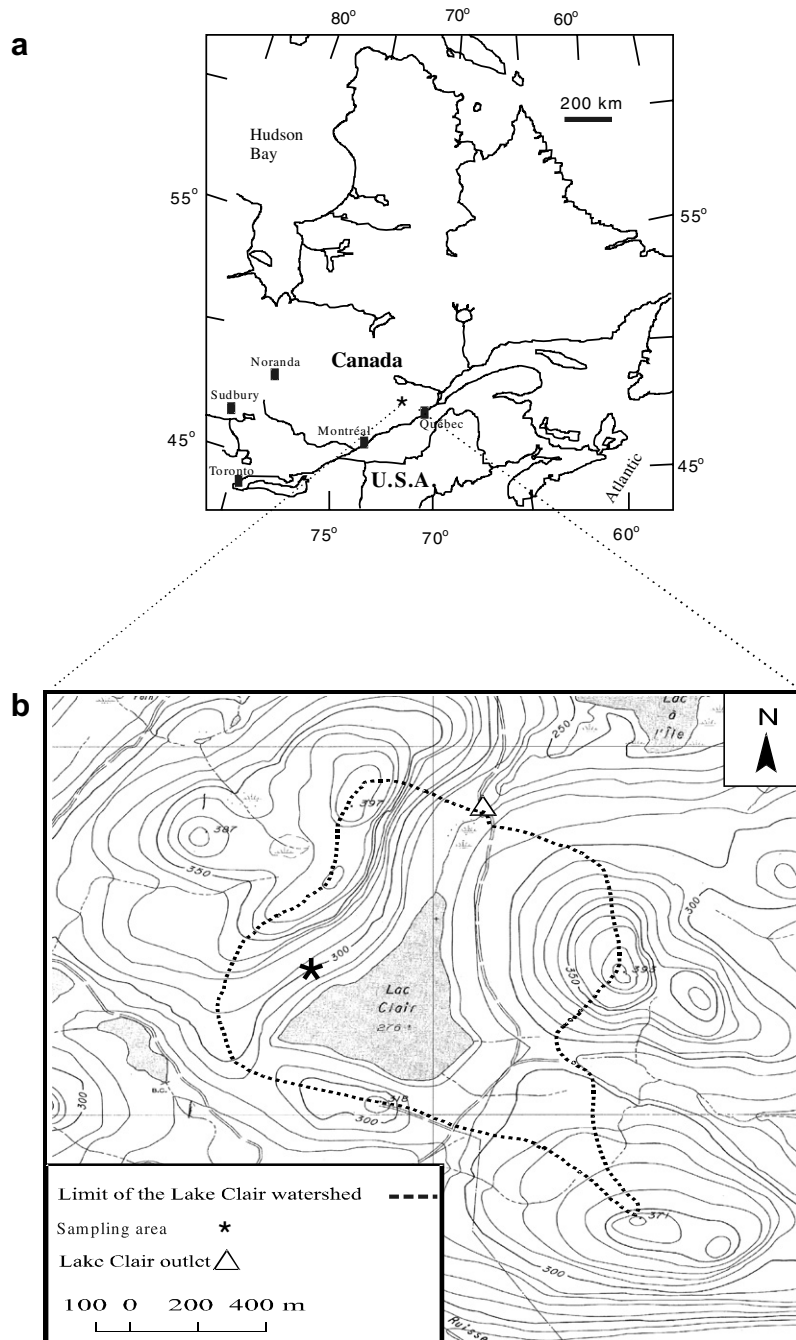


Fig. 1. (a) Map of the study area and (b) topographic map of the Lake Clair watershed showing sampling site and the boundaries of the catchment.

Nriagu and Pacyna, 1988) to ecological and health problems (Patterson, 1980; Needelman, 1984; Pacyna, 1987; Maddaloni et al., 1998; Kurkjian and Flegal, 2003; Filippelli et al., 2005).

In forest soils, contamination has been usually inferred from elevated contents of trace metals in the topsoil layers or by indirect methods such as dendrochemical studies. However, total concentration estimates of trace metals in soils can be of limited usefulness in an evaluation of the environmental risk these metals pose. Indeed, the presence of large amounts of anthropogenic metals in less stable phases might have severe consequences regarding their chemical reactivity, their penetration depth in the soil and eventually their migration into ground waters (Teutsch et al., 2001). The sequential extraction procedure is a much better predictor of the mobility and strength of the metal binding to the soil components (Tessier and Campbell, 1991; Teutsch et al., 2001; Emmanuel and Erel, 2002). Although sequential extraction methods have been widely used in trace metal studies in soils and sedi-

ments (Tessier et al., 1979; Maskall and Thornton, 1998; Wilcke et al., 1998), the validity of such procedures to natural sample is still being debated (Tessier and Campbell, 1991; Marin et al., 1997; Teutsch et al., 2001; Emmanuel and Erel, 2002). Much criticism is due to the selectivity of the extractants for a given phase and difficulties of associating trace metal released during extraction procedures with the discrete phases present in natural samples (Nirel and Morel, 1990). Nevertheless, in the absence of more precise approaches, sequential extraction yields important information regarding the chemical reactivity and the partitioning of trace metals (Tessier and Campbell, 1991; Marin et al., 1997; Teutsch et al., 2001).

