Université du Québec INRS-ETE

# SIGNATURE ISOTOPIQUE DU PLOMB POUR LE MARQUAGE DE LA CONTAMINATION DES SOLS À PROXIMITÉ D'UNE FONDERIE DE MÉTAUX, NORD-OUEST DU QUÉBEC, CANADA

Par

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#### Abstract

The Rouyn-Noranda region is one in which numerous mining and smelting activities have taken place since the opening of the Horne mine in 1922 and the construction of the Horne smelter in December 1927. Before the program "Rouyn-Noranda Ville En Santé" was launched in 1987, the mining and smelting community had earned a reputation as the most polluted city in Canada because of serious environmental problems such as sulfur dioxide plumes, heavy metal fallout as well as acid rain. This project is part of the Metals in the environment (MITE) program of the Geological Survey of Canada. The major objectives of this project are: 1) to determine the extent of Pb contamination of soils exposed to Horne smelter emissions; 2) to distinguish the source of anthropogenic lead in soils using stable Pb isotope ratios; and 3) to estimate the downward migration of Pb in representative mesic soils.

Seventy five (75) samples were collected from podzolic soil profiles at eight (8) sites, six (6) of which lie along a northeast-southwest transect crossing Rouyn-Noranda, northwestern Quebec, while the other two (2) are from Grande Rivière de la Baleine region, approximately 800 km north of Rouyn-Noranda. Pb concentrations and Pb isotopic compositions were determined on the fine-grained fraction of soil samples leached by three extraction methods of increasing agressivity: (1) Mehlich-III, (2) 0.25 M HCl, and (3) total digestion by an acid mixture of HF, HNO<sub>3</sub>, HCl, and HClO<sub>4</sub>.

Pb is enriched in the surface organic horizons at all sites in Rouyn-Noranda. Its concentration decreases by two orders of magnitude from the surface organic horizons to the underlying mineral horizons. Pb isotope ratios are low in surface organic horizons, and they increase sharply in the mineral horizons. Along the NE-SW transect, average Pb concentration is as high as 869 ppm in organic horizons at site 1, closest to the smelter. It decreases exponentially with increasing distance from the smelter, reaching a value of 39 ppm at site 10, 116 km northeast of the Horne smelter. The lowest average <sup>206</sup>Pb/<sup>207</sup>Pb ratio (0.99) is observed at site 1 and the highest ratio (1.15) is found at site 10. At site 1,

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the highest Pb concentration of 1414 ppm is also accompanied by the lowest  ${}^{206}$ Pb/ ${}^{207}$ Pb ratio (0.98), which is close to the isotopic composition of Noranda galena ( ${}^{206}$ Pb/ ${}^{207}$ Pb = 0.92). Both Pb concentrations and isotopic compositions indicate that the Horne smelter is the main source of Pb contamination of soils in the Rouyn-Noranda region. Canadian anthropogenic emissions are also known to contribute modestly to the overall lead levels in soils of the Rouyn-Noranda region, but this contribution cannot be established quantitatively. Two soil profiles from Grande-Baleine display different trend of Pb concentration and isotopic composition in the Rouyn-Noranda soil profiles, it is estimated that anthropogenic lead has migrated downward to a depth of ~10-30 cm, which yields a mobility of ~1-4 mm/a.

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## Résumé étendu

#### 1. Problématique

La région de Rouyn-Noranda a été le siège de nombreuses activités d'extraction et d'affinage de métaux depuis l'ouverture de la mine Horne en 1922 et l'entrée en fonction de la fonderie Horne en 1927. Avant que le programme de "Rouyn-Noranda Ville en santé" n'ait été lancé en 1987, cette communauté minière avait acquis la réputation de ville la plus polluée au Canada en raison des sérieux problèmes environnementaux tels que des nuages d'anhydride sulfureux, des pluies acides et des retombées de métaux lourds. La construction de la fonderie Horne avait eu comme conséquence le rejet de grandes quantités de métaux lourds, tels le plomb, le zinc, le cadmium et le cuivre, dans l'environnement. Les émissions cumulées des métaux lourds de 1965 à 1998 étaient de 40 102 tonnes pour le Pb, de 38 236 tonnes pour le Zn, et de 5 080 tonnes pour le Cu. L'émission annuelle de ces métaux a atteint 2 400 tonnes pour le Pb pour la seule année 1972 et 3 100 tonnes dans le cas du Zn en 1971. Ce n'est qu'après 1987 qu'un effort a été déployé dans le but de réduire de façon importante les émissions de métaux lourds et de gaz provenant de la fonderie Horne et d'améliorer la qualité de l'air dans la ville et ses environs.

Les effets sur l'environnement des émissions de métaux sont évidents autour de la région de Rouyn-Noranda. Aux abords immédiats de la fonderie, on peut clairement observer les dommages à la végétation tels des arbres morts, une diversité biologique réduite, une croissance végétale réduite et l'érosion du sol. Toutefois près de notre site 1, environ 8.7 kilomètres au nord-est de la fonderie Horne, il n'y a pas de dommages évidents à la végétation.

Plusieurs projets de recherche concernant les problèmes environnementaux causés par les émissions de la fonderie Horne ont été conduits jusqu'à présent. Les investigations effectuées par Dumontet *et al.* (1990) indiquent qu'il y a enrichissement en métaux

lourds (Pb, Zn, Cd, Cu, etc.) au sommet des sols tourbeux à un site près de la fonderie Horne et que les concentrations diminuent graduellement avec l'augmentation de la distance de la fonderie. Carignan et Gariépy (1995) ont étudié la concentration en Pb et les rapports <sup>206</sup>Pb/<sup>207</sup>Pb dans les lichens de la région de Rouvn-Noranda et de la vallée du Saint-Laurent, et ont constaté que les concentrations en Pb sont les plus élevées dans les échantillons de lichens recueillis à proximité de la fonderie et qu'elles diminuent progressivement avec la distance de la fonderie. Alors que les rapports <sup>206</sup>Pb/<sup>207</sup>Pb covarient inversement avec les concentrations en Pb, les rapports <sup>206</sup>Pb/<sup>207</sup>Pb les plus bas (1,046) observés au site près de la fonderie sont très proches de celui de la galène de Noranda et dans la plage des valeurs des sulfures de l'Abitibi. En utilisant les rapports <sup>206</sup>Pb/<sup>207</sup>Pb. Carignan et Gariépy (1995) ont pu calculer que les émissions de la fonderie Horne représentent 50-90% du Pb atmosphérique au site le plus proche de Rouyn-Noranda. Dans la vallée du Saint- Laurent, loin de Rouyn-Noranda, c'est un mélange de sources anthropiques canadiennes et américaines qui domine. Simonetti et al. (2000) ont étudié les rapports <sup>206</sup>Pb/<sup>207</sup>Pb dans les accumulations neigeuses au Québec. Ils ont conclu que la pollution atmosphérique dans la région de Québec-Montréal est dominée par un mélange d'émissions anthropiques américaines et canadiennes. Les investigations dendrogéochimiques réalisées par Savard et al. (1999) ont démontré que l'effet des émissions atmosphériques de la fonderie Horne peut être détecté à plus de 40 km en utilisant le signal de l'isotope stable de carbone ( $\delta^{13}$ C) et de nutriments (Ca) dans les épinettes noires. Dans l'étude de géochimie isotopique des cernes de croissance par Savard et al. (accepté), une diminution significative des rapports <sup>206</sup>Pb/<sup>207</sup>Pb et une augmentation concomittante des concentrations en Pb sont observées à un site d'essai 9 km au NE de la fonderie, environ 14 ans après la mise en service de la fonderie, par rapport aux isotopes de l'H et du C qui ont enregistré les changements immédiatement après la mise en service. Le sol, à titre de principal puits des métaux lourds dans l'environnement, joue un rôle important dans le cycle global des métaux. Est-il possible de caractériser les profils de sol typiquement affectés par la contamination atmosphérique issue des émissions de la fonderie et détecter l'effet de la distance des émissions sur ces profils de sol en utilisant les méthodes géochimiques?

#### 2. Objectifs

Bien que plusieurs investigations sur la pollution par les métaux lourds dans différents média aient été réalisées dans la région, aucune recherche approfondie sur les sols exposés aux émissions de la fonderie Horne n'a été effectuée à notre connaissance dans le but de caractériser les profils de sol exposés et de retracer les sources du plomb anthropique dans les sols aux environs de Rouyn-Noranda. Dans ce projet, les concentrations en Pb observées dans différentes fractions dans des profils de sol situés le long d'un transect nord-est-sud-ouest traversant la fonderie Horne et au site de contrôle ont été déterminées dans le but d'examiner l'effet de la fonderie sur la distribution des métaux lourds dans les sols. En même temps, la composition isotopique du plomb a été examinée pour retracer l'origine du plomb dans les sols podzoliques de la région de Rouyn-Noranda. Les objectifs de cette étude sont donc les suivants :

1) déterminer l'ampleur de la contamination en Pb des sols exposés aux émissions de la fonderie Horne ;

2) identifier la ou les sources du plomb d'origine anthropique dans les sols ;

 estimer la migration du Pb vers le bas des profils dans des sols mésiques représentatifs.

#### 3. Méthodologie

#### 3.1 Échantillonnage des sols

La région d'étude est celle de Rouyn-Noranda, dans le nord-ouest du Québec (Fig. 1). Une série de 75 échantillons ont été recueillis dans des profils de sols podzoliques à huit sites, dont six se trouvent le long d'un transect nord-est-sud-ouest au droit de la fonderie Horne alors que les deux autres proviennent de la région de la Grande rivière de la Baleine, environ 800 km au nord de Rouyn-Noranda (Fig. 1). Le substrat de tous les sites était constitué de podzols dérivés de till, une combinaison typique de l'écozone de la forêt



Fig. 1 Carte simplifiée montrant la localisation des sites échantillonnés dans la région d'étude et celles des sites de contrôle.

boréale. Les échantillons de sols ont été prélevés en creusant des tranchées d'environ 60x40 cm à l'aide d'une pelle d'acier. Chaque site comprend de 7 à 12 échantillons de sols, avec au moins un échantillon prélevé de chacun des horizons. Les échantillons recueillis ont été placés dans des sacs de plastique numérotés. Tous les échantillons ont été séchés à l'air ambiant. Les racines vivantes et le matériel ligneux mort ont été retirés manuellement des échantillons. Les échantillons organiques séchés ont été broyés dans un mortier de porcelaine en utilisant de l'azote liquide, et puis ont été passés dans un tamis de 0.5 mm. Les échantillons minéraux ont été tamisés directement à 0.063 mm. Les poudres ont été entreposées dans des fioles de plastique étiquetées pour usage postérieur. Huit échantillons de granules (fraction de 2-4 millimètres) ont été également broyés avant

d'être soumis pour l'analyse des concentrations totales et des compositions isotopiques du Pb.

3.2 Analyse des échantillons en laboratoire

Les concentrations en Pb et la composition isotopique du Pb ont été déterminées sur la fraction fine des échantillons de sol lixiviés à l'aide de trois méthodes d'extraction de force croissante: (1) la méthode Mehlich-III pour l'extraction des métaux échangeables, (2) extraction partielle de 0.25 M HCl pour la fraction extractible des métaux, et (3) digestion totale par un mélange d'acides concentrés (HF, HNO<sub>3</sub>, HCl et HClO<sub>4</sub>). Une partie aliquote des solutions de chacune des méthodes d'extraction a été analysée pour les concentrations en Pb et sa composition isotopique par la spectrométrie de masse couplée à une torche au plasma (ICP-MS). Pour les corrections de masse, la norme NIST 981 a été mesurée après chaque série de 10 échantillons, ce qui résulte en des incertitudes respectives de 0.014 et de 0.004 (2 $\sigma$ ) pour les rapports <sup>206</sup>Pb/<sup>207</sup>Pb et <sup>206</sup>Pb/<sup>208</sup>Pb.

#### 4. Résultats et discussion

4.1 Concentrations en plomb et composition isotopique de la fraction échangeable

Les résultats des concentrations en Pb et des rapports  ${}^{206}$ Pb/ ${}^{207}$ Pb sont présentés aux tableaux 1 et 2. Les profils des concentrations en Pb sont présentés à la figure 2. Les concentrations en Pb dans la fraction échangeable sont de beaucoup inférieures à celles observées dans les extractions partielles et totales (Tableau 1). Elles constituent respectivement de 2.6% à 47% du plomb total dans les échantillons organiques et 0.3% à ~4.6% dans les échantillons minéraux. Le pourcentage plus élevé de plomb échangeable dans les échantillons organiques par rapport aux échantillons minéraux suggère que le plomb présent dans les horizons organiques est plus mobile que celui des horizons minéraux sous-jacents, dans lesquels le Pb est principalement associé aux matériaux parentaux. Les rapports isotopiques du Pb dans les échantillons organiques provenant de la fraction échangeable sont proches de ceux obtenus par extraction partielle (Fig. 3).

Ceci implique que le Pb dans les échantillons organiques est principalement dérivé d'apports atmosphériques, avec des rapports <sup>206</sup>Pb/<sup>207</sup>Pb caractéristiquement plus faibles. Dans le cas des échantillons minéraux, on peut observer un décalage systématique vers des rapports <sup>206</sup>Pb/<sup>207</sup>Pb plus faibles dans la fraction échangeable du Pb, ce qui suggère que la fraction échangeable est de nature différente de celle extraite par lixiviation acide faible.

4.2 Digestion partielle vs digestion totale

Les profils de concentration en Pb et de rapports <sup>206</sup>Pb/<sup>207</sup>Pb dans les fractions partielles et totales ont des tendances semblables, quoiqu'ils affichent des amplitudes différentes (Fig. 2 et 3). Pour les échantillons minéraux, les concentrations totales en Pb sont systématiquement plus élevées que celles des extractions partielles, mais ce n'est pas le cas pour les échantillons organiques. Les concentrations partielles plus élevées en Pb dans certains échantillons organiques résultent probablement d'une moindre homogénéisation des échantillons organiques (fraction < 500 um) ou encore des différences de poids des échantillons utilisés pour les extractions partielles (100 mg) et totales (500 mg). Les niveaux plus élevés en Pb dans les extractions faibles (0.25 M HCl) suggèrent également que le Pb d'origine anthropique est en grande partie retenu dans les horizons organiques de surface et qu'il est facilement libéré par lessivage acide faible. Les rapports isotopiques dans la digestion totale sont plus élevés que dans les extractions partielles (HCl) pour la plupart des échantillons organiques provenant de la région de Rouyn-Noranda. Par contre, dans les horizons minéraux, il y a décalage systématique vers des valeurs plus faibles. Cela contraste avec d'autres études dans lesquelles les extractions partielles sont toujours moins radiogéniques que les digestions totales, mais cela est concordant avec les résultats d'études de sédiments de ruisseau aux USA par Gulson et al. (1992) et Church et al. (1993). L'explication pour les valeurs plus élevées des rapports isotopiques dans les extractions partielles d'échantillons minéraux est que l'altération des silicates libérant le Pb radiogénique des minéraux riches en U et Th laisse la partie résiduelle avec des rapports isotopiques inférieurs. Ceci est en accord avec nos travaux

		Fra	action éch	angeable		Extraction p	artielle	Extraction totale			
Échantillons	Profond (cm)	Horizon	$\frac{^{206}Pb}{^{207}Pb}$	$\frac{\frac{206}{Pb}}{\frac{208}{Pb}}$	[Pb] (ppm)	$\frac{^{206}Pb}{^{207}Pb}$	$\frac{^{206}Pb}{^{208}Pb}$	[Pb] (ppm)	$\frac{^{206}Pb}{^{207}Pb}$	$\frac{^{206}Pb}{^{208}Pb}$	[Pb] (ppm)
Rouyn-Noranda	1				<u> </u>						
97-MITE-1J	2	L	1.00	0.428	$150 \pm 10$	1.00	0.432	$760 \pm 60$	1.03	0.433	$730 \pm 60$
97-MITE-11	5	F	0.97	0.420	49 ± 4	0.98	0.423	$1400 \pm 100$	1.01	0.428	$1400\pm100$
97-MITE-1H	9	FH	0.98	0.425	$10.9\pm0.9$	0.98	0.422	$430\pm30$	1.01	0.428	$420 \pm 30$
97-MITE-1F	12	Ae	1.15	0.487	$0.42\pm0.03$	1.17	0.482	$4.4 \pm 0.5$	1.12	0.464	$9.2 \pm 0.7$
97-MITE-1E	20	Bf	1.13	0.466	$0.070\pm0.006$	1.16	0.471	$2.0 \pm 0.2$	1.08	0.457	$6.2 \pm 0.5$
97-MITE-1D	30	Bf	1.21	0.502	$0.32\pm0.03$	1.18	0.487	$2.6 \pm 0.2$	1.10	0.460	$6.7 \pm 0.5$
97-MITE-1C	40	Bf	1.15	0.475	$0.25\pm0.02$	1.19	0.485	$2.1 \pm 0.2$	1.10	0.458	$6.2 \pm 0.5$
97-MITE-1B	50	BC	1.21	0.490	$0.36 \pm 0.03$	1.21	0.499	$1.5 \pm 0.1$	1.09	0.462	$5.8 \pm 0.5$
97-MITE-1A	60	BC	1.17	0.487	$0.14 \pm 0.01$	1.24	0.504	$2.6 \pm 0.2$	1.11	0.469	$5.8 \pm 0.5$
97-MITE-2J	3	L	1.02	0.439	$104 \pm 8$	1.03	0.441	$240\pm20$	1.02	0.430	$230\pm20$
97-MITE-2I	6	FH	1.07	0.450	27 ± 2	1.07	0.454	$160 \pm 10$	1.09	0.452	$160 \pm 10$
97-MITE-2H	9	Ae	1.16	0.478	$0.65\pm0.05$	1.18	0.482	$2.7 \pm 0.2$	1.12	0.470	$8.0 \pm 0.6$
97-MITE-2G	15	Bf	1.20	0.499	$0.15 \pm 0.01$	1.22	0.492	$2.2 \pm 0.2$	1.13	0.473	$7.0 \pm 0.6$
97-MITE-2F	25	Bf	1.21	0.493	$0.18\pm0.01$	1.25	0.503	$1.7 \pm 0.1$	1.12	0.470	$7.4 \pm 0.6$
97-MITE-2E	35	Bf	1.21	0.495	$0.17 \pm 0.01$	1.26	0.505	$1.7 \pm 0.1$	1.12	0.471	$5.5 \pm 0.4$
97-MITE-2D	45	Bf	1.25	0.518	$0.13\pm0.01$	1.27	0.505	$1.6 \pm 0.1$	1.10	0.465	$6.2 \pm 0.5$
97-MITE-2C	55	BC	1.20	0.496	$0.110 \pm 0.009$	1.25	0.501	$1.5 \pm 0.1$	1.10	0.466	$6.2\pm0.5$
97-MITE-2B	65	BC	1.26	0.510	$0.17\pm0.01$	1.28	0.501	$1.7 \pm 0.1$	1.10	0.462	6.0 ± 0.5

Tableau 1. Concentrations et compositions isotopiques du Pb mesurées dans la fraction échangeable (Mehlich-III), la fraction extractible (0.25 M HCl) et la fraction totale des échantillons de sols des régions de Rouyn-Noranda et de Grande-Baleine.