On the other hand, concentration profiles alone do not always prove unequivocally pollution since elevated trace metal concentrations may also result from pedogenic processes (Nriagu and Pacyna, 1988; Teutsch et al., 1999). Because of both the very strong Pb anthropogenic signal in the environment and the possibility of using stable Pb isotopes



Fig. 2. Photograph of soil profile 1. Boundaries between soil horizons are usually ill-defined and sinuous.

as source indicators, Pb is an effective tracer of metal input and cycling in the atmosphere (Sturges and Barrie, 1987; Graney et al., 1995; Sañudo-Wilhemly and Gill, 1999; Deboudt et al., 1999; Kurkjian and Flegal, 2003; Filippelli et al., 2005). Determination of Pb isotopes can give valuable quantitative source information in the study of atmospheric aerosol transport. These isotopic ratios may be used to identify the atmospheric contamination sources (Sturges and Barrie, 1987; Carignan and Gariépy, 1995; Erel et al., 1997; Deboudt et al., 1999; Teutsch et al., 2001; Kurkjian and Flegal, 2003). This method is based on the differences in isotopic ratios existing among different groups of materials, such as local bedrocks, gasoline additives, and industrial emissions.

In this study, elemental Cr and Pb concentrations as well as Pb isotope ratios are used to assess contamination and to determine the penetration depth of anthropogenic Pb in forest soils from Lake Clair Watershed (LCW). Furthermore, a complete sequential extraction procedure has been applied to help understand the complex partition behaviour of Pb in forest soils.

2. Site description

The LCW is situated 50 km NW of Québec City (Fig. 1). Basement rocks are made of Precambrian Grenvillian felsic gneiss and granites of the Canadian Shield, which is in-filled in places by Quaternary tills of variable thickness. The LCW covers an area of 2.26 km² and the forest stand is dominated by deciduous trees (83%) and conifers (17%). According to recent palynological and paleolimnological studies, the LCW has remained forested during the last 18 centuries (Richard et al., 2000), although locally, selective tree cutting occurred in the mid-1940 s. No significant recent forest fires have been documented in the watershed. From 1974 to 1989, the mean annual air temperature at the site was 3.4 °C and the average precipitation was 1300 mm (Houle et al., 1997). The soils are sandy loam and are classified as a Ferro-Humic Podzols according to The Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Survey, 1987). The sampling sites are located between 270 and 390 m above mean sea level. The LCW has been exposed to weathering during the last 11 Ka since the Wisconsinian glacial ice left the region at the Pliocene–Holocene transition (Occhietti et al., 2001).

3. Methodology

3.1. Sample collection

Mineral soil horizons (Ae, Bhf1, Bhf2, Bf, BC and C; Fig. 2) were carefully collected from two soil profiles (profiles 1 and 2). In each of them, six samples were taken from the surface to a depth of 70 and 76 cm respectively. These samples were examined and described in detail in the field. In the laboratory, they were air-dried at room temperature (22 °C) and sieved at 2 mm. The coarse fraction (>2 mm) was used for petrographic and textural analyses. Representative samples of the fine fraction (<2 mm) were ground with an agate mortar and pestle, and placed in a desiccator for later analysis. To assess anthropogenic net Pb inputs in studied soils, the LFH horizon was also sampled.

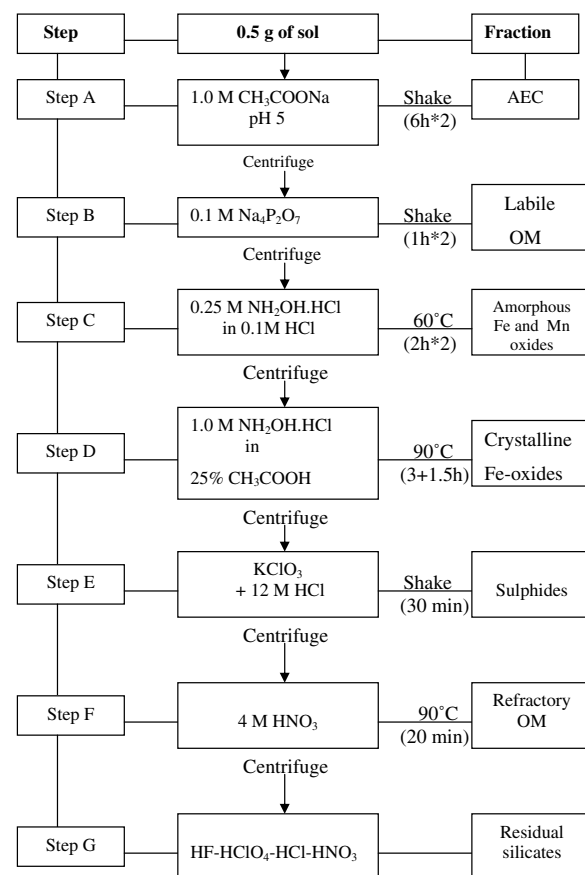


Fig. 3. Summary of the sequential dissolution procedure used in this study. AEC: adsorbed, exchangeable and carbonates; OM: organic matter.

3.2. Chemical and isotopic Analyses

3.2.1. Whole-soil analysis

Milli-Q™ water (>18 MΩ cm) and ultrapure tri-distilled acids (Seastar™) were used during all chemical manipulations. A pulverized 200-mg aliquot of each soil sample (<2 mm fraction) was fused with lithium metaborate at 1000 °C (Ingamells, 1996). Thereafter, the hot fusion products were dissolved in dilute ultrapure HNO₃ and the final solutions were diluted in 100 mL of 5% HNO₃. Titanium concentrations were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; Perkin–Elmer Optima 3000). Total Cr, Pb and Zr concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS; VG Turbo Plasma Quad PQ2⁺). Certified reference materials GXR2 and GXR6 (US Geological Survey) were regularly submitted to the same digestion procedure as the soil samples. Analytical precision was generally better than 1% for the major elements and between 5% and 15% for the trace elements.

3.2.2. Measurements of lead isotopic ratios

To perform Pb isotopic analysis, another 100-mg aliquot of each soil sample (<2 mm fraction) was digested for 5 days at 150 °C in PARR™ metal-jacketed PTFE lined acid digestion bombs with a mixture of concentrated ultrapure HF/HNO₃/HClO₄ acids. Afterwards, Pb separation was achieved by anion-exchange chromatography using the method

described by Bacon et al. (1996). Measurements of Pb isotopic ratios were carried out by ICP-MS (Perkin–Elmer ELAN 3000). This instrument has a good sensitivity and produces a count rate of approximately 5×10^5 cps/μg L⁻¹ for Pb. The NIST 981 Pb reference standard (National Institute of Standards and Technology, Gaithersburg, MD) was used to monitor accuracy. Data were taken in the peak hopping mode (for masses *m/z* between 200 and 210). Natural Tl isotopic ratio was used as an internal standard for calculation of the mass bias correction of the spectrometer (Ketterer et al., 1991). All isotopic ratios used in this study were determined with a precision of $2\sigma < 1\%$.

3.2.3. Sequential and selective extractions

To determine elemental speciation in the studied soils, a sequential extraction procedure has been carried out (Fig. 3). The procedure used in this study was slightly modified from Land et al. (1999). For instance, 0.5 g of sample were used instead of 1.0 g and all steps, including rinsing were done twice. Seven fractions were selected for extraction: (A) CH₃COONa-extractable (adsorbed/exchangeable/carbonate); (B) Na₄P₂O₇-extractable (labile organics); (C) 0.25 M NH₂OH · HCl-extractable (amorphous Fe-oxyhydroxides and Mn-oxides); (D) 1 M NH₂OH · HCl-extractable (crystalline Fe-oxides); (E) KClO₃/HCl-extractable (sulphides); (F) 4 M HNO₃-extractable (refractory organic) and (G) HNO₃/HCl–HF/HClO₄-extractable (residual silicates). After dilution of the extracts with Milli-Q™ water, elemen-

Table 1
Chemical properties of the mineral horizons of the two podzols from the Lake Clair watershed

Horizon	K _{ex} (mg/kg)	Ca _{ex} (mg/kg)	Mg _{ex} (mg/kg)	Mn _{ex} (mg/kg)	Fe _{ex} (mg/kg)	Al _{ex} (mg/kg)	pH (mg/kg)	CEC (meq/100 g)	OM (g/kg)
<i>Profile 1</i>									
Ae	68	76	18	5.6	38	226	4.36	3.7	79
Bhfl	48	85	3.2	1.2	90	446	4.7	4.56	116.5
Bhf2	17	48	5.5	5.1	3.8	317	4.85	3.8	101.4
Bf	10	19	2.5	2	1.3	116	5.12	1.4	39.7
BC	9.3	14	1.6	0.6	2.3	92	5.26	1.1	16.4
C	12	4.7	2	0.3	1.6	40	5.45	0.5	2.6
<i>Profile 2</i>									
Ae	62	69	11.2	4.39	11	153	4.2	2.1	62.9
Bhfl	37	73	2.6	8.4	55	287	4.4	3.1	94.1
Bhf2	20	22	5	5.6	4.1	190	4.5	2.3	91.9
Bf	9.4	8.1	1.3	1.5	0.6	73	5.22	0.9	35.2
BC	7.2	4.6	0.8	0.1	0.7	46	5.31	0.5	6.9
C	8.7	4.4	1	0.1	3.1	35	5.51	0.5	4

Note that both profiles also have a LFH-horizon overlying the mineral horizons. OM: organic matter; ex: exchangeable; CEC: cation exchange capacity.

tal concentrations were determined by ICP-AES and ICP-MS. Since there are mostly no carbonates in the studied soils, most elements extracted from step A are considered to be adsorbed or exchangeable.

Exchangeable fractions of Al, Ca, Fe, K, Mn and Mg were also extracted with unbuffered NH_4Cl (1 N) solution and measured using ICP-AES. Soil pH was measured with water solution using a soil/solution ratio of 1/2.5. Total organic C content was determined by wet combustion (Yeomans and Bremner, 1988).

3.3. Petrographic analyses

Petrographic thin sections of representative samples of each soil horizon were prepared by filling a plastic mold with the soil sample and back-filling the mold with epoxy resin. These epoxy resin blocks were then mounted onto a glass slide, ground to the desired thickness (32 μm) and polished for petrographic analysis. Quantitative major element analyses were performed using an Electron Microprobe analyser (EPMA, CAMECA SX 100) at the University Laval microanalysis laboratory.