							Tableau 1 (	(suite)			
		Fra	action éch	angeable		Extraction p	oartielle		Extraction	totale	
Échantillons	onde m	Horizon	<sup>206</sup> Pb	$^{206}Pb$	[Pb]	$^{206}Pb$	$^{206}Pb$	[Pb]	$^{206}Pb$	$^{206}Pb$	[Pb]
	Prof ((		<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)
97-MITE-2A	75	BC	1.22	0.504	$0.19 \pm 0.01$	1.25	0.496	$1.8 \pm 0.1$	1.10	0.466	$6.3 \pm 0.5$
00-DMITE-4H	4	FL	1.01	0.436	45 ± 4	1.01	0.434	$230\pm20$	1.03	0.432	$200 \pm 20$
00-DMITE-4G	8	HF	1.03	0.439	$5.9 \pm 0.5$	1.03	0.439	$280 \pm 20$	1.05	0.440	$310 \pm 20$
00-DMITE-4F	10	Ae	1.12	0.478	$0.69\pm0.06$	1.12	0.468	$2.6 \pm 0.2$	1.12	0.469	$8.7\pm0.7$
00-DMITE-4E	15	Bhf	1.06	0.476	$0.030\pm0.002$	1.16	0.479	$2.9 \pm 0.2$	1.12	0.476	$9.0\pm0.7$
00-DMITE-4D	25	Bf	1.19	0.504	$0.020\pm0.002$	1.21	0.490	$1.13 \pm 0.09$	1.11	0.471	$4.9 \pm 0.4$
00-DMITE-4C	35	Bf	1.22	0.486	$0.040\pm0.003$	1.23	0.497	$1.14 \pm 0.09$	1.10	0.467	$5.1 \pm 0.4$
00-DMITE-4B	45	BC	1.11	0.468	$0.070 \pm 0.006$	1.17	0.482	$1.4 \pm 0.1$	1.07	0.461	$5.0 \pm 0.4$
00-DMITE-4A	55	Cg	1.16	0.489	$0.030\pm0.002$	1.20	0.490	$1.2 \pm 0.1$	1.07	0.460	$4.9 \pm 0.4$
99-MITE-8L	3	LF	0.98	0.427	85 ± 7	0.99	0.431	$450 \pm 40$	1.02	0.427	$350 \pm 30$
99-MITE-8K	6	H-Ah	1.01	0.435	56 ± 5	1.02	0.435	$240 \pm 20$	1.03	0.433	$190 \pm 10$
99-MITE-8J	12	Ae	1.10	0.458	$4.7\pm0.4$	1.11	0.464	$12 \pm 1$	¥ 1.13	0.458	$16 \pm 1$
99-MITE-8I	20	Bhf	1.12	0.467	$0.050\pm0.004$	1.15	0.469	$2.7 \pm 0.2$	1.13	0.457	$9.0 \pm 0.7$
99-MITE-8H	30	Bf	1.18	0.481	$0.040\pm0.003$	1.25	0.496	1.11 ±0.09	1.13	0.458	$9.3 \pm 0.7$
99-MITE-8G	40	Bf	1.20	0.484	$0.040 \pm 0.003$	1.21	0.485	$1.2 \pm 0.1$	1.13	0.458	$9.6 \pm 0.8$
99-MITE-8F	50	Bf	1.21	0.492	$0.040\pm0.003$	1.24	0.494	$1.4 \pm 0.1$	1.14	0.464	$8.4 \pm 0.7$
99-MITE-8E	60	Bhf	1.20	0.493	$0.030 \pm 0.002$	1.22	0.488	$1.3 \pm 0.1$	1.11	0.455	$9.2 \pm 0.7$
99-MITE-8D	70	Bf	1.20	0.487	$0.070 \pm 0.006$	1.23	0.494	$1.6 \pm 0.1$	1.10	0.452	$10.7 \pm 0.9$
99-MITE-8C	80	Bf	1.16	0.475	$0.080\pm0.006$	1.20	0.484	$2.1 \pm 0.2$	1.15	0.468	$8.9 \pm 0.7$
99-MITE-8B	90	BC	1.19	0.486	$0.090\pm0.007$	1.23	0.490	1.9 ±0.2	1.17	0.479	$8.0 \pm 0.6$

							Tableau 1 (	(suite)				
· · · · · · · ·	au		Fra	action éch	nangeable		Extraction p	artielle		Extraction totale		
Échantillons	onde cm)	Horizon	<sup>206</sup> Pb	<sup>206</sup> Pb	[Pb]	$^{206}Pb$	$^{206} Pb$	[Pb]	$^{206}Pb$	$^{206}\!Pb$	[Pb]	
	Prof ((		<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> Pb	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	
99-MITE-8A	100	С	1.17	0.475	$0.070 \pm 0.006$	1.22	0.486	$1.8 \pm 0.1$	1.16	0.478	$6.8 \pm 0.5$	
99-MITE-9J	10	F	0.98	0.425	$28 \pm 2$	0.98	0.426	$750 \pm 60$	1.00	0.422	$550 \pm 40$	
99-MITE-9I	15	H-Ah	1.02	0.437	$23 \pm 2$	1.04	0.443	$58 \pm 5$	1.04	0.435	57 ± 5	
99-MITE-9H	22	Ae	1.10	0.458	$1.5 \pm 0.1$	1.12	0.465	$4.2 \pm 0.3$	1.12	0.461	$9.0 \pm 0.7$	
99-MITE-9G	30	Bhf	1.19	0.472	$0.3 \pm 0.03$	1.20	0.475	$3.6 \pm 0.3$	1.22	0.499	$9.1 \pm 0.7$	
99-MITE-9F	40	Bf	1.21	0.480	$0.16 \pm 0.01$	1.22	0.487	$2.4 \pm 0.2$	1.12	0.462	$7.8 \pm 0.6$	
99-MITE-9E	50	Bf	1.20	0.478	$0.13\pm0.01$	1.22	0.489	$2.2 \pm 0.2$	1.10	0.457	$7.6 \pm 0.6$	
99-MITE-9D	60	Bf	1.23	0.486	$0.16 \pm 0.01$	1.23	0.493	$2.5\pm0.2$	1.12	0.461	$8.6\pm0.7$	
99-MITE-9C	70	BC	1.20	0.477	$0.17 \pm 0.01$	1.23	0.488	$2.6 \pm 0.2$	1.12	0.460	$8.7\pm0.7$	
99-MITE-9B	80	С	1.21	0.479	$0.21 \pm 0.02$	1.22	0.488	$2.2 \pm 0.2$	1.10	0.456	$8.3 \pm 0.7$	
99-MITE-9A	90	С	1.20	0.480	$0.20\pm0.02$	1.23	0.492	$1.9 \pm 0.2$	1.10	0.454	$8.1 \pm 0.6$	
99-MITE-10J	6	LF	1.10	0.462	$3.2 \pm 0.3$	1.10	0.464	74 ± 6	1.10	0.453	73 ± 6	
99-MITE-10I	15	FH	1.17	0.482	$6.3 \pm 0.5$	1.17	0.488	$25 \pm 2$	1.16	0.469	21 ± 2	
99-MITE-10H	22	Н	1.17	0.479	$2.2 \pm 0.2$	1.17	0.484	$18 \pm 1$	1.14	0.464	$20 \pm 2$	
99-MITE-10G	30	Ae	1.16	0.482	$0.4 \pm 0.3$	1.15	0.476	$0.96\pm0.07$	1.06	0.452	$8.4 \pm 0.7$	
99-MITE-10F	40	Bhf	1.28	0.508	$0.100\pm0.008$	1.28	0.513	$2.8 \pm 0.2$	1.15	0.471	$10.1 \pm 0.8$	
99-MITE-10E	50	Bf	1.05	0.547	$0.070\pm0.006$	1.38	0.537	$1.8 \pm 01$	1.12	0.469	$8.4\pm0.7$	
99-MITE-10D	60	Bf	1.40	0.539	$0.080 \pm 0.006$	1.37	0.541	$1.7 \pm 0.1$	1.11	0.458	$9.0\pm0.7$	
99-MITE-10C	70	BC	1.40	0.539	$0.100\pm0.008$	1.42	0.549	$1.6 \pm 0.1$	1.12	0.461	$8.8\pm0.7$	
99-MITE-10B	80	С	1.51	0.577	$0.090\pm0.007$	1.46	0.577	$1.4 \pm 0.1$	1.11	0.460	$8.2 \pm 0.7$	

							Tableau 1	(suite)				
······································	h		Fra	action éch	angeable		Extraction p	partielle		Extraction totale		
Échantillons	fonde (cm)	Horizon	<sup>206</sup> Pb	<sup>206</sup> <i>Pb</i>	[Pb]	<sup>206</sup> Pb	<sup>206</sup> <i>Pb</i>	[Pb]	<sup>206</sup> Pb	<sup>206</sup> Pb	[Pb]	
	Pro		<sup>207</sup> <i>Pb</i>	$^{208}Pb$	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	
Grande-Baleir	ne							······································				
99-MITE-10A	90	С	1.38	0.545	$0.18\pm0.01$	1.42	0.554	$1.7 \pm 0.1$	1.11	0.463	$9.2 \pm 0.7$	
98-MITE-61	3	LF	1.20	0.490	$5.7\pm0.5$	1.19	0.482	$24 \pm 2$	1.16	0.470	$33 \pm 3$	
98-MITE-6H	7	Ah-H	1.18	0.446	$0.89\pm0.07$	1.19	0.448	$4.6 \pm 0.4$	1.03	0.415	$16 \pm 1$	
98-MITE-6G	11	Ae	1.15	0.442	$1.63 \pm 0.1$	1.16	0.432	$6.4 \pm 0.5$	1.05	0.420	$25 \pm 2$	
98-MITE-6F	17	Bhfj	1.22	0.415	$0.29\pm0.02$	1.27	0.422	$4.0 \pm 0.3$	1.05	0.423	$18 \pm 1$	
98-MITE-6E	28	Bf	1.24	0.415	$0.62\pm0.05$	1.34	0.405	$4.1 \pm 0.3$	1.06	0.413	21 ± 2	
98-MITE-6D	38	Bf	1.23	0.388	$0.66\pm0.05$	1.33	0.398	$4.5 \pm 0.4$	1.04	0.414	$20 \pm 2$	
98-MITE-6C	48	С	1.22	0.387	$0.61\pm0.05$	1.33	0.396	$4.4 \pm 0.4$	1.05	0.413	$20 \pm 2$	
98-MITE-6B	60	С	1.23	0.401	$0.88\pm0.07$	1.34	0.400	$4.5 \pm 0.4$	1.05	0.415	$21 \pm 2$	
98-MITE-6A	70	С	1.19	0.438	$1.9 \pm 0.2$	1.28	0.415	$6.0 \pm 0.5$	1.06	0.419	$21 \pm 2$	
98-MITE-7H	5	HF	1.21	0.490	$1.9 \pm 0.1$	1.20	0.483	$4.2 \pm 0.3$	1.14	0.462	$6.6 \pm 0.5$	
98-MITE-7G	9	Ah-H	1.22	0.392	$0.81\pm0.06$	1.22	0.390	$3.8 \pm 0.3$	1.06	0.415	$10.6\pm0.8$	
98-MITE-7E	16	Bhf	1.25	0.422	$0.080\pm0.006$	1.27	0.421	$6.0 \pm 0.5$	1.10	0.424	$19 \pm 1$	
98-MITE-7D	23	Bhf	1.28	0.413	$0.100\pm0.008$	1.32	0.419	$5.1 \pm 0.4$	1.11	0.428	21 ± 2	
98-MITE-7C	30	Bhf	1.29	0.415	$0.12\pm0.01$	1.35	0.418	$5.5 \pm 0.4$	1.11	0.432	$19 \pm 1$	
98-MITE-7B	35	Bf	1.29	0.414	$0.24\pm0.02$	1.36	0.424	$6.5 \pm 0.5$	1.12	0.435	$21 \pm 2$	
98-MITE-7A	39	Bhf	1.33	0.401	$0.17 \pm 0.01$	1.38	0.414	$6.4 \pm 0.5$	1.12	0.433	$22 \pm 2$	

Échantillons	Profondeur (cm)	Horizon	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>208</sup> Pb	Pb (ppm)
97-MITE-1B-G	50	BC	19.61	16.25	40.20	1.21	0.488	$3.4 \pm 0.3$
97-MITE-2C-G	55	BC	18.52	16.01	39.19	1.16	0.473	$3.1 \pm 0.2$
00-DMITE-4B-G	45	BC	19.03	15.98	39.65	1.19	0.480	$2.1 \pm 0.2$
98-MITE-6C-G	48	С	14.94	15.33	38.34	0.97	0.390	$17 \pm 1$
98-MITE-7B-G	35	Bf	15.98	15.59	38.50	1.03	0.415	$16 \pm 1$
99-MITE-8B-G	90	BC	22.47	16.81	42.73	1.34	0.526	$2.4 \pm 0.2$
99-MITE-8E-G	60	Bhfj	22.63	17.06	42.88	1.33	0.528	$2.7 \pm 0.2$
99-MITE-10C-G	70	BC	16.76	15.35	36.75	1.09	0.456	$4.6 \pm 0.4$

Tableau 2. Concentrations et compositions isotopiques du Pb mesurées par extraction totale dans les granules (2-4 mm) de la roche mère des profils de sols étudiés.

\*99-MITE-10C-G: 99-année d'échantillonnage; MITE = Metals In The Environment; 10- numéro de site; G, échantillon de granules.



xix



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montrant que les rapports <sup>206</sup>Pb/<sup>207</sup>Pb des échantillons de granules (2-4 millimètres) sont inférieurs à ceux observés dans les extractions échangeables et partielles. Le Pb issu de la décroissance radioactive occupe souvent des sites défectueux de la maille des silicates et est libéré préférentiellement lors de la météorisation. Le plomb libéré par l'altération de la roche-mère du sol est ainsi présumément associé aux hydroxydes de fer et de manganèse, ou adsorbé sur la matière organique et les minéraux argileux. Ce type de plomb est facilement libéré lors de l'attaque à l'acide dilué.

La libération d'un Pb plus radiogénique par altération météorique a donc pour conséquence de diluer les rapports isotopiques des échantillons de granules et peut expliquer les valeurs inférieures des rapports isotopiques dans les digestions totales. Cette interprétation s'appuie aussi sur le fait que les rapports isotopiques dans la fraction totale sont un mélange de Pb lixivié par 0.25 M HCl et de Pb dérivé des minéraux parentaux (échantillons de granules). Ceci peut être exprimé par l'équation du bilan de masse suivante:

$$[^{206}Pb/^{207}Pb]_{P} * [Pb]_{P} + [^{206}Pb/^{207}Pb]_{D} * ([Pb]_{T-} [Pb]_{P}) = [^{206}Pb/^{207}Pb]_{T} * [Pb]_{T}$$
$$[^{206}Pb/^{208}Pb]_{P} * [Pb]_{P} + [^{206}Pb/^{208}Pb]_{D} * ([Pb]_{T-} [Pb]_{P}) \approx [^{206}Pb/^{208}Pb]_{T} * [Pb]_{T}$$

où P représente l'extraction partielle, D, la fraction détritique (granules de 2-4 mm), T, la digestion totale.

Cette équation ne s'applique qu'aux échantillons minéraux et à quelques échantillons organiques provenant des sites de contrôle 6 et 7, lesquels ont été présumément moins affectés par les activités humaines. Le degré de météorisation du sol, l'effet des activités anthropiques et la représentativité des échantillons de granules pourraient être autant de raisons pour lesquelles un tel bilan de masse ne peut être appliqué aux sites de la région de Rouyn-Noranda.

4.3 Concentration et composition isotopique du Pb dans les extractions acides faibles

En général, le Pb est fortement concentré dans les horizons organiques au sommet des profils (L, F et H), et les concentrations diminuent brusquement des horizons organiques aux horizons minéraux. Contrairement aux concentrations en Pb, les rapports isotopiques du Pb sont plus élevés dans les échantillons minéraux provenant des horizons plus profonds, et ils diminuent de manière significative vers le sommet.

De faibles teneurs en Pb (~2 ppm) caractérisent les horizons plus profonds de tous les profils (sous 30-40 cm), puis augmentent légèrement dans le Bhf, le Bf supérieur ou l'horizon d'Ae pour atteindre des valeurs maximales dans les horizons organiques supérieurs (Fig. 2). Les rapports <sup>206</sup>Pb/<sup>207</sup>Pb sont plus radiogéniques dans les parties plus profondes des profils de sol, et ils diminuent brusquement de l'horizon illuvial supérieur (Bhf ou Bf) ou de l'horizon éluvial (Ae) aux horizons organiques, atteignant les valeurs minimales au sommet (Fig. 3). Ces profils inversement corrélés des concentrations et des isotopes de Pb sont attribués au dépôt de Pb atmosphérique d'origine industrielle, lequel est généralement caractérisé par des rapports <sup>206</sup>Pb/<sup>207</sup>Pb plus faibles. Une diminution des concentrations en Pb et une augmentation des rapports <sup>206</sup>Pb/<sup>207</sup>Pb caractérisent l'horizon le plus superficiel au site 1, près de la fonderie Horne, reflétant une réduction récente des apports de Pb atmosphérique et/ou la contribution de sources de Pb plus radiogénique. La première hypothèse trouve confirmation dans le fait que les émissions métalliques de la fonderie Horne ont diminué de 50% depuis 1985. La fonderie Horne traite à 100% des minerais provenant d'autres producteurs de métaux non précieux provenant du nord-ouest du Québec ou importés d'Europe depuis la fermeture de la mine Horne (cuivre-or) en 1976. Les signatures isotopiques plus élevées des sulfures de Cu d'Europe (<sup>206</sup>Pb/<sup>207</sup>Pb = ~1.10-1.15) et d'Abitibi ( $^{206}$ Pb/ $^{207}$ Pb = 0.92-1.04) ont pu contribuer aux signatures isotopiques plus élevées au sommet des horizons organiques au site 1, le plus sensible aux apports atmosphériques proximaux.

Les concentrations et rapports isotopiques du Pb varient non seulement verticalement dans les divers profils échantillonnés, mais aussi latéralement entre les sites. Le long du transect nord-est de Rouyn-Noranda, la concentration moyenne en Pb dans les échantillons organiques est très élevée (869 ppm) au site 1, à seulement 8.7 km de fonderie Horne, et elle diminue exponentiellement avec l'éloignement de la fonderie pour atteindre 39 ppm au site 10 situé à 116 km (Figure 4). Des tendances semblables ont été également observées pour d'autres métaux tels le Cu et le Zn dans le cadre de notre étude



Fig. 4 Diagramme montrant les concentrations et compositions moyennes du Pb dans les horizons organiques de surface en fonction de la distance par rapport à la fonderie Horne.

(données non publiées) et de plusieurs autres études. Au contraire des concentrations en Pb, les rapports isotopiques du Pb augmentent graduellement de 0.99 au site 1 à 1.15 au site 10 (Figure 4), indiquant une contribution décroissante du Pb anthropique avec l'éloignement de la source ponctuelle de pollution au Pb. Au site 1, l'échantillon montrant la concentration la plus élevée en Pb (1 414 ppm) présente également le plus bas rapport <sup>206</sup>Pb/<sup>207</sup>Pb (0.98). Cette valeur est proche de la valeur <sup>206</sup>Pb/<sup>207</sup>Pb de la galène de Noranda (0.92) (Franklin *et al.*, 1983) et dans la plage des sulfures de l'Abitibi. La diminution des concentrations en Pb et l'augmentation des rapports isotopiques avec l'éloignement de la fonderie Horne suggèrent que celle-ci est la source ponctuelle de la contamination en métaux lourds des sols de la région de Rouyn-Noranda. Cette conclusion s'appuie aussi sur le fait que les compositions isotopiques du Pb mesurées

dans les sols se situent le long d'une ligne de mélange entre la composition isotopique de la galène de Noranda et celle du matériel minéral dans les horizons plus profonds des profils (Fig. 5). La valeur <sup>206</sup>Pb/<sup>207</sup>Pb la plus basse observée (0.98) au site le plus proche de la fonderie Horne est inférieure à celles de 1.046 et de 1.172 enregistrées respectivement dans des échantillons de lichens (Carignan et Gariépy, 1995) et dans des



Fig. 5 Diagramme montrant les rapports  ${}^{206}Pb/{}^{207}Pb$  et  ${}^{206}Pb/{}^{208}Pb$  dans la fraction extractible (0.25 M HCl) des échantillons de sols. Notez l'apport de Pb moins radiogénique dans les horizons organiques de surface. Les rapports isotopiques de la Galène de Noranda (Franklin, *et al.*, 1983), et les émissions anthropiques des États-Unis (Simonetti *et al.*, 2000) et du Canada (Carignan and Gariépy, 1995) sont aussi été indicués.

échantillons de neige (Simonetti *et al.*, 2000) dans la région de Rouyn-Noranda. Cette différence peut être attribuée à l'éloignement plus grand de l'échantillon de lichen par rapport à la fonderie Horne (~ 100 km), ou encore aux signatures spécifiques du Pb dans les aérosols pendant la croissance des lichens ou pendant la période nivale.

La figure 6 montre le rapport <sup>206</sup>Pb/<sup>207</sup>Pb vs la concentration en Pb pour tous les échantillons provenant des huit (8) profils. La contamination des sols dans la région de Rouyn-Noranda est caractérisée par des concentrations plus élevées en plomb et des rapports isotopiques inférieurs dans les horizons organiques. Tous les échantillons minéraux provenant de Rouyn-Noranda ont une teneur en Pb inférieure (< 12 ppm) et des rapports plus radiogéniques  ${}^{206}Pb/{}^{207}Pb$  ( ${}^{206}Pb/{}^{207}Pb = 1.11-1.46$ ), suggérant que les horizons minéraux des profils de sols ont été peu ou pas affectés par les apports de Pb anthropique.



Fig. 6 Diagramme montrant le rapport <sup>206</sup>Pb/<sup>207</sup>Pb versus la concentration en Pb dans la fraction extractible (0.25 M HCl) de tous les échantillons de sols. Les rapport <sup>206</sup>Pb/<sup>207</sup>Pb de la galène de Noranda (Franklin *et al.*, 1983) et sulfures de l'Abitibi sont aussi indiqués (Carignan et Gariépy, 1995).

Les concentrations et rapports isotopiques de Pb dans les profils de sol de Grande-Baleine sont caractérisés par des tendances n'affichant pas de changement vertical marqué. Tous les échantillons provenant de Grande-Baleine ont des valeurs proches des échantillons minéraux provenant de Rouyn-Noranda (Fig. 6) mais à l'extérieur de la ligne de mélange <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>206</sup>Pb/<sup>208</sup>Pb (Fig. 5), suggérant que cette région est moins affectée par des activités anthropiques.

Les rapports <sup>206</sup>Pb/<sup>207</sup>Pb moyens de 1.25 pour les sites 1, 2, 8, 9 et 4 et de 1.4 (site 10) déterminés sur l'extraction à 0.25 M HCl représentent les rapports <sup>206</sup>Pb/<sup>207</sup>Pb du Pb naturel puisque les rapports <sup>206</sup>Pb/<sup>207</sup>Pb des échantillons minéraux les plus élevés proviennent de l'extraction partielle. Le rapport <sup>206</sup>Pb/<sup>207</sup>Pb de 0.92 est considéré comme typique des émissions de la fonderie Horne. En utilisant ces valeurs et les équations standard de dilution isotopique, la proportion estimée des émissions de la fonderie dans les sols de la région de Rouyn-Noranda peut être calculée. Les résultats sont présentés à la figure 7. Le Pb anthropique provenant des émissions de la fonderie a probablement été transporté jusqu'à 100 km.





Sur la foi des concentrations en Pb et des rapports <sup>206</sup>Pb/<sup>207</sup>Pb dans les profils de sols, la migration du Pb anthropique dans les sols est estimée atteindre une profondeur de ~10-30 cm. Si le dépôt du Pb provenant des émissions de la fonderie a commencé à compter de l'entrée en service de la fonderie Horne en décembre 1927 ou juste après, une mobilité de 1 à 4 mm/a est estimée, ce qui concorde avec les résultats d'autres recherches.

Introduction

### 1. Pb contamination of the environment

Heavy metals occur naturally in the environment and are thus present, generally at low concentrations, in rocks, soils, sediments, plants and animals. But with the advent of the industrial revolution, large amounts of heavy metals were released to the atmosphere through various human activities. Of all the heavy metals concerned, lead continues to be the subject of significant environmental concern because of its widespread use and its toxicity and persistence in the environment. Large quantities of lead were introduced into the environment through human activities, such as burning of leaded gasoline in automobiles, mining, smelting and refining, industrial and municipal waste disposal, combustion of coal, *etc.* The burning of leaded gasoline was once the largest source of lead in the environment (Harrison and Luxen, 1981), but industrial releases such as lead mining, smelting and refining are now the major sources due to the drastic reduction of leaded gasoline used in automobiles.

In the absence of reliable historical data on lead emissions, past records of lead in the environment has to be obtained indirectly. Soils, sediments, peat, ice and trees have provided indirect evidence of lead pollution in the environment. Elevated anthropogenic lead concentrations have been documented in aquatic sediments (Öhlander *et al.*, 1993, Moor *et al.*, 1996; Farmer *et al.* 1996, 1997), soils (Rieuwerts and Farago, 1996; Verner *et al.*, 1996), peat bogs (Cortizas *et al.*, 1997; Görres and Frenzel, 1997), corals from the Atlantic and Pacific oceans (Shen and Boyle, 1987), snow and ice from polar regions (Boutron *et al.*, 1991, 1994; Rosman *et al.*, 1993, 1994), and trees near a copper smelter (Savard *et al.*, accepted).

The measurement of lead concentrations in sediments or soils cannot elucidate alone its origin, since elevated Pb and other heavy metal accumulations do occur in areas with high

background Pb levels. To study the source of Pb in the environment, Pb isotope geochemistry can provide crucial information for identifying its provenance (Doe, 1970; Kramers and Tolstikhin, 1997). The measurement of Pb concentrations and isotope ratios, together with the <sup>210</sup>Pb, <sup>137</sup>Cs, or <sup>14</sup>C dating in the profiles of aquatic sediments, peat bogs and polar ice provides an indirect record of the history of human civilization. Emissions of anthropogenic Pb dating from Greek and Roman times have been recorded both in Greenland ice (Hong et al., 1994) and lake sediments (Renberg et al., 1994). In Scotland sediments, Farmer et al. (1996) demonstrated that the anthropogenic lead inputs have started as early as 1630 A.D. The rapid increase of Pb concentration together with the drop of Pb isotope ratios starting from the 1920s was attributed to the introduction of leaded petrol in the 1920s. In addition to lake sediments and polar ice, anthropogenic Pb emissions have also been recorded in peat bogs. These records have documented an ancient peak in Pb production in Roman times (Shotyk et al., 1997; Farmer et al., 1997), elevated Pb emissions during the Medieval period (Brännvall et al., 1997) and a rapid increase of Pb inputs during the industrial revolution (Farmer et al., 1997; Shotyk et al., 1997), especially massive Pb inputs in peat during the 1950s, 1960s and 1970s, as a result of the widespread introduction of leaded gasoline. The significant reduction of atmospheric Pb inputs both in North America (Norton et al., 1997) and in Europe (Brännvall et al., 1997; Farmer et al., 1997; Shotyk et al., 1997) is a measure of the success of efforts to eliminate leaded gasoline.

Soils, as the major sink of heavy metals in the environment, play an important role in global metal cycling; consequently, anthropogenic lead contamination of soils has received much attention. Numerous investigations have been conducted in soils in the vicinity of smelters (Linzon *et al.*, 1976; Bisessars, 1982; Dumontet *et al.*, 1990; Karczewska, 1996; Rieuwerts and Farago, 1996; Verner and Ramsey, 1996) and near traffic roads (Chow, 1970; Erel *et al.*, 1997) to study the heavy metal contamination. These studies found that heavy metal concentrations are extremely high in the upper horizons of the soils close to smelters and highways and that they decrease progressively with increasing distance from the contaminant sources. Such distribution patterns of Pb in soils have been attributed to smelter emissions (Rabinowitz and Wetherill, 1972) and to

the increased use of leaded gasoline (Chow, 1970; Gulson, 1981; Erel et al., 1997) by using lead isotope signatures.

The detection of Pb pollution in soils is based on the fact that Pb isotopic ratios in natural background materials, such as crustal rocks and soils, are significantly different from those of industrial pollutants, such as smelter emissions or leaded gasoline. Ore leads used in industrial activities usually have <sup>206</sup>Pb/<sup>207</sup>Pb significantly lower than the natural ratios of soils and soil related components, because the accumulation of <sup>206</sup>Pb from radioactive decay of <sup>238</sup>U stops when lead is separated from uranium during the formation of the ore bodies, while it continues in crustal rocks from which soils are derived. Lead concentration in soil profiles is often enhanced in the uppermost horizon and decreases with depth. If natural processes had caused this enrichment, Pb should have an isotope pattern related to soil parent materials throughout the soil profile. When soils are exposed to industrial pollution, their Pb concentrations and isotope rations usually display an inverse trend with depth in soil profiles (Pouchelt *et al.*, 1993).

#### 2. Previous work in the study area

Rouyn-Noranda is a region where numerous mining and smelting activities have taken place since the opening of the Horne mine in 1922 and construction of the Horne smelter in 1927. Before the "Rouyn-Noranda Ville En Santé" program was launched in 1987, the mining and smelting community earned the reputation of "the most polluted city in Canada", because of the severe environmental problems such as clouds of sulfur dioxide, acid rain, lead and other heavy metal contamination. Many research projects pertaining to Horne smelter emission-related environmental problems were conducted (*e.g.* Dumontet *et al.*, 1990; Henderson *et al.*, 1999; Carignan and Gariépy, 1995). Investigations carried out by Dumontet *et al.* (1990) revealed that heavy metals (Pb, Zn, Cd, Cu, *etc.*) are enriched in top soils at sites near the Horne smelter and decrease gradually with increasing distance away from the smelter. In a comparative study, Savard *et al.* (accepted) investigated the Pb concentration and Pb isotope ratios in spruce rings near Rouyn-Noranda. They found that Pb concentrations in spruce rings show a major increase

starting in 1944 which coincides with a decrease of <sup>206</sup>Pb/<sup>207</sup>Pb ratios. It is suggested that the delay of 14 years is mainly generated by the buffering effect of soils. Carignan and Gariépy (1995) investigated the Pb concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb ratios in lichens in Rouyn-Noranda region and in the St. Lawrence Valley. They found that Pb concentrations are highest in lichen samples collected at sites close to the smelter, and decline progressively with distance away from the smelter. While <sup>206</sup>Pb/<sup>207</sup>Pb ratios inversely covary with Pb concentrations, the lowest <sup>206</sup>Pb/<sup>207</sup>Pb ratio of 1.046 found at site close to smelter is very close to that of the typical Noranda galena and within the range of Abitibi copper sulfides. By using <sup>206</sup>Pb/<sup>207</sup>Pb ratios, they were able to calculate that emissions from Horne smelter accounted for 50%-90% of the atmospheric Pb at site nearest Rouyn-Noranda. In the St. Lawrence Valley, far away from Rouyn-Noranda, a mixture of Canadian and U.S. anthropogenic Pb sources is found. Simonetti *et al.* (2000) investigated the <sup>206</sup>Pb/<sup>207</sup>Pb ratios of snow pack from Quebec. They found that atmospheric pollution in the Quebec-Montreal region is dominated by a mixture of anthropogenic emissions from U.S. and Canadian sources.

#### 3. Objectives of this project

Although many investigations of heavy metal pollution have been conducted in the Rouyn-Noranda area, no thorough investigation of soils exposed to Horne smelter emissions has yet been carried out to trace the sources of anthropogenic lead in soils. In this project, Pb concentrations as well as Pb isotope ratios of different extracted fractions in soil profiles along a north-east south-west transect crossing the Horne smelter and at control sites were analyzed to examine the smelter effect on the heavy metal distribution in soils and to trace the origins of lead in surface soils near the smelter. This work has three (3) main objectives:

- 1) To determine the extent of Pb contamination of soils exposed to Horne smelter emissions;
- 2) To distinguish the source(s) of anthropogenic lead in soils;
- 3) To estimate the downward migration of Pb in representative mesic soils.

## 4. The structure of the thesis

In chapter 1, the author briefly discusses the presence of Pb in the environment, including its sources, speciation, contamination of the environment and its health effects. Chapter 2 and chapter 3 are mainly focused on the sources and environmental fate of Pb in soils. Chapter 4 describes the methodology applied in this project, including sampling methods, sample preparation procedures, analytical methods and data quality control approaches. The last chapter presented the results and discussions of Pb concentrations and Pb isotope ratios in soil profiles in the study area and at control sites.

### Chapter 1

### The presence of Pb in the environment

#### **1. Sources of Pb in the environment**

The major sources of lead in the environment are emissions from vehicles burning leaded gasoline, from mining and smelting industry, and from domestic waste combustion. According to Ter Haarand and Bayard (1971), exhaust particles emitted from automobiles consist mainly of PbBr<sub>2</sub>, PbBrCl, Pb(OH)Br, (PbO)<sub>2</sub>PbBr<sub>2</sub> and (PbO)<sub>2</sub>PbBrCl and they are relatively unstable and readily converted into other mineral forms. After 18 hours of disposal to the air, about 75% of the Br has volatilized, and 30% - 40% of the Cl compounds are also lost. The Pb compounds are converted to Pb carbonates, oxycarbonates and oxides. The main Pb pollutants emitted from smelters occur as PbSO<sub>4</sub> and PbS, and to a lesser extent PbO (Clevenger et al., 1991). In the atmosphere, lead exists primarily in the form of PbSO<sub>4</sub> and Pb(CO<sub>3</sub>) (EPA, 1986). In addition to anthropogenic sources, natural processes also contribute to the presence of Pb in the environment. Eroded soils containing Pb particles may end up in rivers and then be transported to lakes and to the ocean. Pb-bearing soil particles may be transported over long distances by wind. Volcanic emissions also contribute materials containing metals from the Earth's mantle and crust into the atmosphere. Pb that has been part of vegetation can be released and spread by forest fires.

#### 2. Speciation of Pb in the environment

The fate of Pb in the environment depends to a large extent on its speciation, the chemical form under which Pb is present. Pb has two oxidation states,  $Pb^{2+}$  and  $Pb^{4+}$ , both of which are stable. The environmental chemical behavior of the element is dominated by the plumbous ion,  $Pb^{2+}$ . The inorganic forms include galena (PbS), lead carbonate (cerussite,

PbCO<sub>3</sub>), sulphate (anglesite, PbSO<sub>4</sub>), Pb phosphates (e.g. pyromorphite,  $Pb_5(PO_4)_3Cl$ ) and Pb oxides (e.g.  $Pb_3O_4$ ). Pb tends to form low solubility compounds with the major anions found in natural water (lead acetate, chloride, chromate, nitrate, oxide and sulphate). Many inorganic Pb compounds like lead hydroxides, carbonate, and sulfide are not readily soluble in water and are precipitated from water and sequestered in sediments. The organolead compounds in the environment are mainly anthopogenic in origin. The most widely used forms are the tetraalkyllead (tetramethyllead and tetraethyllead) in antiknock gasoline, in which Pb exists as Pb<sup>4+</sup>. These organoleads are volatile, insoluble in water, can be adsorbed onto particles and accumulate in living organisms. The tetraalkyllead can degrade into trialkyllead and dialkyllead that are soluble in water. Organic lead compounds are fat-soluble and are more toxic than other forms. In rivers, lakes and oceans, Pb is strongly associated with particles by adsorption or coprecipitation on solid organic or inorganic phases, by precipitating of insoluble compounds or by association with organisms. Pb can also be uptaken by plants, animals and aquatic organisms, and the principal factors controlling Pb uptake in aquatic systems include temperature, pH, salinity and the presence of organic matter.

#### 3. Pb concentrations in the environment

The Pb concentrations reported in the environment vary greatly depending on sample location, the time of sampling, the analytical method applied, the extent of local pollution, *etc.* In pre-technological times, Pb concentrations in the atmosphere were less than 0.1 ng/m<sup>3</sup>, but in present day, it has exceeded several nanograms even in remote areas (RSC, 1986). The natural Pb content in soils is about 20 ppm, while in the surface horizons of soils close to Pb source such as smelters, the Pb content can be as high as tens of thousands ppm. Pb concentration is usually higher at surface of the ocean or lakes than in the deeper parts of the water column due to the input from atmospheric deposition. The baseline Pb concentration in Lake Erie was found to range from 17 to 18.9 ppm (at the depth of 45-60 cm) (Ritson *et al.*, 1994), while the maximum dissolved Pb concentration in surface waters was as high as 135 ppm in Lake Erie and 291.5 ppm in lake Ontario (Flegal *et al.*, 1989), which is likely related to the amount of Pb input to the individual

lakes. Similar patterns were observed in lake sediments. For example, in surface lake sediments of Sweden, Pb occurs at a level as high as 400 ug/g by dry weight, which is about 40-100 times the background value.