4. Results and discussion

4.1. Soil properties

The LCW soils are mainly sandy loams classified as typical Ferro-Humic Podzols. Typical exchange-

able cations, pH (H_2O), cation exchange capacity (CEC) and organic matter (OM) contents of their mineral horizons are listed in Table 1 (profiles 1 and 2). The CEC values are relatively low throughout the profiles with maxima in the Bhf1-horizons (4.6 and 3 meq/100 g) and very low values in the basal Quaternary till (values ≤ 0.5 meq/100 g). Organic matter content, negligible in the C-horizons of both profiles (< 5 g/kg), increases upward to values above 60 g/kg in the Ae and Bhf-horizons. Once again, maximum values are observed in the Bhf1-horizons (116 and 94 g/kg, respectively, in profiles 1 and 2). In both profiles, pH values increase significantly from 4.2 in the Ae-horizon to 5.5 in the C-horizon. As pH increases, exchangeable Ca and Mg contents decrease downwards in the soil profiles. Both elements show their highest exchangeable abundances in the Bhf1 and Ae-horizons. From the Ae to C-horizon, exchangeable Al (Al_e) also shows a decreasing trend. This element is strongly enriched in the Bhf-horizons, where pH becomes < 5 .

4.2. Soil mineralogy

The mineralogical composition of the C-horizon indicates that the sources of Quaternary tills are dominated by felsic gneiss and granites. The parent materials in both profiles are medium to fine grain size tills dominated by quartz (40%), plagioclase (25%), K-feldspar (15%) and micas (10%). Minor

Table 2
Depth, densities, total trace metal contents and Ti/Zr ratios in the mineral horizons of the soil profiles

Horizon	Thickness (cm)	Density (kg/m^3)	IVC (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ti (mg/kg)	Zr (mg/kg)	Ti/Zr (mg/kg)
<i>Profile 1</i>								
Ae	4	1160	-0.065	159	34.5	4176	430	9.7
Bhf1	6	980	0.125	110	23.1	4871	424	11.5
Bhf2	10	1040	0.184	84	16.6	3415	379	9
Bf	15	1140	0.086	87	17.1	2941	377	7.8
BC	30	1230	0.032	84	17.4	3128	368	8.5
C	0	1330	0	76	17.9	3090	351	8.8
<i>Profile 2</i>								
Ae	3	1160	-0.219	167	50	5059	649	7.8
Bhf1	5	980	-0.044	151	34.8	4766	627	7.6
Bhf2	12	1040	-0.084	94	19	4561	616	7.4
Bf	25	1140	0.054	91	18.2	4939	489	10.1
BC	20	1230	0.174	99	16.6	3336	407	8.2
C	0	1330	0	87	15.5	3401	442	7.7

IVC: index of volume change.

components are amphiboles (5%) and Fe-Ti oxides (<5%). Biotite and amphibole enclose many accessory minerals such as zircon, apatite and monazite. In the tills, these primary minerals are relatively well preserved. Much petrographic evidence indicates increasing rates of alteration in the B and A-horizons. For example, chloritization of biotite, Fe crust developments on biotite, sericitisation and corrosion of plagioclases reflect progressive alteration of primary metamorphic minerals. In the most altered Ae-horizon, quartz and K-feldspar

remain relatively fresh whereas biotite is significantly altered to chlorite with minor amounts of clay minerals. Despite its minor proportion in the till, hornblende is still present in the Ae-horizon and is only partially altered along cleavages and grain boundaries.

4.3. Total elemental concentrations

Total Cr, Pb, Ti and Zr concentrations are presented in Table 2. Chromium and Pb distributions