#### 4. The health effect of Pb

Pb is hazardous to human beings and animals in two ways - inhalation of Pb-bearing soil dust and consumption of foods with high levels of Pb. Studies on the quantitative relationship between exposure to lead contaminated soil and Pb blood levels in children have indicated that Pb blood levels increase with exposure to increased lead concentrations in soils (Duggan, 1980). Lead toxicity may occur at Pb blood levels of 10-15 mg/dl or possibly less. The exposure of children to high levels of Pb can cause a variety of adverse health effects, including impaired mental and physical development, decreased biosynthesis, elevated hearing threshold, and decreased serum levels of vitamin D. Long-term exposure of adults to lead at work has resulted in decreased performance in some tests that measure functions of the nervous system. Lead exposure may also cause weakness in fingers, wrists, or ankles. At high levels of exposure, lead can severely damage the brain and kidneys in adults or children. In pregnant women, high levels of exposure to lead may cause miscarriage. High-level exposure in men can damage the organs responsible for sperm production [1]. Another pathway of Pb into human body is food uptake. Lead accumulates in the gill, liver, kidney and bone of fish. Although Pb occurs naturally in all plants, it has not been shown to play an essential role in their metabolism. Pb is present naturally in plants as trace amounts. However, in the proximity of mining and smelting areas, much higher Pb concentrations are common in plants growing on contaminated soils.

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### Chapter 2

#### Sources of Pb in soils

Lead is introduced in the environment through diverse sources, such as burning of leaded gasoline in automobiles, mining, smelting and refining, industrial and municipal waste disposal, combustion of coal, *etc.* Since the fallout of airborne Pb onto soils contributes more to the total Pb concentrations than that from natural source (*e.g.* parental rocks) from which the soils are derived (Jaworski, 1978), the sources of Pb in the atmosphere will be discussed prior to soils.

#### 1. Sources of Pb in the atmosphere

#### **1.1 Mining and smelting industry**

Base metal mining is an important point source of heavy metals in the environment. Mining and milling operations together with grinding and concentrating ores, the disposal of mine wastes and dispersion from tailings provide obvious sources of metal contamination (Adriano, 1986). Elevated levels of heavy metals from metalliferous mines are found in soils and plants growing on the contaminated soils near mine areas due to the discharge and dispersion of mine wastes into the ecosystem (Davies and Ballinger, 1990, Davies and Roberts, 1975; Merrington and Alloway, 1994). Jung and Thornton (1996) reported that Pb concentration in surface soils near a Pb-Zn mine in Korea was as high as 29 900 ppm.

Smelting and refining heavy metals generate a considerable amount of fumes containing Pb and other heavy metal particles. Total particulate emissions into the atmosphere from the production of primary (originating directly from ore concentrate) and secondary (referring to recycled or recovered Pb) lead in the US were estimated to be 30 000 and 4
000 tons per year, respectively (Vandegrift *et al.*, 1971). The lead content of such emissions is estimated to be in the range of 0.1-100 mg/kg. In addition to emissions from Pb production, other metallic production, such as the production of iron and steel, or that of primary and secondary copper also contribute great amounts of Pb and other heavy metals into the atmosphere.

Canada is a major producer and emitter of lead. Primary lead productions peaked at about 400 000 tons in 1971, and have declined to about 300 000 tons in 1984 (Stokes, 1986). In 1982, atmospheric emissions of Pb from primary production of metals were estimated to be 3 574 tons, which account for 31% of the total atmospheric Pb emissions of 11 466 tons (Jacques, 1985). The Horne smelter, as the major emitter in Canada, has released large amounts of heavy metals (Pb, Zn, Cu, Cd, As, *etc.*) in the environment. The total emissions of heavy metals from 1965 to 1998 were estimated to be 40 102 tons, 38 236 tons and 5 080 tons for Pb, Zn and Cu, respectively.

Elevated levels of Pb and other metals were reported in soils in the vicinity of smelters. Many investigations show that heavy metals are enriched in surface soils near a smelter, and they decline exponentially with increasing distance from smelter (*e.g.* Rieuwerts and Farago, 1996). In Ontario, Pb concentration in soils near a secondary Pb smelter was estimated to be 21 200 ppm (Linzon *et al.*, 1976).

Modern devices are extremely efficient in controlling the release of heavy metals from industrial and mining plants, and emissions into the atmosphere are greatly reduced. But due to the low solubility of Pb compounds in soils and their resistance to microbial degradation, Pb will remain in soils for a relatively long time.

#### **1.2 Gasoline combustion**

Lead was added to gasoline in the early 1920s as organic tetraalkyllead additives to increase the octane ratings and to avoid uneven combustion in engine cylinders. The first leaded gasoline was sold in 1923 and its use rapidly became standard. In 1973, the UK

consumption of lead antiknock additives was 12 000 tons per year (CUEP, 1974). Of this, about 70% - 75% was emitted from the exhaust as inorganic salts of lead, and about 1% was emitted unchanged as tetraalkyllead. Evaporative loss of fuel from fuel tanks also contributed tetraalkyllead compounds to the atmosphere. The remaining 20% - 25% of lead remained trapped in the exhaust system and engine oil. Concentrations of lead in vehicle exhaust gases are typically 2000-10000 ug (Pb)/m<sup>3</sup>. The organic tetraalkyllead compounds are volatile and exist in air in vapor phase, while the inorganic salts are emitted as particles that will be subject to rapid growth in ambient air by coagulation with other particles. In Canada, atmospheric emissions of Pb from petrol (including alkyl lead manufacture) were estimated to be 7 278 tons in 1982, which represented 63% of the total Pb emissions that year (Jacques, 1985).

Leaded gasoline combustion as a source of soil contamination has been reported by many researchers. Warren and Delavault (1960) reported that soil and vegetation samples collected near roads contained unusually high levels of Pb. In Israel, Erel *et al.* (1997) found that Pb concentrations in soil samples collected near traffic roads are much higher than those collected from remote area. Contamination of soils and vegetation near traffic roads has been reported by many researchers in many countries. Other sources of Pb into the atmosphere include fossil fuel combustion, waste incineration, battery manufacturing, *etc.* 

Pb in the atmosphere may also come from natural sources such as silicate dusts, volcanic halogen aerosols, forest fires, sea salt aerosols, meteoric and meteoritic smoke and Pb derived from the decay of radon. But these sources contribute only a small amount of airborne lead in comparison to lead derived from mining and smelter emissions as well as vehicle emissions.

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# 2. Sources of lead in soils

# **2.1 Parent rocks**

# 2.1.1 Background levels of Pb in rocks

Geological materials from which soils are derived are important contributors of lead in soils. In unpolluted soils, mean lead concentrations relate closely to the lead concentration of parent rocks. Lead makes up less than 0.1% by weight in rocks and soils. The primary Pb form in the natural state is galena (PbS), as Pb has highly chalcophilic properties. Lead can also substitute Zn in sphalerite, Cu in chalcopyrite. It can also easily replace K, Sr, Ba, Ca and sometimes Na in certain silicates. The natural lead content of soil is closely related to the type of bedrock. Generally, there is an increase in lead concentrations from ultramafic to felsic igneous rocks because Pb isomorphously replaces potassium in silicate lattices. For sedimentary rocks, argillaceous sediments, shales, which are rich in organic matter, tend to have higher lead contents due to their ability to adsorb metal ions (Table 2-1).

	Rock type	Pb concentration
		(ppm)
	Ultramafic rocks	0.1-1.0
	Mafic rocks(Basalt, Gabbro)	3-8
Magmatic rocks	Intermediate rocks	12-15
	Felsic rocks (Granite, Gneisses)	15-24
	Felsic rocks (Volcanic)	12-20
	Argillaceous sediments	20-40
Sedimentary	Shales	18-25
rocks	Sandstones	5-10
	Limestone, dolomite	3-10

Table 2-1 Lead concentrations in representative rock types.

From Kabata-Pendias and Pendias, 1992

The influence of parent materials on the total content of lead in soils is modified to varying degrees by pedogenetic process such as gleyfication, leaching, surface organic matter accumulation and podzolization, which may lead to the redistribution of heavy metals within the soil profile. For example in podzols, metals like Cu, Zn and Hg are often leached from the surface layers of podzols and enriched in the upper B horizons of soil profiles.

### 2.1.2 Natural contents of Pb in soils

Estimates of Pb concentration in uncontaminated soils vary greatly depending on the local geology and the distance from possible pollution source. Nriagu (1978) reported a mean value of 17 ppm. In order to establish the background Pb levels in soils, Pierce *et al.* (1982) examined metal concentrations in 16 soil series in Minnesota, USA, and he found that the total lead concentration was below 25 ppm for all the soils. Holmgren *et al.* (1983) reported Pb concentrations for 3 001 surface soil samples from cultivated land in the USA. The mean Pb concentration was 18 ppm. Kabata-Pendias and Pendias (1992) collected from the literature lead concentration data of uncontaminated soils from various countries. Lead concentrations vary from 3 to 189 ppm, while mean values for different soil types range from 10 ppm to 67 ppm, with an average of 32 ppm. The relatively high lead levels (>100 ppm) probably reflect the influence of pollution. Soils in Alaska contain relatively low levels of Pb. About 90% of the samples contained only up to 20 ppm Pb with a geometric mean of 12 ppm. These low concentrations of Pb in soils from this remote region suggest that baseline values of this metal in most world soils should not be much higher than 20 ppm (Kabata-Pendias and Pendias, 1992).

## 2.2 Atmospheric deposition of airborne lead

When emitted from smelters and automobiles, airborne lead is subject to dry and wet depositions. Its residence time is very short, of about 10 days, in the northern hemisphere (Stokes, 1986). Gravitational settling and deposition onto surfaces due to impaction are

the two major mechanisms of dry deposition. Gravitational settling is significant for all particles of >10 um, but is rapid only for the large particles (>50 um). Deposition onto surfaces due to impaction is significant only for small particles. Consequently, larger particles will deposit right away near the pollution sources, while smaller ones will be transported a long distance before settling onto surfaces. Differences in surface properties can also have an effect on deposition efficiency. Rough or hairy leaf surfaces are up to eight times more efficient at collecting airborne lead than smooth surfaces. Lead deposited onto vegetation reaches the soil sooner or later mainly through rainwater washout and the decomposition of plant debris. In forests, deposition of heavy metals on leaf surfaces is the main source of heavy metal input into soils.

Precipitation scavenging processes such as rainout and washout are also efficient means of removing particulate Pb pollutants from the atmosphere. Rainout refers to the scavenging of airborne lead by water droplets within the cloud layer, while washout involves the scrubbing of airborne lead by falling raindrops or snow. Total atmospheric deposition of Pb ranged from 3.1 to 31 mg/m<sup>2</sup>/a in remote and rural areas, and from 27 to 140 mg/m<sup>2</sup>/a in suburban and industrial regions (Alloway, 1990). In the northern hemisphere, anthropogenic flux to soils from the atmosphere is 60 to 200 mg/m<sup>2</sup>/a in urban areas, compared with 30-60 mg/m<sup>2</sup>/a in rural areas (Stokes, 1986). The decreasing concentrations of Pb, Cd, Zn, As, Sb, and Se from south to north in Norwegian, Swedish, and Finnish lakes were attributed to the long-range transport from sources in Central Europe. In central Greenland, Boutron *et al.* (1991) and Candelone *et al.* (1995) found a 6.5-fold decrease in atmospheric Pb recorded in snow samples between ~1970 and 1992 due to the reduction of leaded gasoline.

# 2.3 Sewage sludge disposal

The application of sewage sludge as a soil amendment to farmland provides another means of introduction for heavy metals such as lead, zinc and cadmium to farmland. Sewage sludges are the solids separated during the treatment of wastewater. Sewage sludges have long been recognized as a desirable soil amendment material because they are rich in nitrogen and phosphorus and so as to make use of important plant nutrients and to ease the problems of sludge disposal. Unfortunately, sewage sludge can have an undesirable chemical property, a high content of heavy metals. It is common practice for industrial effluents to be passed into the foul sewer and the organic residues effectively remove metal ions by complexation. Thus, the metal contaminants are retained in the sewage sludge. In 1982, effluents discharged into Canadian environment contained a total of 562 tons of Pb, of which 412 were contained in municipal sewage, accounting for 73% of the total Pb content in liquid effluents.

Sewage sludges contain high levels of Pb and other heavy metals. Berrow and Webber (1972) analysed 42 sludges from rural and industrial towns in England and Wales. The lead contents of the dried materials ranged from 120 to 3 000 ug/g (mean 820 and median 700 ug Pb/g, respectively). Sommers (1977) reported a range of 545-7 431 ug/g Pb for sludges from eight Indiana (USA) cities. The application of sewage sludge to agricultural soils resulted in high Pb concentrations in soils. The possibility that Pb and other heavy metals might accumulate in plants to dangerous levels has led several countries and cities to formulate guidelines for the use of sludge as a fertilizer. In the UK, total lead addition over a 30-year period should not exceed 1000 kg/ha, corresponding to about 450 mg/kg of soil of 200 mm depth. In Germany, the lead content of sludge should not exceed 1 200 mg/kg dry weight. In Ontario, the maximum allowable Pb concentration in sludge is 1100 ug/g of solids (OMAF, 1986). Other sources of Pb into soils include the application of fertilizers and pesticides, *etc.* 

# Chapter 3

# The environmental fate of lead in soils

## 1. Chemical behavior of lead in soils

Under reducing conditions, Pb primarily occurs as galena. During weathering, Pb sulfides are readily oxidized and may then precipitate as Pb carbonates and Pb phosphates. Pb can also be incorporated in clay minerals, in Fe and Mn oxides, and in organic matter. The fate of lead in soil is affected by the specific or exchange adsorption at mineral interfaces, the precipitation of sparingly soluble solid phases, and the formation of relatively stable organo-metal complexes or chelates with the organic matter in soil (EPA, 1986).

## **1.1 The adsorption of metal ions and their constituents**

Lead in soils is associated mainly with clay minerals, Fe and Mn oxides, hydroxides and organic matter. Two adsorption patterns are involved in the adsorption of Pb ions and Pb compounds by soil particles. One is the non-specific adsorption, and the other is the specific adsorption.

### **1.1.1 Non-specific adsorption**

In non-specific adsorption, the force involved in the adsorption of ionic species at charged surfaces is electrostatic. The adsorption of heavy metals (as cations in the soil solution) depends on the density of negative charges on the surface of the soil colloids. According to Alloway (1990), there are two types of surface negative charges in soils. One is permanent charge, the other is pH dependent charge. The surface negative charge is balanced by an equal quantity of oppositely charged counter-ion to maintain electrical neutrality. Ion exchange refers to the exchange between the counter ions balancing the

surface charge on the colloids and the ions in the soil solutions. The cation exchange capacity (CEC) of a soil is a measure of its ability to provide sites for non-specific adsorption. Generally, soil solids with large surface areas have high CEC, as shown for the clay minerals in Table 3-1.

Clay minerals	Surface area	CEC
Kaolinite	5-100 m <sup>2</sup> /g	3-20 meq/100g
Illite	100-200 m <sup>2</sup> /g	10-40 meq/100g
Vermiculite	300-500 m <sup>2</sup> /g	100-150 meq/100g
Smectites	700-800 m <sup>2</sup> /g	80-120meq/100g
· · · · · · · · · · · · · · · · · · ·		From Alloway, 1990

Table 3-1 Cation exchange capacity of some clay minerals.

higher pH values, which can be described as follows.

The permanent charge is formed by the isomorphous substitution of a lower charged ion for a higher charged ion  $(e.g. Mg^{2+} \text{ for } Al^{3+} \text{ and } Al^{3+} \text{ for } Si^{4+})$  within 2:1 clay minerals and edge effects on clay minerals. The negative charges on humus polymers are due to the removal of protons from carboxyl and phenolic hydroxyl groups, whereas those on the surface of hydrous oxides are created by proton dissociation from O and OH groups at

$$CO-OH + OH^{-} \rightleftharpoons CO-O^{-} + H_2O$$

$$> Al-OH + OH^{-} \rightleftharpoons > Al-O^{-} + H_2O$$

$$> Al-(OH)_2^{-} \cdot Al-(OH)_2^{-} + OH^{-} \rightleftharpoons Al-(OH)_2^{-} + Al(OH)_2$$

Below a pH of 8, there is little or no negative charge because the hydrogen ion concentration inhibits proton dissociation. Consequently, the hydrous oxides of Fe and Al contribute little to the CEC of soils. But as the pH increase, the hydrogen dissociates from the colloid OH group, and negative charges result. In contrast, carboxyl groups (CO–OH) in humic polymers have dissociation constants (pK) of 3-5 and phenolic groups have pK values of greater than 7. Thus the high adsorptive capacity of humic substances at pHs above 5 contributes significantly to the overall CEC of a soil. In general, humic acids in

soil can bind large amounts of Pb very strongly, and the bound Pb is less susceptible to release by acidification than is Pb bound to mineral portions of the soil.

#### **1.1.2 Specific adsorption**

Specific adsorption involves the exchange of heavy metal cations and most anions with surface ligands to form partly covalent bonds with lattice ions. It results in metal ions being adsorbed to a far greater extent than would be expected from the CEC of a soil. Specific adsorption is strongly pH dependent and is related to the hydrolysis of the heavy metal ions, which can be expressed by the equation below. Metals most able to form hydroxylcomplexes are specifically adsorbed to the greatest extent.

 $M^{2+} + H_2O = MOH^+ + H^+$ 

So specific adsorption increases with decreasing pK (equilibrium constant) values. Pb with a pK of 7.7 is more strongly adsorbed than Cd with a pK of 10.1. The order of increasing specific adsorption of metals concern is: Cd<Zn<Cu<Pb. The hydrous oxides of Al, Fe and Mn are considered to be the main soil constituents involved in the specific adsorption reaction.

#### **1.2 Precipitation and co-precipitation**

Chemical precipitation of Pb is another means of immobilizing metal in soils. In uncontaminated soils, the formation of insoluble lead phosphates acts as an important control on Pb (Nriagu, 1974). The average Pb content in soils is about 20 ppm, and the average phosphorus content is about 600 ppm, so it is possible that phosphorus acts as a control on Pb. The Pb phosphates have very low solubility, which is shown by their low solubility products in Table 3-2. The insoluble nature of most Pb phosphate minerals was applied to remediate soils contaminated by Pb, Zn and Cd (Lambert *et al.*, 1997). Lead added to soils may react with available soil anions such as  $PO_4^{2-}$  or  $CO_3^{2-}$  to form relatively insoluble salts, such as basic lead carbonate PbCO<sub>3</sub>, and pyromorphite.

Pyromorphite ( $Pb_5(PO_4)_3Cl$ ) is the most stable lead mineral under acidic to neutral conditions (Nriagu, 1984). Under alkaline conditions, when alumium or iron is present, the formation of less soluble minerals such as plumbogummite, hinsdalite and corkite is expected. At all pH values, pyromorphite  $Pb_5(PO_4)_3Cl$  is less soluble than other lead phosphates and cerussite (PbCO<sub>3</sub>). Under alkaline conditions, cerussite is less soluble than fluoropyromorphite  $Pb_5(PO_4)_3F$ . The highly insoluble nature of most Pb compounds makes it less mobile than other metals (Cd, Hg, As or Zn) in soils.

The solubility of Pb can be greatly decreased by liming. A high soil pH may precipitate Pb as hydroxides, phosphate or carbonate, as well as promote the formation of Pb-organic complexes which are rather stable. Increasing acidity may increase the Pb solubility, but this mobilization is usually slower than the accumulation in organic-rich layer of soils.

Minerals	Chemical formula	Log Ksp	-
Anglesite	PbSO <sub>4</sub>	-7.7	-
Cerussite	PbCO <sub>3</sub>	-12.8	
Fluoropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	-76.8	
Hydroxypyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	-82.3	
Chloropyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	-84.4	
Hinsdalite	PbAl <sub>3</sub> (PO <sub>4</sub> )(OH) <sub>6</sub> SO <sub>4</sub>	-99.1	
Plumbogummite	PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> H <sub>2</sub> O	-99.3	
Corkite	PbFe <sub>3</sub> <sup>3+</sup> (PO <sub>4</sub> )(OH) <sub>6</sub> SO <sub>4</sub>	-112.6	

Table 3-2 Solubility products (log Ksp) at 25 °C of representative lead minerals.

From Lambert et al., 1997

Co-precipitation is defined as the simultaneous precipitation of a minor chemical agent incorporation with other elements by any mechanism and at any rate. The types of mixed solid commonly formed include clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred. In addition to co-precipitation, replacement of  $Ca^{2+}$  cations by  $Cd^{2+}$  can also occur in the surface layer of calcite when it comes into contact with solutions containing Cd. Table 3-3 lists the trace metals normally found co-precipitated with secondary minerals in soils.

Mineral	Co-precipitated trace metals
Fe oxides	V, Mn, Ni, Cu, Zn, Mo
Mn oxides	Fe, Co, Ni, Zn, Pb
Ca carbonates	V, Mn, Fe, Co, Cd
Illites	V, Ni, Co, Cr, Zn, Cu, Pb
Smectites	V, Ni, Co, Cr, Zn, Cu, Pb
Vermiculites	Ti, Mn, Fe

Table 3-3 Coprecipitated trace metals in secondary soil minerals.

From Thornton, 1983

# 1.3 Organic complexation

In addition to being involved in cation exchange reactions described earlier in this chapter, solid-phase humic substances such as humic acids also adsorb metals by forming chelate complexes. Low molecular-weight organic ligands, not necessarily humic in origin, can form soluble complexes with metals and prevent them from being adsorbed or precipitated. The stability constants of chelates with metals tend to be in the following order: Cu>Fe=Al>Mn=Co>Zn (Alloway, 1990). Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. It is reported that soil humus, especially high-molecular-weight humic acids, contributes most to the immobilization of Pb added to the soil and that Pb is bound through coordinate binding by free electron pairs (Alloway, 1990).

Pb is always enriched in surface soils and the localization of Pb near the soil surface in most soil profiles is primarily related to the accumulation of organic matter. Therefore, organic matter should be considered as important sink of Pb in polluted soils (Kabata-Pendias and Pendias, 1992).

# 2. Chemical forms of Pb in soils

The chemical form of Pb in soils is the mean factor that determines the potential risk of Pb mobilization and availability to plant uptake. As a consequence, the method of sequential extraction was applied in many studies to estimate the chemical forms of heavy metals in soils (Kersten and Förstner, 1986; Li *et al.*, 1995; Verner *et al.*, 1996). The chemical forms of lead in soils are summarized in Table 3-4.

Classification	Chemical forms
Soluble (Mobile)	Metal precipitate; porewater
Exchangeable	Unspecifically adsorbed
Carbonate phase	Precipitate or co-precipitate, specifically adsorbed
Fe-Mn oxide phase	Specifically adsorbed, co-precipitate
Organic phase, sulphides	Complexed, adsorbed
Residual	Bound in silicate lattice

Table 3-4 Chemical forms of Pb in soils.

Pb in soil solution is believed to be the immediate source of metals for plant roots, but this water-soluble Pb represents only a minor portion of total Pb in soils. This is evidenced by the extremely low concentrations of Pb in soil solution. Soil solution Pb accounts for 0.005-0.13% of total soil Pb (Alloway, 1990). The soluble and exchangeable fractions of Pb indicate the forms of Pb that are most available to plant uptake. Specifically adsorbed Pb and the Pb bound to carbonate can easily become mobile and be available under conditions of lower soil pH. The Pb associated with Fe-Mn oxides, organic/sulphides and structurally associated with silicate minerals is generally strongly held with the soil constituents and normally unavailable to plants.

# 3. Pb isotope geochemistry

The element lead has four stable isotopes: <sup>204</sup>Pb (1.4%), <sup>206</sup>Pb (25.2%), <sup>207</sup>Pb (21.7%) and <sup>208</sup>Pb (51.7%). <sup>204</sup>Pb is non-radiogenic. <sup>206</sup>Pb is formed by radioactive decay of <sup>238</sup>U, <sup>207</sup>Pb

is formed from <sup>235</sup>U, and <sup>208</sup>Pb from <sup>232</sup>Th. The three elements decay at different rates. The half-life, abundances and decay constant of U and Th are listed in Table 3-5. The radioactive decay of Uranium and Thorium to their daughter can be summarized as follows:



Table 3-5 Abundances, half-lives, and decay constants of the principal naturally occurring isotopes of uranium and thorium.

Isotope	Abundances	Half-life (years)	Decay constant
<sup>238</sup> U	99.2743	4.468 x10 <sup>9</sup>	1.55125 x10 <sup>-10</sup>
<sup>235</sup> U	0.7200	0.7038 x10 <sup>9</sup>	9.8485 x10 <sup>-10</sup>
<sup>232</sup> Th	100	14.010 x10 <sup>9</sup>	4.9475 x10 <sup>-11</sup>

From Faure, 1986

The differences in parent isotope decay rates result in systematic variations in the ratios of <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb to each other as well as to <sup>204</sup>Pb. Most geological uses of Pb isotopes are based on the ratios of radiogenic isotopes to <sup>204</sup>Pb. Converting the data to <sup>206</sup>Pb/<sup>207</sup>Pb, <sup>206</sup>Pb/<sup>208</sup>Pb shows that these ratios also change in a predictable pattern with respect to geological age. Therefore, the <sup>206</sup>Pb-based <sup>207</sup>Pb-based ratios also have meaning with respect to the age of Pb in rocks and ores. <sup>206</sup>Pb/<sup>207</sup>Pb ratio is generally used for environmental tracer studies because it can be most accurately measured (Maring *et al.*, 1987).

The lead isotopic ratio of an ore depends on how long lead and its radioactive parents were together in the mantle and crust before the lead was segregated into an ore body. For example, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio is ~ 1.10 in some 1 000-Ma-old ore deposits, ~1.15 in 500-Ma-old ores, and ~1.19 in 30-Ma-old ores (Doe, 1970). Metallic Pb is produced from the mineral galena, PbS, which contains no U or Th, and its Pb isotopic composition has usually not changed since ore formation. Many silicates, on the other hand, contain both U and Th resulting in continuous change of their isotopic composition. Most ore leads have <sup>206</sup>Pb/<sup>207</sup>Pb ratios measurably less than the natural leads of soil and soil related components, because the accumulation of <sup>206</sup>Pb from <sup>238</sup>U radioactive decay stops when lead is separated from uranium during the formation of ore bodies. But it continues in crustal rocks from which soils are derived. In general, <sup>206</sup>Pb/<sup>207</sup>Pb ratios of most ore bodies are generally less radiogenic (e.g. having lower <sup>206</sup>Pb/<sup>207</sup>Pb values) ranging from ~0.92-1.20 (Sturges and Barrie, 1987), which is caused mainly by ore deposits of different geological ages and in many cases are less radiogenic than rock or soil Pb. The isotope ratios of anthropogenic Pb released to the atmosphere depend largely on the Pb isotope ratios of the ore bodies used for the production of leaded gasoline or for metal production in smelting and refining industries.

The detection of Pb pollution in soils is based on the fact that Pb isotopic ratio in natural background materials, such as crustal rocks and soils, is significantly different from that of industrial pollutants, such as emissions from smelter or leaded gasoline. In soils not affected by industrial pollution, the Pb concentration and isotope ratios are usually constant within the soil profile (Pouchelt *et al.*, 1993), any variation of the Pb isotope ratio within a sediment core or soil profile reflects changes in the relative proportion of Pb from sources with distinct Pb isotopic compositions. While in soils contaminated by anthropogenic activities, Pb concentration and isotope ratio profiles usually display an inverse trend with depth in soils (Hansmann and Köppel, 2000).

## Chapter 4

# Study area and methodology

### 1. Background

The study area is located in the Rouyn-Noranda region, northwestern Quebec (Fig. 4-1). The region surrounding the Horne smelter is typical of the Precambrian low-relief shield terrane. The surface of the area is a mosaic of glaciolacustrine plains and bedrock bosses and knolls. Sparse glaciofluvial sand and gravel deposits also occur in the region. The bedrock bosses and knolls are discontinuously covered by glacial sediments (till) which were locally reworked by waves during the Glacial Lake Ojibway episode (Veillette, 1989). Good humoferric and ferrohumic podzolic soil profiles developed on well drained, unreworked till deposits. Coniferous boreal community is the major forest type in the study area. This region is underlain by the Abitibi-greenstone belt, which consists of Archean metasedimentary and metavolcanic rocks and associated intrusives.

The Rouyn-Noranda mining district is well known for its rich polymetallic deposits. Until 1990, 22 massive sulfide deposits and 17 gold deposits had been discovered in the Noranda Camp (Gibson and Watkinson, 1990), the premier base metal and gold camps in Canada. The Horne Au-Cu mine, located near the northern limit of the city of Rouyn-Noranda, was the first and largest massive sulfide deposit discovered in Noranda region. The huge estimated reserves of the Horne Mine resulted in the birth of the company Noranda Mines Ltd. as well as the Horne Smelter in December 1927. Since the beginning of ore mining in 1927, a total of 92 Mt of ores has been mined out. Among these, 416 tons metal Au, 2.1 Mt Cu, 1.2 Mt Zn and 2 240 tons Ag were smelted from the Noranda Camp (Kerr and Mason, 1990). The operation of the Horne smelter resulted in emissions of large amounts of heavy metals, in particular metallurgical metals such as lead, zinc, cadmium and copper into the environment. The cumulative emissions of heavy metals from 1965 to 1998 were 40 102 tons for Pb, 38 236 tons for Zn, and 5 080 tons for Cu. Yearly emissions of these metals were as high as 2 400 tons for Pb in 1972 and 3 100 tons for Zn in 1971. Only after 1987, when an effort was taken to control the emissions of heavy metals and gases from Horne smelter to curtail air pollution, were the emissions of heavy metals reduced significantly. In 1976, the Horne Mine closed because metal reserves had run out. The Horne smelter became a 100%-custom smelter with feeds from the Louvicourt Cu-Zn-Au mine and other base metal producers in northwest Quebec as well as imported feeds from Europe and elsewhere [2]. Today, the Horne smelter ranks as one of the world's leading producers of copper and precious metals.



Fig. 4-1 Simplified location map showing the sampling sites in the study area as well as the control sites.

The environmental effects of metal emissions are obvious in the Rouyn-Noranda region. Immediately adjacent to the smelter stack and several kilometers distant, the vegetation damage such as tree mortality, reduction in species diversity, reduced growth and soil erosion can be clearly observed. Between the smelter and our sampling site 1, about 8.7 kilometers northeast, numerous trees had died, especially in areas closest to the smelter where the ground became almost barren with only struggling bushes (Photos 4 - 1, 4 - 2).



Photo 4-1 Tree mortality and soil erosion near Rouyn-Noranda.



Photo 4-2 Tree mortality and soil erosion near Rouyn-Noranda.

## 2. Soil sampling and sample preparation

A series of 75 soil samples were collected from podzolic soil profiles at 8 sites between 1997 and 2000, with sites 1 and 2 sampled in 1997, sites 6 and 7 in 1998, sites 8, 9 and 10 in 1999, and site 4 in 2000. Sites 8, 1, 9, 2, 4, and 10 lie along a northeast-southwest transect crossing the Horne smelter (Fig. 4-1). This direction is the prevailing wind direction during the growth season in this region. Sites 6 and 7 are control sites situated in the region of Grande rivière de la Baleine (Grande-Baleine) region, approximately 800 km north of Rouyn-Noranda, an area that is assumed least affected by human activities. All profiles were sampled from till-derived podzolic soils at mesic sites (Fig. 4-2). The characteristics of podzolic soil profiles sampled are summarised in Table 4-1.

The soil classification in this project is based on the Canadian system of soil classification (SCWG, 1998). In this system, the podzolic order is defined on morphological and chemical properties of the B horizon, which are associated with humid conditions, sandy to loamy parent materials and forest or heath vegetation. Podzols are relatively welldrained acidic soils characteristic of boreal coniferous forests, which cover large areas of North Europe and America. A typical podzol profile is characterized by the presence of organic surface layers (L, F, H and O), a light-colored eluvial horizon Ae, a reddish brown to black B (Bh, Bhf, Bf) horizon, and yellowish-grey or greenish-grey lower layers of less altered parent till (BC, or C) (Fig. 4-2). The soil horizons are divided into organic horizons (L, F, H and O) and mineral horizons (A, B, C) based on the organic C content. The organic horizons (L, F, H) develops primarily from the accumulation of leaves, twigs and woody materials at various stages of decomposition, which are normally associated with upland forest soils with imperfect drainage or drier. The O horizon, which is not present in our sampled profiles, is developed mainly from mosses, rush, and woody materials. Ae horizon is characterized by the eluviation of clay, Fe, Al, or organic matter. In the illuvial B horizon, Al, Fe and organic complexes have accumulated from above horizons. The C horizon is composed of comparatively unaltered parent materials.



Fig. 4-2 Ferrohumic and humoferric podzols developed on unreworked matrix dominated till.

Table 4-1 A brief description of podzolic soil profiles.

Horizon		Description
L		Characterized by an accumulation of organic matter in which the originally structures like leaves, twigs and woody materials can be easily recognized.
F	Organic horizons	Characterized by an accumulation of partly decomposed organic matter. Some of the original structures are difficult to recognize.
H/ Ah		Characterized by an accumulation of dark-colored organic matter mixed with mineral materials in which the original structures are indiscernible. It differs from the F by having greater humification due chiefly to the action of organisms. It is frequently intermixed with mineral grains.
Ae		Characterized by the eluviation of clay, Fe, Al, or organic matter alone or in combination. It is generally recognized by its light, ashy color in the field.
Bh	Mineral horizons	Bh horizon is characterized by accumulated organic matter, and it is usually evidenced by dark colors relative to C horizon.
Bhf, Bf		Enriched with amorphous material principally Al and Fe combined with organic matter. Bhf contains more than 5% organic matter; Bf contains 0.5-5% organic matter. It is always reddish brown to black in color.
BC		Transitional from B to C horizon
С		Comparatively unaffected by the pedogenic processes operating in A and B horizons, except the process of gleying (Cg), and the accumulation of calcium and magnesium carbonates and more soluble salts. Color becomes

All the samples were collected in podzolic soils to avoid heavy metal concentration variation from soil characteristics and for easier comparison. Soil samples were taken by digging an area approximately 60 x 40 cm using a steel spade. In each profile, 7 to 12 soil samples were collected, with at least one sample taken from each horizon. The collected samples were stored in identified plastic bags. The depths of the profiles range from 40 to 100 cm depending on the depth of bedrock or the depth of BC or C horizons. All the organic samples from the upper layers of the profiles and the mineral samples from the lower horizons were air-dried at room temperature. The living roots and the dead wood fragments were removed manually. The dried organic samples were ground in a china pot

using liquid nitrogen, and then were passed through a 0.5 mm-sieve. The mineral samples were disaggregated and passed through a sieve of 0.063 mm. The powders were kept in labelled plastic vials.

Eight granule samples (2-4 mm fraction) were chosen to estimate the approximate Pb concentrations and isotopic compositions of parent materials at individual sites. These samples were from BC or C-horizon or Bhf, Bf horizon, when BC or C-horizon was not available. The tills (parent material) in the sampled area are sedimentologically mature and lithologically well mixed, hence the geochemical composition of the granules can be used as a proxy for the 'original' (prior to weathering) composition of the fine matrix (0.063 mm fraction) which was utilized for the analytical work. The granules were washed with 10% HCl in an ultra-sonic bath to remove surface coatings. The washed samples were air-dried and ground in a shatter-box. The powdered material was kept in labelled plastic vials.

# **3. Experiment procedures**

To eliminate possible Pb contamination from chemical reagents, chemicals used in sample preparation were of the highest grade available. Acids (HNO<sub>3</sub>, HCl, HF, and HClO<sub>4</sub>) were of the commercial Seastar<sup>®</sup> grade. The Teflon bombs and the syringes used in this experiment were cleaned and soaked in 10% HCl for at least 72 hours. After being thoroughly rinsed with Milli-Q water, they were oven-dried at 90 °C and 50 °C, respectively.

To estimate the Pb contamination of soils around the Horne smelter, total Pb concentrations were measured on fine-grained soil samples (0.5 mm for organic samples, 0.063 mm for mineral samples) by  $H_2O_2$  followed by an acid mixture of concentrated HF, HClO<sub>4</sub>, HNO<sub>3</sub> and HCl digestion. The granule samples were also treated by this total

extraction for their Pb concentration and isotopic composition. The total concentrations of heavy metals in soils are the most frequently reported parameter in investigations of metal contamination, but to estimate the potential risk of heavy metal contamination in soils, the exchangeable fractions of heavy metals are needed because they are the most available for plant uptake. Mehlich-III extracting method (Tran and Simard, 1993), widely used in Canada for measuring exchangeable metal concentrations in soils, was applied in this study to estimate the exchangeable Pb contents. It has also been demonstrated that anthropogenic lead is more mobile and can be separated from total lead by dilute acid leaching (Erel *et al.*, 1997), and that Pb isotopic ratios in the leached fraction are different from those of natural lead (Erel *et al.*, 1997, Monna. *et al.*, 2000). To differentiate the anthropogenic lead from natural source Pb, soil samples were also leached by dilute acid (0.25M HCl) for their Pb concentrations and isotope ratios. The three extracting procedures are described below:

1) Exchangeable fraction

- a. Weigh 3 g of soil sample into a 250-ml Erlenmeyer flask.
- b. Add 30 ml Mehlich–III extracting solution (0.2 M NH<sub>4</sub>NO<sub>3</sub>, 0.015 M NH<sub>4</sub>F, 0.013 M HNO<sub>3</sub> and 0.001 M EDTA) into the flask.
- c. Shake immediately on a rotative shaker for 5 minutes (120 oscillations/min).
- d. Filter through No. 41 Whatman filter paper, transfer the filtrate into a syringe and filter through Millipore 0.45 um filter into a tube (Falcon Blue Max 2098).
- e. Pipet 2.5 ml of Seastar® HNO<sub>3</sub> 70% into the above tube. The resulting solution is ready for analysis.