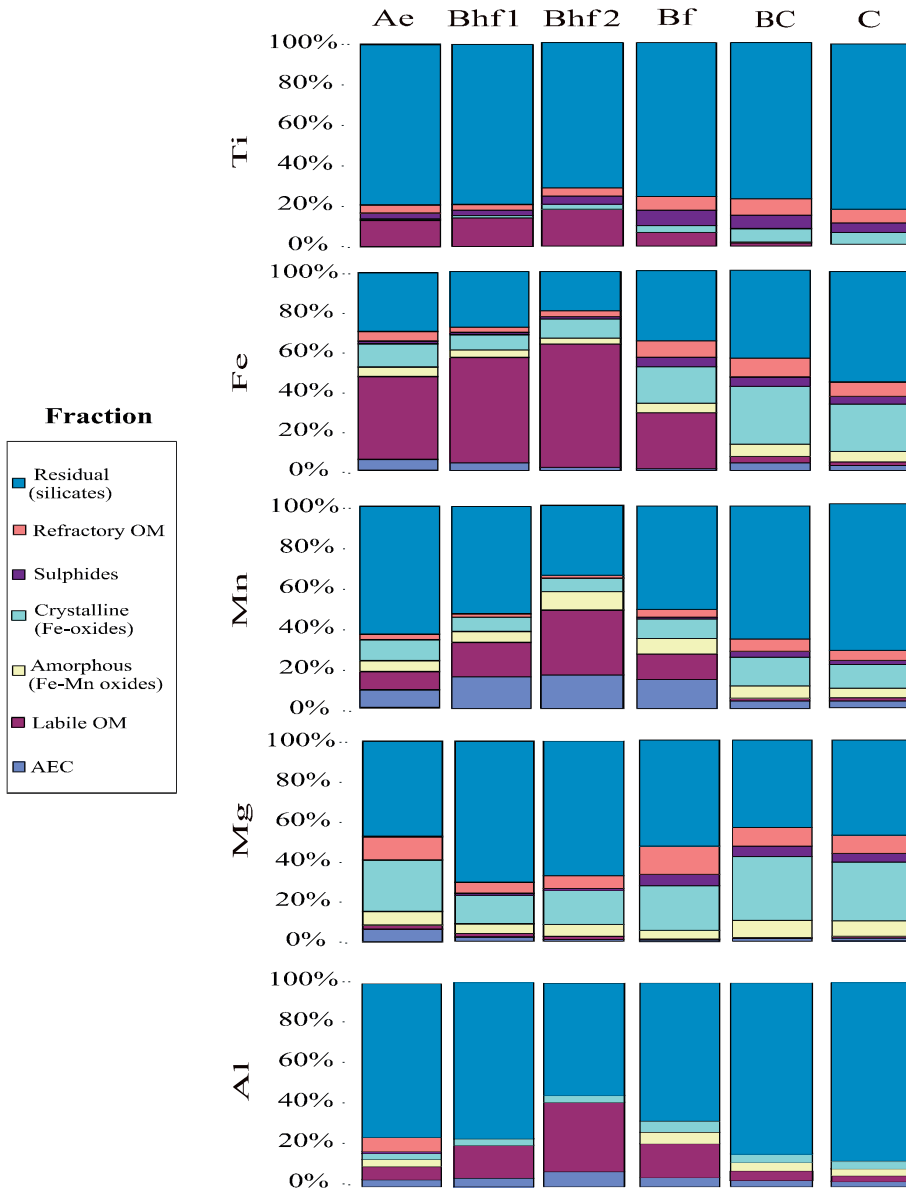


Fig. 4. Major element chemical speciation in the mineral horizons of the LCW soil profiles, illustrated by Ti, Fe, Mn, Mg and Al (profile 1).

are characterized by relatively stable concentrations in the lower soil horizons and by strong enrichment in the upper Bhf1 and Ae-horizons where concentrations in the Ae-horizons are 2–3 times higher than in the C-horizons (Table 2). In the studied soils, Ti/Zr ratios are nearly constant (Table 2). Since these two elements are present in minerals with different sizes and physical properties (e.g. Ti in ilmenite; Zr in small zircon inclusions in biotite), the near constancy of the Ti/Zr ratios argues against selective transport of fine particles within the soil profiles, which may, in some cases, explain some Al depletions in soil profiles (e.g., Van der Weijden and Van der Weijden, 1995).

5. Elemental mass balance calculations

Since Zr and Ti may be considered as relatively immobile elements in the studied soil profiles and that selective dispersion of fine minerals is not supported by the observations, these elements may be used in simple mass balance calculations to estimate long-term elemental mass balances. In this study, elemental long-term fluxes and mass balances have been calculated using the method proposed by Brimhall et al. (1991a) (see Appendix 1).

5.1. Volume changes

In this study, Zr was used instead of Ti in the calculation of the index of volume change (IVC). This choice results from the chemical speciation study which shows that between 99.4% and 99.9% of the total Zr content is partitioned in the residual fraction (silicates) whereas in some soil horizons (e.g. Bhf2), a small proportion of the total Ti content is associated with labile OM and to a lesser extent with amorphous or crystalline oxides (Fig. 4).

IVC values calculated for the mineral horizons are listed in Table 2. Negative values are noticed in the Ae-horizon of profile 1 and in the Ae, Bhf1 and Bhf2-horizons of profile 2. For example, these data suggest that materials from the actual Ae-horizon in profile 2 lost 22% of its initial volume when compared to the C-horizon, which is assumed to have maintained this volume since its formation. Volume losses in the Ae (profile 1) and Bhf-horizons (profile 2) are small, ranging from 4% to 8% of the initial material (Table 2). These volume losses mainly result from the weathering of primary minerals and progressive collapse of the soil microstructure.

In the other soil horizons, IVC values are positive reflecting volume expansion that may reach values up to 18% (Bhf2-horizon, profile 1; BC-horizon, profile 2; Table 2). The main processes contributing to soils expansion (increasing volume) are root growth, accumulation of OM, formation of Fe and Al amorphous compounds and the creation of biopores by burrowing animals (Brimhall et al., 1991 b; Egli et al., 2001). Volumetric expansion of soil horizons in profile 1 is mainly related to the accumulation of organic matter and to the formation of secondary Fe and Al solid phases (Table 1, Fig. 4). In profile 2, the Ae and both Bhf1 and Bhf2-horizons show volumetric losses, which probably reflects lower organic matter and exchangeable Al and Fe contents as well as local collapse of the soil microstructure (Tables 1 and 2). Calculated IVC values in this study are similar to those reported for other podzolic soils in North America (Jersak et al., 1995; Lichter, 1998) and in Europe (Egli et al., 2001).