2) Partial extraction

- a. Weigh about 0.5 g of soil sample into a Teflon bomb.
- b. Add 10 ml 0.25 M HCl solution into the above bomb.
- c. Close the bomb and place it in a water bath for 2 hours at 90 °C.

- d. After cooling, transfer the mixture into a tube (Falcon Blue Max 2098), making to 50 ml with 0.25 M HCl solution. Centrifuge and filter through Millipore 0.45 um filter.
- e. Analyze the solution directly for metal concentrations and Pb isotope ratios.

3) Total extraction

- a. Weight 0.1 g of soil sample into a clean Teflon bomb.
- b. Add 10 ml of HNO<sub>3</sub> 70% and place in a dry heating block on a hot plate at 180 °C until it dries.
- c. After cooling, add 3 ml of 30% H<sub>2</sub>O<sub>2</sub>; heat at about 90 °C on a hot plate to ca. 1-ml volume. After cooling, add another 5 ml of 30% H<sub>2</sub>O<sub>2</sub>, and heat to dryness.
- d. Add 10 ml of the acid mixture 48% HF (5 ml), 70% HClO<sub>4</sub> (3 ml), 70% HNO<sub>3</sub> (2 ml).
   Evaporate on a hot plate at ca. 180 °C overnight to incipient dryness.
- e. After cooling, redissolve the residue by adding 1 ml of HCl 35% and 3 ml of 70% HNO<sub>3</sub>. Swirl until the residue dissolves and then wash down the sides of the bomb with a few ml of Milli-Q water. Gently heat for about 10 minutes.
- f. Cool and transfer the resulting solution into a 50 ml test tube (Falcon Blue Max 2098) and make to 25 ml with Milli-Q water.

### 4. Sample analysis

An aliquot of the solutions from each of the extracting methods was measured for Pb concentrations and Pb isotopic compositions by inductively coupled plasma-mass spectrometry (ICP-MS). To reduce mass bias in relation to concentration differences, the solutions were diluted with 2% HNO<sub>3</sub> to a concentration of ca. 50 ppb before analysis. Blank samples were prepared at every batch of 12 samples. Measurements of Pb concentration on the blanks of reagents for partial and total digestions were found negligible compared to the Pb contents in sample solutions. Pb in blank reagents for exchangeable fraction was systematically subtracted. Measurements of Pb concentration on certified samples of AGV-2 (USGS, Guano Valley Andesite) and BCR-2 (USGS,

Columbia River Basalt) yielded a relative uncertainty better than 8% for total Pb concentration analysis. For mass bias correction, NIST 981 standard was measured for their Pb concentration and isotope ratios after each batch of 10 samples (n = 10), yielding an uncertainty of 0.014, 0.004 ( $2\sigma$ ) for <sup>206</sup>Pb/<sup>207</sup>Pb, and <sup>206</sup>Pb/<sup>208</sup>Pb respectively. Although there are 4 stable isotopes of Pb, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio is generally used for tracer purposes because it can be measured most accurately (Maring *et al.*, 1987). Consequently, the <sup>206</sup>Pb/<sup>207</sup>Pb ratio is used in this paper as the main Pb isotope tracer although for graphical representation, the <sup>206</sup>Pb/<sup>208</sup>Pb ratio is also used.

### Chapter 5

### **Results and discussion**

## 1. Pb concentrations and isotopic compositions in exchangeable fraction

Pb concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb ratios in the exchangeable fraction (Mehlich-III) are listed in Table 5-1 and shown in Fig. 5-1 and 5-2. Pb contents in surface organic horizons ranged from 2.2 to 154.1 ppm, while in the underlying mineral horizons, they are much lower, ranging from 0.2 to 1.5 ppm. Plots of Pb isotopic compositions vs depth in the exchangeable fraction (Mehlich-III method) mimic those of the 0.25 M HCl leachates (Fig. 5-2). Pb isotope ratios in the exchangeable fraction of organic samples are similar to those in partial extraction (Fig. 5-2), implying that Pb in organic samples is predominantly derived from atmospheric deposition with similar <sup>206</sup>Pb/<sup>207</sup>Pb ratios. For those of mineral samples, a systematic shift to lower <sup>206</sup>Pb/<sup>207</sup>Pb ratios is observed in the exchangeable fraction, suggesting that Pb in the exchangeable fraction originates from a different source than that extracted by dilute acid leaching. As expected, the Pb concentrations in the exchangeable fraction are lower, and often much lower than in partial and total extractions (Table 5-1). They respectively account for 2.6%-47% and 0.3%-4.6% of total lead in organic samples and in mineral samples. The higher percentage of exchangeable lead in organic samples suggests that lead in surface organic horizons is more mobile than that in underlying mineral horizons in which Pb is mainly associated with parent materials.

### 2. Partial digestion vs total digestion

All data from partial and total digestions are listed in Table 5-1 and 5-2. The total Pb levels are lower than partial levels in a few organic samples, while they are consistently a few ppm higher in mineral samples obtained with 0.25 M HCl extraction (Fig. 5-1). Analytical precision explains all but three of these illogical results. The higher partial Pb

	Exchangeable fraction Partial extraction				action	Total extraction					
Sample No.	Depth	Horizon	<sup>206</sup> <i>Pb</i>	$^{206}Pb$	[Pb]	$^{206}Pb$	$^{206}Pb$	[Pb]	<sup>206</sup> Pb	$^{206}Pb$	[Pb]
_	(cm)		<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)
Rouyn-Noranda	region										
97-MITE-1J	2	L	1.00	0.428	$150 \pm 10$	1.00	0.432	$760 \pm 60$	1.03	0.433	$730 \pm 60$
97-MITE-11	5	F	0.97	0.420	49 ± 4	0.98	0.423	$1400 \pm 100$	1.01	0.428	$1400\pm100$
97-MITE-1H	9	FH	0.98	0.425	$10.9 \pm 0.9$	0.98	0.422	$430 \pm 30$	1.01	0.428	$420\pm30$
97-MITE-1F	12	Ae	1.15	0.487	$0.42\pm0.03$	1.17	0.482	$4.4\pm0.5$	1.12	0.464	$9.2 \pm 0.7$
97-MITE-1E	20	Bf	1.13	0.466	$0.070\pm0.006$	1.16	0.471	$2.0 \pm 0.2$	1.08	0.457	$6.2 \pm 0.5$
97-MITE-1D	30	Bf	1.21	0.502	$0.32 \pm 0.03$	1.18	0.487	$2.6 \pm 0.2$	1.10	0.460	$6.7\pm~0.5$
97-MITE-1C	40	Bf	1.15	0.475	$0.25\pm0.02$	1.19	0.485	$2.1 \pm 0.2$	1.10	0.458	$6.2 \pm 0.5$
97-MITE-1B	50	BC	1.21	0.490	$0.36 \pm 0.03$	1.21	0.499	$1.5 \pm 0.1$	1.09	0.462	$5.8 \pm 0.5$
97-MITE-1A	60	BC	1.17	0.487	$0.14 \pm 0.01$	1.24	0.504	$2.6 \pm 0.2$	1.11	0.469	$5.8 \pm 0.5$
97-MITE-2J	3	L	1.02	0.439	$104 \pm 8$	1.03	0.441	$240\pm20$	1.02	0.430	$230 \pm 20$
97-MITE-2I	6	FH	1.07	0.450	27 ± 2	1.07	0.454	$160 \pm 10$	1.09	0.452	$160 \pm 10$
97-MITE-2H	9	Ae	1.16	0.478	$0.65\pm0.05$	1.18	0.482	$2.7 \pm 0.2$	1.12	0.470	$8.0 \pm 0.6$
97-MITE-2G	15	Bf	1.20	0.499	$0.15 \pm 0.01$	1.22	0.492	$2.2 \pm 0.2$	1.13	0.473	$7.0 \pm 0.6$
97-MITE-2F	25	Bf	1.21	0.493	$0.18\pm0.01$	1.25	0.503	$1.7 \pm 0.1$	1.12	0.470	$7.4 \pm 0.6$
97-MITE-2E	35	Bf	1.21	0.495	$0.17\pm0.01$	1.26	0.505	$1.7 \pm 0.1$	1.12	0.471	$5.5\pm0.4$
97-MITE-2D	45	Bf	1.25	0.518	$0.13 \pm 0.01$	1.27	0.505	$1.6 \pm 0.1$	1.10	0.465	$6.2 \pm 0.5$
97-MITE-2C	55	BC	1.20	0.496	$0.110\pm0.009$	1.25	0.501	$1.5 \pm 0.1$	1.10	0.466	$6.2 \pm 0.5$
97-MITE-2B	65	BC	1.26	0.510	$0.17 \pm 0.01$	1.28	0.501	1.7 ± 0.1	1.10	0.462	6.0 ± 0.5

Table 5-1 Pb concentrations and isotopic compositions determined on the exchangeable fraction (Mehlich-III), the partial fraction (0.25 M HCl) and the total fraction for all soil samples from Rouyn-Noranda and Grande-Baleine.

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<u> </u>			Ex	changeabl	e fraction	_, <u>,                                    </u>	Partial extr	action		Total extr	action
Sample No.	Depth (cm)	Horizon	<sup>206</sup> <i>Pb</i>	$^{206}Pb$	[Pb]	<sup>206</sup> <i>Pb</i>	$^{206}Pb$	[Pb]	<sup>206</sup> <i>Pb</i>	<sup>206</sup> <i>Pb</i>	[Pb]
·····			<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> Pb	(ppm)
97-MITE-2A	75	BC	1.22	0.504	$0.19 \pm 0.01$	1.25	0.496	$1.8 \pm 0.1$	1.10	0.466	$6.3 \pm 0.5$
00-DMITE-4H	4	FL	1.01	0.436	$45 \pm 4$	1.01	0.434	$230\pm20$	1.03	0.432	$200 \pm 20$
00-DMITE-4G	8	HF	1.03	0.439	$5.9 \pm 0.5$	1.03	0.439	$280\pm20$	1.05	0.440	$310 \pm 20$
00-DMITE-4F	10	Ae	1.12	0.478	$0.69 \pm 0.06$	1.12	0.468	$2.6 \pm 0.2$	1.12	0.469	$8.7 \pm 0.7$
00-DMITE-4E	15	Bhf	1.06	0.476	$0.03\pm0.002$	1.16	0.479	$2.9 \pm 0.2$	1.12	0.476	$9.0\pm0.7$
00-DMITE-4D	25	Bf	1.19	0.504	$0.02\pm0.002$	1.21	0.490	$1.13 \pm 0.09$	1.11	0.471	$4.9 \pm 0.4$
00-DMITE-4C	35	Bf	1.22	0.486	$0.04 \pm 0.003$	1.23	0.497	$1.14 \pm 0.09$	1.10	0.467	$5.1 \pm 0.4$
00-DMITE-4B	45	BC	1.11	0.468	$0.07\pm0.006$	1.17	0.482	$1.4 \pm 0.1$	1.07	0.461	$5.0 \pm 0.4$
00-DMITE-4A	55	Cg	1.16	0.489	$0.03 \pm 0.002$	1.20	0.490	$1.2 \pm 0.1$	1.07	0.460	$4.9\pm0.4$
చ్ర?9-MITE-8L	3	LF	0.98	0.427	85 ± 7	0.99	0.431	$450\pm40$	1.02	0.427	$350 \pm 30$
99-MITE-8K	6	H-Ah	1.01	0.435	56 ± 5	1.02	0.435	$243\pm20$	1.03	0.433	$190 \pm 10$
99-MITE-8J	12	Ae	1.10	0.458	$4.7 \pm 0.4$	1.11	0.464	$12 \pm 1$	<b>,</b> 1.13	0.458	$16 \pm 1$
99-MITE-8I	20	Bhf	1.12	0.467	$0.05\pm0.004$	1.15	0.469	$2.7 \pm 0.2$	1.13	0.457	$9.0 \pm 0.7$
99-MITE-8H	30	Bf	1.18	0.481	$0.04 \pm 0.003$	1.25	0.496	1.11 <b>±0.09</b>	1.13	0.458	$9.3 \pm 0.7$
99-MITE-8G	40	Bf	1.20	0.484	$0.04 \pm 0.003$	1.21	0.485	$1.2 \pm 0.1$	1.13	0.458	$9.6 \pm 0.8$
99-MITE-8F	50	Bf	1.21	0.492	$0.04\pm0.003$	1.24	0.494	$1.4 \pm 0.1$	1.14	0.464	$8.4 \pm 0.7$
99-MITE-8E	60	Bhf	1.20	0.493	$0.03\pm0.002$	1.22	0.488	$1.3 \pm 0.1$	1.11	0.455	$9.2 \pm 0.7$
99-MITE-8D	70	Bf	1.20	0.487	$0.07\pm0.006$	1.23	0.494	$1.6 \pm 0.1$	1.10	0.452	$10.7\pm0.9$
99-MITE-8C	80	Bf	1.16	0.475	$0.08\pm0.006$	1.20	0.484	$2.1\pm0.2$	1.15	0.468	$8.9 \pm 0.7$
99-MITE-8B	90	BC	1.19	0.486	$0.09\pm0.007$	1.23	0.490	$1.9 \pm 0.2$	1.17	0.479	$8.0 \pm 0.6$
99-MITE-8A	100	C	1.17	0.475	$0.07 \pm 0.006$	1.22	0.486	$1.8 \pm 0.1$	1.16	0.478	$6.78\pm0.5$

			Ex	changeab	le fraction		Partial ext	raction		Total extra	action
Sample No.	Depth	Horizon	$^{206}Pb$	<sup>206</sup> Pb	[Pb]	<sup>206</sup> Pb	<sup>206</sup> Pb	[Pb]	$^{206}Pb$	$^{206}Pb$	[Pb]
	(em)		<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)
99-MITE-9J	10	F	0.98	0.425	28 ± 2	0.98	0.426	$750\pm60$	1.00	0.422	$550 \pm 40$
99-MITE-9I	15	H-Ah	1.02	0.437	$23 \pm 2$	1.04	0.443	58 ± 5	1.04	0.435	57 ± 5
99-MITE-9H	22	Ae	1.10	0.458	$1.5 \pm 0.1$	1.12	0.465	$4.2 \pm 0.3$	1.12	0.461	$9.0 \pm 0.7$
99-MITE-9G	30	Bhf	1.19	0.472	$0.3 \pm 0.03$	1.20	0.475	$3.6 \pm 0.3$	1.22	0.499	$9.1 \pm 0.7$
99-MITE-9F	40	Bf	1.21	0.480	$0.16 \pm 0.01$	1.22	0.487	$2.4 \pm 0.2$	1.12	0.462	$7.8 \pm 0.6$
99-MITE-9E	50	Bf	1.20	0.478	$0.13\pm0.01$	1.22	0.489	$2.2 \pm 0.2$	1.10	0.457	$7.6 \pm 0.6$
99-MITE-9D	60	Bf	1.23	0.486	$0.16 \pm 0.01$	1.23	0.493	$2.5 \pm 0.2$	1.12	0.461	$8.6 \pm 0.7$
99-MITE-9C	70	BC	1.20	0.477	$0.17\pm0.01$	1.23	0.488	$2.6\pm0.2$	1.12	0.460	$8.7\pm0.7$
99-MITE-9B	80	С	1.21	0.479	$0.21 \pm 0.02$	1.22	0.488	$2.2 \pm 0.2$	1.10	0.456	$8.3 \pm 0.7$
99-MITE-9A	90	С	1.20	0.480	$0.20\pm0.02$	1.23	0.492	$1.9 \pm 0.2$	1.10	0.454	$8.1 \pm 0.6$
99-MITE-10J	6	LF	1.10	0.462	$3.2 \pm 0.3$	1.10	0.464	$74 \pm 6$	1.10	0.453	$73 \pm 6$
99-MITE-10I	15	FH	1.17	0.482	$6.3 \pm 0.5$	1.17	0.488	$25 \pm 2$	1.16	0.469	21 ± 2
99-MITE-10H	22	Н	1.17	0.479	$2.2 \pm 0.2$	1.17	0.484	$18 \pm 1$	1.14	0.464	$20 \pm 2$
99-MITE-10G	30	Ae	1.16	0.482	$0.4 \pm 0.3$	1.15	0.476	$0.96\pm0.07$	1.06	0.452	$8.4\pm0.7$
99-MITE-10F	40	Bhf	1.28	0.508	$0.100 \pm 0.008$	1.28	0.513	$2.8 \pm 0.2$	1.15	0.471	$10.1 \pm 0.8$
99-MITE-10E	50	Bf	1.05	0.547	$0.070 \pm 0.006$	1.38	0.537	$1.8 \pm 01$	1.12	0.469	$8.4 \pm 0.7$
99-MITE-10D	60	Bf	1.40	0.539	$0.080 \pm 0.006$	1.37	0.541	$1.7 \pm 0.1$	1.11	0.458	$9.0 \pm 0.7$
99-MITE-10C	70	BC	1.40	0.539	$0.100 \pm 0.008$	1.42	0.549	$1.6 \pm 0.1$	1.12	0.461	$8.8\pm0.7$
99-MITE-10B	80	С	1.51	0.577	$0.090 \pm 0.007$	1.46	0.577	$1.4 \pm 0.1$	1.11	0.460	$8.2 \pm 0.7$
99-MITE-10A	90	С	1.38	0.545	$0.18 \pm 0.01$	1.42	0.554	$1.7 \pm 0.1$	1.11	0.463	$9.2 \pm 0.7$

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			Ех	changeab	le fraction	· · · · · · · · · · · · · · · · · · ·	Partial extr	action		Total extr	action
Sample No.	Depth	Horizon	<sup>206</sup> Pb	$^{206}Pb$	[Pb]	$^{206}Pb$	<sup>206</sup> Pb	[Pb]	$^{206}Pb$	$^{206}Pb$	[Pb]
	(011)		<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)	<sup>207</sup> <i>Pb</i>	<sup>208</sup> <i>Pb</i>	(ppm)
Grande-Balein	e region										
98-MITE-6I	3	LF	1.20	0.490	$5.7 \pm 0.5$	1.19	0.482	$24 \pm 2$	1.16	0.470	$33 \pm 3$
98-MITE-6H	7	Ah-H	1.18	0.446	$0.89\pm0.07$	1.19	0.448	$4.6 \pm 0.4$	1.03	0.415	$16 \pm 1$
98-MITE-6G	11	Ae	1.15	0.442	$1.63 \pm 0.1$	1.16	0.432	$6.4 \pm 0.5$	1.05	0.420	$25 \pm 2$
98-MITE-6F	17	Bhfj	1.22	0.415	$0.29\pm0.02$	1.27	0.422	$4.0 \pm 0.3$	1.05	0.423	$18 \pm 1$
98-MITE-6E	28	Bf	1.24	0.415	$0.62 \pm 0.05$	1.34	0.405	$4.1 \pm 0.3$	1.06	0.413	21 ± 2
98-MITE-6D	38	Bf	1.23	0.388	$0.66 \pm 0.05$	1.33	0.398	$4.5 \pm 0.4$	1.04	0.414	$20 \pm 2$
98-MITE-6C	48	С	1.22	0.387	$0.61 \pm 0.05$	1.33	0.396	$4.4 \pm 0.4$	1.05	0.413	$20 \pm 2$
98-MITE-6B	60	С	1.23	0.401	$0.88\pm0.07$	1.34	0.400	$4.5\pm0.4$	1.05	0.415	$21 \pm 2$
98-MITE-6A	70	C	1.19	0.438	$1.9 \pm 0.2$	1.28	0.415	$6.0 \pm 0.5$	1.06	0.419	$21 \pm 2$
98-MITE-7H	5	HF	1.21	0.490	$1.9 \pm 0.1$	1.20	0.483	$4.2 \pm 0.3$	1.14	0.462	$6.6 \pm 0.5$
98-MITE-7G	9	Ah-H	1.22	0.392	$0.81\pm0.06$	1.22	0.390	$3.8 \pm 0.3$	<b>*</b> 1.06	0.415	$10.6\pm0.8$
98-MITE-7E	16	Bhf	1.25	0.422	$0.080\pm0.006$	1.27	0.421	$6.0 \pm 0.5$	1.10	0.424	$19 \pm 1$
98-MITE-7D	23	Bhf	1.28	0.413	$0.100\pm0.008$	1.32	0.419	$5.1 \pm 0.4$	1.11	0.428	21 ± 2
98-MITE-7C	30	Bhf	1.29	0.415	$0.12 \pm 0.01$	1.35	0.418	$5.5 \pm 0.4$	1.11	0.432	$19 \pm 1$
98-MITE-7B	35	Bf	1.29	0.414	$0.24 \pm 0.02$	1.36	0.424	$6.5 \pm 0.5$	1.12	0.435	21 ± 2
98-MITE-7A	39	Bhf	1.33	0.401	$0.17 \pm 0.01$	1.38	0.414	$6.4 \pm 0.5$	1.12	0.433	$22 \pm 2$

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Sample No.	Depth (cm)	Horizon	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	<sup>206</sup> Pb/ <sup>207</sup> Pb	<sup>206</sup> Pb/ <sup>208</sup> Pb	Pb concentration (ppm)
97-MITE-1B-G	50	BC	19.61	16.25	40.20	1.21	0.488	3.4 ± 0.3
97-MITE-2C-G	55	BC	18.52	16.01	39.19	1.16	0.473	$3.1 \pm 0.2$
00-DMITE-4B-G	45	BC	19.03	15.98	39.65	1.19	0.480	$2.1 \pm 0.2$
98-MITE-6C-G	48	С	14.94	15.33	38.34	0.97	0.390	$17 \pm 1$
98-MITE-7B-G	35	Bf	15.98	15.59	38.50	1.03	0.415	$16 \pm 1$
99-MITE-8B-G	90	BC	22.47	16.81	42.73	1.34	0.526	$2.4 \pm 0.2$
99-MITE-8E-G	60	Bhfj	22.63	17.06	42.88	1.33	0.528	$2.7 \pm 0.2$
99-MITE-10C-G	70	BC	16.76	15.35	36.75	1.09	0.456	$4.6 \pm 0.4$

Table 5-2 Pb concentrations and isotopic compositions determined on total extraction for granule (2-4 mm) samples from the parent materials of studied soil profiles.

\*Sample number prefix indicates year of sample collection. MITE= Metals In The Environment. A, B, C... indicate different samples from the same site. The number before letter A, B, C ... refers to site number. G = Granule sample.



Fig. 5-1 Concentration profiles for soil sites in the Rouyn-Noranda and Grande-Baleine regions. ▲ Total extraction, ● Exchangeable fraction, □ Partial extraction

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Fig. 5-2 <sup>206</sup>Pb/<sup>207</sup>Pb profiles for soil sites in the Rouyn-Noranda and Grande-Baleine regions. ▲ Total extraction, ● Exchangeable fraction, □ Partial extraction

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levels in certain organic samples may result from the lesser homogenization of the analyzed fraction of organic samples (<500 um) as well as from the weight difference of subsamples between partial (100 mg) and total extractions (500 mg). The high Pb levels in 0.25 M HCl extraction suggest that anthropogenic Pb is largely retained by organic matter and readily released by this dilute acid leaching.

The <sup>206</sup>Pb/<sup>207</sup>Pb ratios in total extractions are higher than or similar to those in HCl leachates for most of the organic samples from Rouyn-Noranda region (Table 5-1). This may result from the release of mineral materials of higher <sup>206</sup>Pb/<sup>207</sup>Pb signatures that were integrated in organic horizons, or from the admixion of previously cycled organic matter with higher <sup>206</sup>Pb/<sup>207</sup>Pb ratios. In mineral layers, a systematic shift to lower values is observed (Fig. 5-2). This is in contrast to other studies in which the leachates are always less radiogenic than untreated bulk samples and residues (Monna et al., 1999), but is in accordance with results from stream sediment studies in the US by Gulson et al. (1992) and Church et al. (1993), and in Canada by Gobeil et al., (1995). This higher Pb isotope values in partial fraction in mineral soils can be attributed to the weathering of silicate minerals which releases more radiogenic Pb from U- and Th-rich minerals, leaving the residual part with lower Pb isotopic compositions (Erel et al., 1990, 1991; Keinonen, 1992). Pb derived from radioactive decay often occupies defect lattice positions in silicates (Faure, 1986) and is liberated by weathering in preference to the original Pb (Öhlander et al., 1992). The lead released from weathering of parent materials in soils is believed to be associated with Fe and Mn hydroxides, or adsorbed onto organic matter and of clay minerals (Erel et al., 1990, 1997) and is readily removed by dilute acid leaching (Erel et al., 1997).

At control sites 6 and 7, total lead concentrations of mineral samples are about 10 ppm higher than at sites in the Rouyn-Noranda region (Table 5-1), thus indicating that the parent materials in the Grande-Baleine region contain more Pb. Unlike the sites in Rouyn-Noranda region, Pb isotope ratios in total extraction are systematically lower than in acid leaching for both mineral samples and organic samples (Fig. 5-2, sites 6 and 7). The lower <sup>206</sup>Pb/<sup>207</sup>Pb ratios in the total extraction of organic samples relative to the partial

extraction probably results from the relatively low <sup>206</sup>Pb/<sup>207</sup>Pb ratios of mineral materials at these two sites.

Total lead concentrations and isotope ratios of granule samples (2-4 mm) from selected horizons are listed in Table 5-2. The total lead concentrations of soil samples are higher at all sites than those of granule samples of the corresponding horizon, indicating that a certain amount of Pb has been released to soils, possibly through weathering. <sup>206</sup>Pb/<sup>207</sup>Pb ratios in the total extraction of granule samples vary greatly from 0.97 at control site 7 to 1.34 at site 8. They are consistently less radiogenic (having lower isotope ratios) than in partial extraction at the corresponding site, except at site 8. This is likely due to preferential leaching of most soluble minerals with higher <sup>206</sup>Pb/<sup>207</sup>Pb ratios. This hypothesis is supported by the fact that <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>206</sup>Pb/<sup>208</sup>Pb ratios measured in the total fraction of soil samples are an admixing of Pb leached by 0.25 M HCl and Pb derived from the mineral framework (granule samples). This can be expressed by the mass balance equations below where P refers to partial extraction, D, to detrital part, and T, to total extraction:

$$[^{206}\text{Pb}/^{207}\text{Pb}]_{P} * [Pb]_{P} + [^{206}\text{Pb}/^{207}\text{Pb}]_{D} * ([Pb]_{T-} [Pb]_{P}) \approx [^{206}\text{Pb}/^{207}\text{Pb}]_{T} * [Pb]_{T}$$
$$[^{206}\text{Pb}/^{208}\text{Pb}]_{P} * [Pb]_{P} + [^{206}\text{Pb}/^{208}\text{Pb}]_{D} * ([Pb]_{T-} [Pb]_{P}) \approx [^{206}\text{Pb}/^{208}\text{Pb}]_{T} * [Pb]_{T}$$

These equations apply only for mineral and certain organic samples from control sites 6 and 7, which are assumed to have been least affected by human activities. This could be explained by the fact that Pb present in soils near Rouyn is mainly derived from anthropogenic sources external to the profile (wet/dry deposition). Other factors such as, the degree of soil weathering, and the representativity of the granule samples could also be the reasons that the mass balance does not apply at the sites in the Rouyn-Noranda region.

Pb concentration data show that anthropogenic lead in organic samples is readily removed by 0.25 M HCl leaching, and the Pb isotope signatures of these leachates show the highest difference between organic and mineral horizons (Fig. 5-2). So the foregoing discussion on soils contamination will mainly focus on the results from partial extraction (0.25 M HCl leaching).

### 3. Lead concentrations and isotopic compositions in dilute acid leachates

# 3.1 Rouyn-Noranda region

In general, Pb is highly concentrated in organic samples from the upper layers of the profiles (L, F and H), and its concentrations decrease markedly from organic horizons to mineral horizons. In contrast to Pb concentration, Pb isotope ratios are higher in mineral samples collected at deeper horizons, and they decline significantly at the top of the profiles.

As shown in Fig. 5-1, low Pb contents ( $\sim 2$  ppm) are observed in deeper horizons of all the profiles (below 30-40 cm), and they increase slightly in the upper Bhf or Bf and Ae horizon, finally reaching the maximum values in the uppermost humus layers. The <sup>206</sup>Pb/<sup>207</sup>Pb ratios are higher in the deeper parts of the soil profiles, and they decrease sharply from the upper illuvial horizon (Bhf or Bf) or eluvial horizon (Ae) to organic horizons, reaching the minimum ratios at the top (Fig. 5-2). These inversely correlated Pb concentration and isotope ratios have been attributed to atmospheric fluxes of Pb from industrial pollutants with lower <sup>206</sup>Pb/<sup>207</sup>Pb ratios by many investigators (Farmer et al., 1996; Brännvall et al., 1997; Hansmann and Köppel, 2000). A small decrease of Pb concentration and increase of <sup>206</sup>Pb/<sup>207</sup>Pb ratios are observed in the uppermost surface organic sample at site 1 (Fig. 5-2), located closest to the Horne smelter, reflecting either a recent reduction of smelter-Pb deposition (Gobeil, et al., 1995; Brännvall et al., 1997; Cortizas et al., 1997; Görres et al., 1997; Norton, 1997) or an input of another Pb type. The former hypothesis is consistent with the fact that metal emissions from the Horne smelter have decreased by 50% since 1985 [3]. The Horne smelter has become a 100%custom smelter after the Horne copper-gold mine was closed in 1976, and its feeds come from other base metal producers in northwestern Quebec and from Europe. The higher Pb isotope signatures for Europe (<sup>206</sup>Pb/<sup>207</sup>Pb= ~1.10-1.15) (Simonetti et al., 2000) and

Abitibi Cu Sulphides ( $^{206}$ Pb/ $^{207}$ Pb= ~0.92-1.04) (Carignan and Gariépy, 1999) may have contributed to the higher Pb isotope signatures of topsoil at site 1, which is proximal to the smelter. At site 1, the regular decline of  $^{206}$ Pb/ $^{207}$ Pb ratios from ~1.24 at the bottom of the profile to 1.17 in the Ae horizon probably resulted from the addition of a minor amount of lower isotopic ratio Pb from upper organic horizons into the soil, though the Pb concentrations remain relatively stable. No clear inverse trend of Pb concentration and  $^{206}$ Pb/ $^{207}$ Pb profiles was observed at site 10. There, the Pb concentrations are much lower and  $^{206}$ Pb/ $^{207}$ Pb ratios are much higher than at other sites along the transect, implying that the farthest site along the transect is least affected by smelting activity.

The Pb concentrations and isotope ratios vary not only vertically in individual sample profiles, but also laterally between different sample sites. There is distinct difference in Pb concentrations and isotope ratios between the sites nearest to the Horne smelter and the other sites. Along the northeast transect in Rouyn-Noranda, the average Pb concentration in humus layers is as high as 869 ppm at site 1, only 8.7 km from the smelter. It decreases exponentially with increasing distance from the smelter, reaching 39 ppm at site 10, 116 km from Rouyn (Fig 5-3). Similar trends have been observed in many other investigations (Rieuwets and Farago, 1996; Verner and Ramsey, 1996; Karczewska, 1996) and this was attributed to the anthropogenic emissions from both smelter stacks and fugitive sources such as stockpiles and waste heaps (Harrison and Luxen, 1981; Rolfe and Jennett, 1975). The average Pb concentration in organic samples at site 8, 13 km in the upwind direction of the Horne smelter is of the same magnitude as at site 9, which is at a similar distance but in the downwind direction. All these suggest a point source of Pb input into the soils. This conclusion is supported by the similar distribution pattern of other metals (Cu and Zn) in soils (unpublished data). In contrast, Pb isotope ratios increase gradually from 0.99 at site 1 to 1.15 at site 10 (Fig. 5-3), indicating a decreasing proportion of anthropogenic Pb at increasing distance from point source of Pb pollution.


Fig. 5-3 Plot of average Pb concentration and isotope ratios in surface organic horizons as a function of distance from the Horne smelter. A Pb concentration of about 1 000 ppm at Horne smelter is assumed.  $^{206}$ Pb/ $^{207}$ Pb ratio at Horne smelter (0.92) is that of Noranda galena (Franklin *et al.*, 1983)

At site 1, the sample showing the highest Pb concentration (1 414 ppm) also presents the lowest ratio (0.98). This value is close to the <sup>206</sup>Pb/<sup>207</sup>Pb value of Noranda galena (0.92) and within the range of Abitibi Cu sulfides (Franklin *et al.*, 1983;, Carignan and Gariépy, 1995) (<sup>206</sup>Pb/<sup>207</sup>Pb= ~ 0.92-1.04). Both the decrease of Pb concentrations and the increase of isotope ratios with increasing distance from Rouyn-Noranda suggest that the Horne smelter is the cause of Pb contamination of soils in the region. This conclusion is further supported by the fact that the Pb isotopic compositions measured in soils lie on a mixing line between the Pb-isotopic compositions of deep mineral soils and of the Rouyn-Noranda galena (Fig. 5-4). This is also supported by the trends of Pb concentrations and isotope ratios in spruce rings in this area (Savard *et al.*, accepted). The lowest observed <sup>206</sup>Pb/<sup>207</sup>Pb value of 0.98 at the nearest site is lower than those of 1.046 and 1.172 respectively reported in lichen samples (Carignan and Gariépy, 1995) and in snow samples (Simonetti *et al.*, 2000) near Rouyn-Noranda. This can be attributed to the greater distance of lichen sample from the Horne smelter (~ 100 km) than that of our sample (8.7 km), or to the specific Pb signatures of aerosols during the life span of

lichens, or to the short period recorded by snow samples (Simonetti, *et al.*, 2000). Even at an equivalent distance from Horne smelter (100 km), the lowest observed  ${}^{206}Pb/{}^{207}Pb$ value of 1.10 at site 10, 116 km from Horne smelter is higher than that of the lichen samples ( ${}^{206}Pb/{}^{207}Pb = 1.046$ ). The higher  ${}^{206}Pb/{}^{207}Pb$  values in soils may be attributed to the fact that  ${}^{206}Pb/{}^{207}Pb$  values in lichen samples are representative of that of atmospheric Pb in the region, while  ${}^{206}Pb/{}^{207}Pb$  ratios in the soils are a mixing of anthropogenic Pb from the atmosphere and the natural background Pb in the soils, which is usually characterized by higher  ${}^{206}Pb/{}^{207}Pb$  ratios. However, the smelter contribution to soil Pb at site 10 is similar to that estimated by using lichen samples by Carignan and Gariépy (1995) (see section 4 in this chapter).



Fig. 5-4 Plot of  ${}^{206}$ Pb/ ${}^{207}$ Pb vs  ${}^{206}$ Pb/ ${}^{208}$ Pb for all the soil samples digested by 0.25 M HCl showing an influence of less radiogenic Pb input into soils. Samples from Grande-Baleine are plotted off the mixing line. Pb isotopic ratios representing Noranda Galena (Franklin *et al.*, 1983), US anthropogenic emissions (Simonetti *et al.*, 2000) and Canadian anthropogenic emissions (Carignan and Gariépy, 1995) are also plotted.

Figure 5-5 shows the  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio vs Pb concentration for all samples from 8 profiles. Contamination of soils in Rouyn-Noranda region can be recognized by higher lead concentrations and lower Pb isotope values. All the mineral samples from Rouyn-Noranda have lower Pb contents (<12 ppm) and more radiogenic  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratios ( ${}^{206}\text{Pb}/{}^{207}\text{Pb} = 1.11-1.46$ ), suggesting that the mineral horizons of the soil profiles were less affected or not affected by anthropogenic Pb deposition.

# **3.2 Grande-Baleine region**

The soil profiles from Grande-Baleine generally display trends of Pb concentration and isotope ratios without major vertical change. Pb concentrations are much lower and <sup>206</sup>Pb/<sup>207</sup>Pb ratios are much higher (in organic horizons) at these two sites. At site 6, the highest Pb concentration in surface organic sample is 32 ppm, which is a somewhat



Fig. 5-5 Plot of <sup>206</sup>Pb/<sup>207</sup>Pb ratio against Pb concentration for all soil samples extracted by 0.25 M HCl leaching. Also shown are the <sup>206</sup>Pb/<sup>207</sup>Pb ratios of Noranda galena (Franklin *et al.*, 1983) and Abitibi Cu sulphides (Carignan and Gariépy, 1995).

higher than the average total Pb level (20 ppm) of the mineral samples at this site, but it is within the range of natural Pb concentration in soils presented in many reports (Nriagu 1978, Pierce et al., 1982; Alina and Henryk, 1992). Site 7 shows slightly different trends from those in Rouyn-Noranda region. Pb concentrations decrease from the bottom to the top, with slight variations within the profile, and lead isotope ratios decline continuously from the bottom to the top. The continuous increase of Pb concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb ratios with increasing depth at site 7 is probably related to the sandier texture of the soil at this site. This presumably favored the migration of Pb at depth. On the <sup>206</sup>Pb/<sup>207</sup>Pb vs Pb concentration diagram (Fig. 5-5), all samples from Grande-Baleine are plotted in the range of, or close to, mineral samples from Rouyn-Noranda. They also plot outside the mixing line on the <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>206</sup>Pb/<sup>208</sup>Pb diagram (Fig. 5-4). Although at control sites, Pb concentrations are much lower and Pb isotope ratios are much higher than those of organic samples in Rouyn-Noranda region, there still exist some differences in <sup>206</sup>Pb/<sup>207</sup>Pb ratios between surface organic samples and underlying mineral samples. In the dendrogeochemical investigation by Savard et al. (accepted), the Pb concentrations in spruce rings at the control site present relatively flat trends through time, but there is a gentle increase after 1960. However there is no <sup>206</sup>Pb/<sup>207</sup>Pb data available due to very low Pb concentrations in tree ring samples. Based on these data, we can not rule out the possibility of contamination by anthropogenic Pb at the control site. The decline of <sup>206</sup>Pb/<sup>207</sup>Pb ratios in the surface organic samples at control sites is likely due to the long range transport of Canadian airborne Pb, which is characterized by  ${}^{206}Pb/{}^{207}Pb = 1.147$ , as recorded by lichen samples collected approximately 700 km northwest of Rouyn-Noranda (Carignan and Gariépy, 1995).