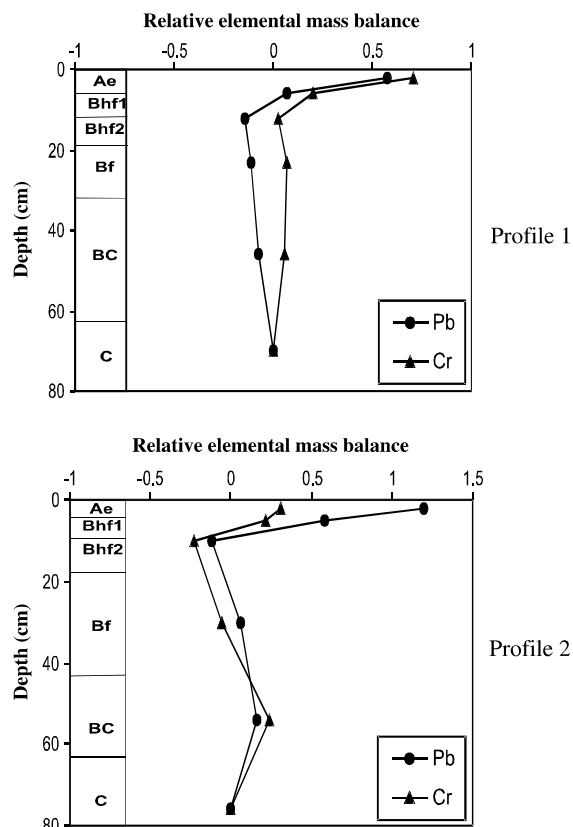


Fig. 5. Calculated relative elemental mass balances of Cr and Pb vs. depth.

5.2. Elemental mass balances and chemical speciation

Fig. 5 shows the relative elemental mass balances (Eq. (2); Appendix 1) for Cr and Pb. These two elements are characterized by strong positive mass balances in the Bhf1 and Ae-horizons (Fig. 5). For example, in profile 2, Pb enrichment reaches a maximum value of about 119%. In profile 1, both Cr and Pb mass balances increased by more than 50%. Depletions in Pb are observed in the BC, Bf and Bhf2-horizons in profile 1, whereas in profile 2, losses are only observed in the Bhf2-horizon. These losses may be related to the weathering of primary minerals and subsequent leaching of dissolved metals as shown by the Pb chemical speciation (Fig. 6). On the other hand, since Pb is quite soluble or exchangeable in the upper soil horizons, increasing Pb abundances toward the soil–atmosphere interface cannot be explained by a residual enrichment as observed for other relatively immobile elements such as Ti and Zr (Table 2). The simplest way to explain such enrichment is by accumulation of atmospheric contaminants in the upper horizons of the soils (e.g., Sañudo-Wilhemly and Gill, 1999; Kurkjian and Flegal, 2003; Filippelli et al., 2005). Finally, from the Ae to the C-horizon, Cr and Pb abundances progressively increase in the residual siliceous fraction, reflecting mineralogical control of these trace metals in the lower soil horizons (e.g., Chlopecka et al., 1996; Lee et al., 1997; Filipp-

elli et al., 2005). Indeed, chemical speciation of Pb shows that this metal is mainly partitioned in refractory minerals in the C-horizon (85%) whereas in the upper Bhf1 and Ae-horizons less than 50% of Pb is associated with this fraction. It is noteworthy that Pb associated with exchangeable, labile OM and amorphous Fe–Mn oxides fractions strongly increase toward the top of the soil profile, in as much, in the Ae horizon, 35%, 30% and 12% of total Pb, respectively, is associated with the exchangeable, labile OM and amorphous Fe–Mn oxides fractions (Fig. 6).

5.3. Lead isotope constraints on the accumulation of atmospheric contaminants in the soils

Contamination of the soils can also be demonstrated using Pb isotope ratios. Uncontaminated soils are usually characterized by nearly constant Pb concentrations and isotopic ratios throughout the soil profiles whereas, in contaminated areas, increasing Pb concentrations, with corresponding decrease in Pb isotope ratios, should be observed upwards in the soil profiles. Fig. 7 shows variations of elemental and isotopic Pb values in the studied soils vs. depth. Lead concentrations show limited variations from the C to the Bhf2-horizons (~17 mg/kg) in both profiles and increase significantly in the Bhf1 and Ae-horizons to maximum values of 36 and 50 mg/kg respectively in profiles