## 4. Estimation of smelter contribution to Pb in soils

As shown on the <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>206</sup>Pb/<sup>208</sup>Pb diagram (Fig. 5-4), all samples from Rouyn-Noranda region plot on a straight line between Pb isotope ratios of Noranda galena and that of local mineral soils, indicating a significant contribution of a less radiogenic lead source to the natural lead source in soils. Samples from Grande-Baleine plot well outside this straight line. Pb isotope ratios of US and Canadian anthropogenic emissions also plot on the above straight line. US anthropogenic emissions as a source of Pb in soils in Rouyn-Noranda can be ruled out on the basis of their absence in lichen samples from this region (Carignan and Gariépy, 1995). The linear relationship of soil samples from Rouyn-Noranda area indicates a simple mixing of two components whose two end-members are anthropogenic lead from Horne smelter emissions ( $^{206}Pb/^{207}Pb = 0.92$ ) and natural background Pb in the deeper horizons of soil profiles. On a regional scale, Canadian atmospheric emissions are also a source of Pb in soils. Due to the multiple sources of lead in soils, the exact contribution of smelter emissions to soils cannot be calculated directly. In order to at least estimate this contribution, two extreme situations can be considered. That is, the background Pb in the Rouyn-Noranda region is either from mineral Pb in soils only, or from Canadian atmospheric emissions only ( $^{206}Pb/^{207}Pb = 1.15$ ).

To calculate the relative contributions of smelter emissions to soils, it is necessary to define the Pb isotopic compositions of natural lead in soils. Figure 5-6 shows the  $^{206}Pb/^{207}Pb$  against sampling site for all soil samples digested by the three extracting methods. The base line for  $^{206}Pb/^{207}Pb$  in 0.25 M HCl extractions averages 1.25 for site 1, 2, 8, 9 and 4, and 1.4 for site 10. These values are assumed to best represent the  $^{206}Pb/^{207}Pb$  ratios of natural background Pb because the  $^{206}Pb/^{207}Pb$  ratios of mineral samples are the highest in the partial HCl extraction (Fig. 5-2). Using these values and

Smelter  
contribution = 
$$\frac{\binom{206 \text{Pb} / 207 \text{Pb}}{\text{End Mb2} - (206 \text{Pb} / 207 \text{Pb})_{\text{sample}}}}{\binom{206 \text{Pb} / 207 \text{Pb}}{\text{End Mb2} - (206 \text{Pb} / 207 \text{Pb})_{\text{End Mb1}}}} X 100$$

Where End Mb1 = 0.92 (Noranda Galena),

End Mb2 = 1.25 or 1.4 (background soils); 1.15 (CDN emissions),

Sample = Average organic samples.

standard isotope dilution equation presented here, then the proportion of smelter emissions in the organic samples at each site falls within the range as shown in Figure 5-7. The real contributions of smelter emissions to soils in Rouyn-Noranda region should



Exchangeable fraction

Fig. 5-6  $^{206}$ Pb/ $^{207}$ Pb profiles of all sites as a function of relative distance from smelter for three extracting methods.

lay between these two lines, but since the anthropogenic Pb in soils will have predominantly low Pb ratios, as shown by the lower ratios in surface organic samples, the proportion of anthropogenic Pb from smelter emissions should lay close to



Fig. 5-7 Contributions of smelter emissions to the anthropogenic Pb in soils in Rouyn-Noranda region. Solid and hollow circles assume to be contributions from airborne emissions and from background soils to the measured ratios, respectively.

the smelter vs background soil line. As shown in Figure 5-7, anthropogenic Pb from smelter emissions can be recognized as far as 116 km downwind from the Horne smelter.

The proportion of smelter emissions at site 10, 116 km from the Horne smelter, accounts for 53 % of anthropogenic Pb in soils. If Pb isotopic compositional range of Abitibi Cu sulphides (0.92-1.04) is used to estimate the contribution of smelter emissions to anthropogenic Pb in the uppermost surface organic sample at site 10, the proportion of anthropogenic Pb in soils will increase to 63-84 %. This is within the range (50-90 %) estimated by Carignan and Gariépy (1995) using lichen samples collected at 100 km from the Horne Smelter.

## 5. Pb migration in soils

Unlike other metals such as Cu, Zn and Hg (Lucotte et al., 1999), Pb is not depleted in eluvial horizon (Ae) or enriched in upper illuvial horizons (Bhf or Bf). Pb concentration is relatively higher in eluvial and upper illuvial horizons than in the corresponding BC or C horizon at all sites in the Rouyn-Noranda region (Fig. 5-1). The higher Pb value probably indicates that Pb has migrated to eluvial or upper illuvial horizon. This assumption is further evidenced by the relatively lower Pb isotope ratios in these two horizons than in corresponding BC or C-horizon (Fig. 5-2). Based on the abrupt change of Pb concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb rations in soil profiles, it is estimated that anthropogenic Pb in soil profiles has reached a depth of  $\sim 10-30$  cm. The mobility of Pb in soils can be estimated by the depth penetration of Pb (Öhlander et al., 1992; Erel et al., 1997). If Pb deposition from smelter emissions began only and immediately after the set up of the Horne smelter in December 1927, a mobility range of 1 to 4 mm/a is estimated. This is in fair agreement with investigations by other researchers. By using Pb isotopes, Pouchelt et al. (1993) was able to estimate a maximum mobility of 8 mm/a in southwest Germany, and Erel et al. (1997) estimated an infiltration velocity of 5 mm/a in Israel soils. Whitehead et al. (1997) estimated a mean migration rate of  $8 \pm 2$  mm/a in fractured sandstone in London. The mechanisms involved in the migration of Pb in soils include migration of Pb in soil solutions, with clay minerals, especially those of colloidal sizes (< 10 um), and with soil organic matter (Miller *et al.*, 1994).

#### Conclusions

Pb concentrations coupled with Pb isotopic signatures provide useful methods for recognizing Pb contamination of soils and for distinguishing anthropogenic lead from natural lead in soils. The study of elemental Pb and Pb isotopic compositions in Rouyn-Noranda suggests that the Horne smelter is the point source of Pb contamination of soils in the region. High levels of Pb from smelter emissions were largely retained in the organic horizons (L, F and H) of soil profiles, but at heavily contaminated sites, Pb is present at relatively high concentrations at the deeper portions of the soil profile. Pb pollution in individual soil profiles is generally recognized by inverse trend of Pb concentration and isotopic composition *vs* depth profiles.

Pb concentrations and isotope values vary not only vertically within individual soil profiles, but also laterally between different sites. In organic horizons, Pb levels peaked at the site closest to the Horne smelter and decreased exponentially with increasing distance from Rouyn-Noranda, while Pb isotope ratios display an opposite pattern.  $^{206}$ Pb/ $^{207}$ Pb ratio of 0.98 are observed in organic horizons at sites closest to Horne smelter, and this value is very close to Pb isotopic composition of Noranda galena ( $^{206}$ Pb/ $^{207}$ Pb =0.92) and within the range of Abitibi Cu sulphides. Along the southwest-northeast transect, Pb from smelter emissions has been transported as far as 116 km downwind from Rouyn-Noranda. Based on Pb concentration and isotopic composition results, Pb has migrated downward to a depth of ~10-30 cm, and a mobility range of 1-4 mm/a is thus estimated.

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[3] www.noranda.com/annual-rps/enviroreport95/mingand metals.html



Fig. 1 Carte simplifiée montrant la localisation des sites échantillonnés dans la région d'étude et celles des sites de contrôle.

boréale. Les échantillons de sols ont été prélevés en creusant des tranchées d'environ 60x40 cm à l'aide d'une pelle d'acier. Chaque site comprend de 7 à 12 échantillons de sols, avec au moins un échantillon prélevé de chacun des horizons. Les échantillons recueillis ont été placés dans des sacs de plastique numérotés. Tous les échantillons ont été séchés à l'air ambiant. Les racines vivantes et le matériel ligneux mort ont été retirés manuellement des échantillons. Les échantillons organiques séchés ont été broyés dans un mortier de porcelaine en utilisant de l'azote liquide, et puis ont été passés dans un tamis de 0.5 mm. Les échantillons minéraux ont été tamisés directement à 0.063 mm. Les poudres ont été entreposées dans des fioles de plastique étiquetées pour usage postérieur. Huit échantillons de granules (fraction de 2-4 millimètres) ont été également broyés avant dans les sols se situent le long d'une ligne de mélange entre la composition isotopique de la galène de Noranda et celle du matériel minéral dans les horizons plus profonds des profils (Fig. 5). La valeur <sup>206</sup>Pb/<sup>207</sup>Pb la plus basse observée (0.98) au site le plus proche de la fonderie Horne est inférieure à celles de 1.046 et de 1.172 enregistrées respectivement dans des échantillons de lichens (Carignan et Gariépy, 1995) et dans des



Fig. 5 Diagramme montrant les rapports  ${}^{206}$ Pb/ ${}^{207}$ Pb et  ${}^{206}$ Pb/ ${}^{208}$ Pb dans la fraction extractible (0.25 M HCl) des échantillons de sols. Notez l'apport de Pb moins radiogénique dans les horizons organiques de surface. Les rapports isotopiques de la Galène de Noranda (Franklin, *et al.*, 1983), et les émissions anthropiques des États-Unis (Simonetti *et al.*, 2000) et du Canada (Carignan and Gariépy, 1995) sont aussi été indiqués.

échantillons de neige (Simonetti *et al.*, 2000) dans la région de Rouyn-Noranda. Cette différence peut être attribuée à l'éloignement plus grand de l'échantillon de lichen par rapport à la fonderie Horne (~ 100 km), ou encore aux signatures spécifiques du Pb dans les aérosols pendant la croissance des lichens ou pendant la période nivale.

La figure 6 montre le rapport <sup>206</sup>Pb/<sup>207</sup>Pb vs la concentration en Pb pour tous les échantillons provenant des huit (8) profils. La contamination des sols dans la région de Rouyn-Noranda est caractérisée par des concentrations plus élevées en plomb et des rapports isotopiques inférieurs dans les horizons organiques. Tous les échantillons minéraux provenant de Rouyn-Noranda ont une teneur en Pb inférieure (< 12 ppm) et des rapports plus radiogéniques <sup>206</sup>Pb/<sup>207</sup>Pb (<sup>206</sup>Pb/<sup>207</sup>Pb = 1.11-1.46), suggérant que les horizons minéraux des profils de sols ont été peu ou pas affectés par les apports de Pb anthropique.



Fig. 6 Diagramme montrant le rapport <sup>206</sup>Pb/<sup>207</sup>Pb versus la concentration en Pb dans la fraction extractible (0.25 M HCl) de tous les échantillons de sols. Les rapport <sup>206</sup>Pb/<sup>207</sup>Pb de la galène de Noranda (Franklin *et al.*, 1983) et sulfures de l'Abitibi sont aussi indiqués (Carignan et Gariépy, 1995).

Les concentrations et rapports isotopiques de Pb dans les profils de sol de Grande-Baleine sont caractérisés par des tendances n'affichant pas de changement vertical marqué. Tous les échantillons provenant de Grande-Baleine ont des valeurs proches des échantillons minéraux provenant de Rouyn-Noranda (Fig. 6) mais à l'extérieur de la ligne de mélange <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>206</sup>Pb/<sup>208</sup>Pb (Fig. 5), suggérant que cette région est moins affectée par des activités anthropiques.

Les rapports <sup>206</sup>Pb/<sup>207</sup>Pb moyens de 1.25 pour les sites 1, 2, 8, 9 et 4 et de 1.4 (site 10) déterminés sur l'extraction à 0.25 M HCl représentent les rapports <sup>206</sup>Pb/<sup>207</sup>Pb du Pb naturel puisque les rapports <sup>206</sup>Pb/<sup>207</sup>Pb des échantillons minéraux les plus élevés proviennent de l'extraction partielle. Le rapport <sup>206</sup>Pb/<sup>207</sup>Pb de 0.92 est considéré comme typique des émissions de la fonderie Horne. En utilisant ces valeurs et les équations standard de dilution isotopique, la proportion estimée des émissions de la fonderie dans les sols de la région de Rouyn-Noranda peut être calculée. Les résultats sont présentés à la figure 7. Le Pb anthropique provenant des émissions de la fonderie a probablement été transporté jusqu'à 100 km.



Fig. 7 Contribution estimée des émissions provenant de la fonderie par rapport au Pb dérivé de source anthropique et par rapport au bruit de fond des sols de la région de Rouyn-Noranda.

Sur la foi des concentrations en Pb et des rapports <sup>206</sup>Pb/<sup>207</sup>Pb dans les profils de sols, la migration du Pb anthropique dans les sols est estimée atteindre une profondeur de ~10-30 cm. Si le dépôt du Pb provenant des émissions de la fonderie a commencé à compter de l'entrée en service de la fonderie Horne en décembre 1927 ou juste après, une mobilité de 1 à 4 mm/a est estimée, ce qui concorde avec les résultats d'autres recherches.

from 1965 to 1998 were 40 102 tons for Pb, 38 236 tons for Zn, and 5 080 tons for Cu. Yearly emissions of these metals were as high as 2 400 tons for Pb in 1972 and 3 100 tons for Zn in 1971. Only after 1987, when an effort was taken to control the emissions of heavy metals and gases from Horne smelter to curtail air pollution, were the emissions of heavy metals reduced significantly. In 1976, the Horne Mine closed because metal reserves had run out. The Horne smelter became a 100%-custom smelter with feeds from the Louvicourt Cu-Zn-Au mine and other base metal producers in northwest Quebec as well as imported feeds from Europe and elsewhere [2]. Today, the Horne smelter ranks as one of the world's leading producers of copper and precious metals.



Fig. 4-1 Simplified location map showing the sampling sites in the study area as well as the control sites.

The environmental effects of metal emissions are obvious in the Rouyn-Noranda region. Immediately adjacent to the smelter stack and several kilometers distant, the vegetation damage such as tree mortality, reduction in species diversity, reduced growth and soil erosion can be clearly observed. Between the smelter and our sampling site 1, about 8.7 kilometers northeast, numerous trees had died, especially in areas closest to the smelter where the ground became almost barren with only struggling bushes (Photos 4 - 1, 4 - 2).



Photo 4-1 Tree mortality and soil erosion near Rouyn-Noranda.



Photo 4-2 Tree mortality and soil erosion near Rouyn-Noranda.



Fig. 4-2 Ferrohumic and humoferric podzols developed on unreworked matrix dominated till.

lichens, or to the short period recorded by snow samples (Simonetti, *et al.*, 2000). Even at an equivalent distance from Horne smelter (100 km), the lowest observed  ${}^{206}Pb/{}^{207}Pb$ value of 1.10 at site 10, 116 km from Horne smelter is higher than that of the lichen samples ( ${}^{206}Pb/{}^{207}Pb = 1.046$ ). The higher  ${}^{206}Pb/{}^{207}Pb$  values in soils may be attributed to the fact that  ${}^{206}Pb/{}^{207}Pb$  values in lichen samples are representative of that of atmospheric Pb in the region, while  ${}^{206}Pb/{}^{207}Pb$  ratios in the soils are a mixing of anthropogenic Pb from the atmosphere and the natural background Pb in the soils, which is usually characterized by higher  ${}^{206}Pb/{}^{207}Pb$  ratios. However, the smelter contribution to soil Pb at site 10 is similar to that estimated by using lichen samples by Carignan and Gariépy (1995) (see section 4 in this chapter).



Fig. 5-4 Plot of <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>206</sup>Pb/<sup>208</sup>Pb for all the soil samples digested by 0.25 M HCl showing an influence of less radiogenic Pb input into soils. Samples from Grande-Baleine are plotted off the mixing line. Pb isotopic ratios representing Noranda Galena (Franklin *et al.*, 1983), US anthropogenic emissions (Simonetti *et al.*, 2000) and Canadian anthropogenic emissions (Carignan and Gariépy, 1995) are also plotted.

Figure 5-5 shows the  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratio vs Pb concentration for all samples from 8 profiles. Contamination of soils in Rouyn-Noranda region can be recognized by higher lead concentrations and lower Pb isotope values. All the mineral samples from Rouyn-Noranda have lower Pb contents (<12 ppm) and more radiogenic  ${}^{206}\text{Pb}/{}^{207}\text{Pb}$  ratios ( ${}^{206}\text{Pb}/{}^{207}\text{Pb} = 1.11-1.46$ ), suggesting that the mineral horizons of the soil profiles were less affected or not affected by anthropogenic Pb deposition.

# 3.2 Grande-Baleine region

The soil profiles from Grande-Baleine generally display trends of Pb concentration and isotope ratios without major vertical change. Pb concentrations are much lower and <sup>206</sup>Pb/<sup>207</sup>Pb ratios are much higher (in organic horizons) at these two sites. At site 6, the highest Pb concentration in surface organic sample is 32 ppm, which is a somewhat



Fig. 5-5 Plot of <sup>206</sup>Pb/<sup>207</sup>Pb ratio against Pb concentration for all soil samples extracted by 0.25 M HCl leaching. Also shown are the <sup>206</sup>Pb/<sup>207</sup>Pb ratios of Noranda galena (Franklin *et al.*, 1983) and Abitibi Cu sulphides (Carignan and Gariépy, 1995).



Exchangeable fraction

Fig. 5-6  $^{206}$ Pb/ $^{207}$ Pb profiles of all sites as a function of relative distance from smelter for three extracting methods.

lay between these two lines, but since the anthropogenic Pb in soils will have predominantly low Pb ratios, as shown by the lower ratios in surface organic samples, the proportion of anthropogenic Pb from smelter emissions should lay close to



Fig. 5-7 Contributions of smelter emissions to the anthropogenic Pb in soils in Rouyn-Noranda region. Solid and hollow circles assume to be contributions from airborne emissions and from background soils to the measured ratios, respectively.

the smelter vs background soil line. As shown in Figure 5-7, anthropogenic Pb from smelter emissions can be recognized as far as 116 km downwind from the Horne smelter.

The proportion of smelter emissions at site 10, 116 km from the Horne smelter, accounts for 53 % of anthropogenic Pb in soils. If Pb isotopic compositional range of Abitibi Cu sulphides (0.92-1.04) is used to estimate the contribution of smelter emissions to anthropogenic Pb in the uppermost surface organic sample at site 10, the proportion of anthropogenic Pb in soils will increase to 63-84 %. This is within the range (50-90 %) estimated by Carignan and Gariépy (1995) using lichen samples collected at 100 km from the Horne Smelter.