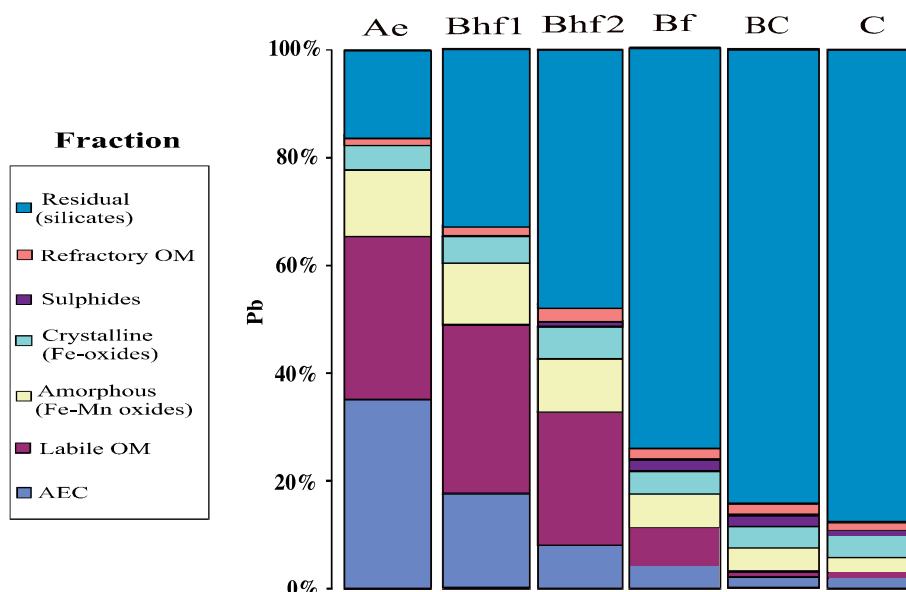


Fig. 6. Pb chemical speciation in the mineral horizons of the soil (profile 1).

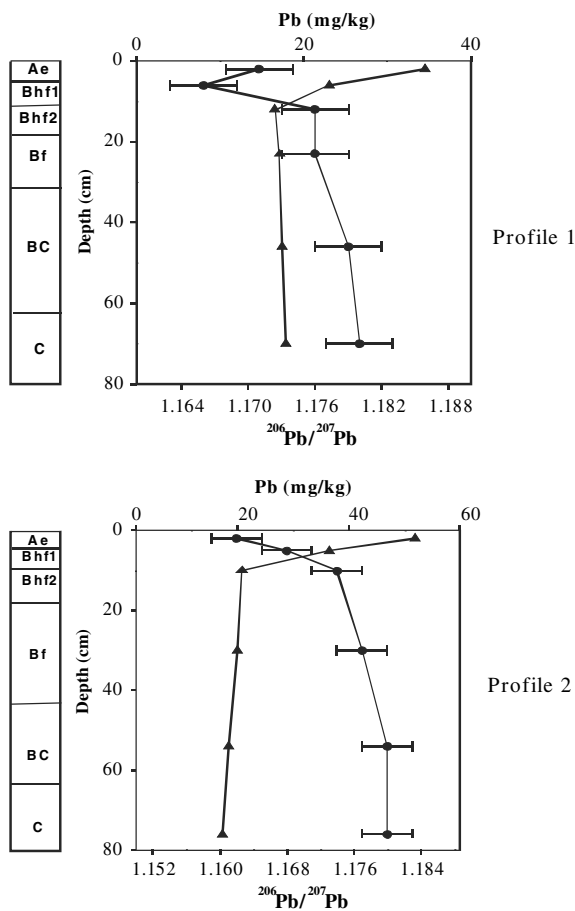


Fig. 7. Variations of Pb concentrations and isotopic ratios in the mineral horizons of the two soil profiles. ▲: Pb concentrations; ●: Pb isotopic ratios.

1 and 2. In the same way, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are relatively stable below the Bhf1-horizon (1.176 ± 0.003 in profile 1 and 1.177 ± 0.003 in profile 2) and decrease to less radiogenic values in the Bhf1 and Ae-horizons (Fig. 7). Constancy of Pb isotopic ratios and elemental concentrations below the Bhf1-horizons most probably represents the natural Pb background in the soils. The important Pb enrichments observed in the Bhf1 and Ae-horizons are accompanied by significant decreases in Pb isotope ratios (Fig. 7). This strong negative correlation implies the presence of anthropogenic Pb in these upper soil horizons (Weiss et al., 1999; Hansmann and Köppel, 2000; Bing-Quan et al., 2001). The lack of industrial and/or agricultural activities in the watershed implies that this anthropogenic component comes essentially from the atmosphere (Deboudt et al., 1999; Kurkjian and Flegal, 2003;

Filippelli et al., 2005). Previous study on the Lake Clair sediments concluded that anthropogenic Pb, accumulated since the beginning of the industrial era, comes from American and Canadian sources and that its isotopic composition principally reflects the mixing of Pb from wood and coal burning and alkyl Pb from gasoline (Ndzangou et al., 2005).

5.4. Net anthropogenic Pb inputs in the studied soils

Simultaneous use of Pb concentrations and Pb isotope ratios enables not only recognition of contamination in the studied soils, but also determination of the penetration depth of the atmospheric pollution. Lead isotope data show that, in the studied soils, only the upper Bhf1 and Ae-horizons are affected by contamination (Fig. 7). Accordingly, in both soil profiles, penetration depth of anthropogenic Pb does not exceed 10 cm. Therefore, the net anthropogenic Pb inputs (in g/m^2) can be calculated using Eq. (1). To do this, Pb concentrations in the LFH-horizon have also been measured (152 mg/kg in profile 1 and 118 mg/kg in profile 2, respectively). Study of Lake Clair sediments (Ndzangou et al., 2005) showed that anthropogenic trace metal contamination of the LCW began around 1872. Therefore, Pb fluxes ($\text{g}/\text{m}^2/\text{a}$) have been estimated for the 127a spanning from 1872 to 1999, which was the year of soil sampling. The calculations show that, during the last 127a, the LCW soils have received between 1.24 and 1.8 g/m^2 of Pb from anthropogenic sources. From these data, annual fluxes of 0.01 and 0.014 $\text{g}/\text{m}^2/\text{a}$ have been estimated.

6. Conclusions

During the last 127a, LCW forest soils have received significant amounts of trace metals from anthropogenic activities. Chemical speciation of Pb shows that 85% of this metal is mainly partitioned in refractory minerals in the C-horizon whereas in the upper Bhf1 and Ae-horizons, less than 50% of the Pb is associated with this fraction. In the Ae-horizon, for example, 35%, 30% and 12% of total Pb, respectively, is associated with the exchangeable, labile organic matter and amorphous Fe–Mn oxide fractions. Elevated Cr and Pb concentrations as well as low $^{206}\text{Pb}/^{207}\text{Pb}$ values observed in the upper soil horizons indicate the presence of an anthropogenic component in the studied soils. In both soil profiles, penetration of anthropogenic

Pb does not exceed 10 cm depth. Below this depth, both Pb concentrations and isotopic ratios remain approximately constant and similar to values measured in pre-anthropogenic sediments from the Lake Clair. These values represent the natural geochemical backgrounds of the watershed. Calculated net anthropogenic Pb inputs since 1872 amounted to between 1.24 and 1.8 g/m².

Acknowledgements

We thank Jean Gagné, M. St.-Germain and S. St.-Laurent (Forêts Québec) for their help during sampling of the soils. Special thanks are given to the Ministère des Ressources naturelles de la Faune et des Parcs du Québec (MRNFP) for access to the Lake Clair experimental station. Pierre Dumas of the Institut National de la Santé Publique du Québec is acknowledged for the determination of Pb isotopic ratios. S.O. Ndzangou acknowledges financial support by a Gabon Government doctoral fellowship. M. Richer-LaFlèche acknowledges financial support from the Fond de la Recherche Forestière (MRNQ) and from the Natural Sciences and Engineering Research Council of Canada (Grant OGP 0138413-01). Gratitude is also given to I. Bélanger, R. Gosselin and C. De Blois for their generous help in analyzing the samples by ICP-AES and ICP-MS.

Appendix 1. Method used to calculate elemental fluxes and mass balances in studied soils

A.1. Elemental mass balance calculations

In this study, elemental long-term fluxes and mass balances have been calculated using the method proposed by Brimhall et al. (1991a). Such estimations take into consideration volume changes related to pedogenic processes such as eluviation, biological activity, organic matter accumulation, degradation and alteration of primary minerals (Johnson and Watson-Stegner, 1987). Volume variation, which results in contraction or expansion of the soil horizons, is an important parameter, which has to be considered in elemental mass balance calculations (Brimhall et al., 1991a).

Such mass balance calculations imply 3 basic assumptions: (1) the original material of a given soil profile is texturally and mineralogically uniform at the time of their formation; (2) the properties of the actual C-horizon are identical to those of the original material; (3) the soil profile has at least

one conservative element such as Zr, which can be used for normalization. Assuming Zr immobility during chemical weathering of the studied soils, gains or losses of any element relative to their initial content in the fresh Quaternary till (c-horizon) can be calculated.

As suggested by Brimhall et al. (1991a), absolute elemental mass balance in a given soil horizon can be calculated as follows:

$$\delta_{x,h} = [(\rho_h C_{x,h})(\varepsilon_{zr,h} + 1) - (\rho_c C_{x,c})] \quad (1)$$

where absolute mass balance δ (g/m³ of original material) of any element x is linked to the density of materials ρ (kg/m³), to the total concentration of the element C (g/kg) and to the index of volume change ε . In Eq. (1), h and c represent respectively a given weathered soil horizon and the unweathered C-horizon.

In the same way, the relative elemental mass balances (fractional unity relative to initial content in the original material) of an element x may be calculated according to:

$$\tau_{x,h} = [(\rho_h C_{x,h})/(\rho_c C_{x,c})](\varepsilon_{zr,h} + 1) - 1 \quad (2)$$

Positive and negative values of τ suggest that element x has been added or lost, respectively, from the soil profile. The index of volume change (IVC) $\varepsilon_{zr,h}$ is calculated using total Zr (mg/kg) concentrations in the parent material (C-horizon) and in the weathered soil horizon (h) as follows:

$$\varepsilon_{zr,h} = [(\rho_c C_{zr,c})/(\rho_h C_{zr,h})] - 1 \quad (3)$$

Positive $\varepsilon_{zr,h}$ values denote expansion of the soil horizon, negative values reflect contraction processes and the lack of net volume change is marked by a value equal to zero (isovolumetric conditions).

For the time elapsed since the initial formation of the soil profile, summation of the absolute mass balances of each individual soil horizon, according to their thickness and respective density, gives the total elemental mass balance by surface unity (kg/ha or g/ha). Annual elemental mass balances (kg/ha/a or g/ha/a) are calculated by dividing the total mass balance by the age of the soil profile, which is approximately 11 Ka in the studied area (Occhietti et al., 2001). Such an age is compatible with the fact that the studied post-glacial soils in the region were emplaced directly over Quaternary glacial tills. Negative and positive mass balance values indicate elemental depletion or enrichment, respectively, in the actual soil relative to the composition of unweathered material. Negative values are generally

interpreted as equivalent to the weathering rate of the considered element.

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