

# Lead Isotopic Compositions of Soil and Near-Surface Till Profiles from a Watershed Containing Arsenic-Enriched Groundwater in Coastal Maine



USGS Scientific Investigations Report 2005–5112

**Cover.** Soil and till sites were selected for detailed chemical and lead isotope analysis from an area of coastal Maine known to have groundwater with anomalously high arsenic contents, in order to determine the source of the lead and, by inference, possible sources of arsenic.

# **Lead Isotopic Compositions of Soil and Near-Surface Till Profiles from a Watershed Containing Arsenic-Enriched Groundwater in Coastal Maine**

By Robert Ayuso, Nora Foley, Gregory Wandless, Jeremy Dillingham, and Anna Colvin

Scientific Investigations Report 2005-5112

**U.S. Department of the Interior  
U.S. Geological Survey**

**U.S. Department of the Interior**  
Gale A. Norton, Secretary

**U.S. Geological Survey**  
P. Patrick Leahy, Acting Director

U.S. Geological Survey, Reston, Virginia: 2005

For product and ordering information:

World Wide Web: <http://www.usgs.gov/pubprod>

Telephone: 1-888-ASK-USGS

For more information on the USGS--the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment:

World Wide Web: <http://www.usgs.gov>

Telephone: 1-888-ASK-USGS

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Ayuso, Robert; Foley, Nora; Wandless, Gregory; Dillingham, Jeremy; Colvin, Anna; 2005, Lead Isotopic Compositions of Soil and Near-surface Till Profiles from a Watershed Containing Arsenic-enriched Groundwater in Coastal Maine: Reston, Virginia.

**Library of Congress Cataloging-in-Publication Data**

Ayuso, Robert.

Title of book/ Author List

p. cm. --(U.S. Geological Survey Science Investigations Report 2005-5112)

Includes bibliographic references.

1. Subject heading. 2. Subject heading. 3. Subject heading. I. Main entries.

II. Main entries. III. Main entries.

TN24.M9 M55 2002

553'.09786'6—dc21

2001051109

## Contents

Abstract.....	1
Introduction.....	1
The Penobscot Formation.....	3
Bedrock in the Northport area .....	3
Previous work.....	3
Near-surface soil profiles in the Northport area .....	3
Analytical Techniques.....	4
Results .....	5
Lead isotope data.....	5
Major and trace element contents: Penobscot formation.....	11
Lead and arsenic contents: Soils and near-surface till profiles .....	12
Discussion.....	13
Conclusions.....	16
Acknowledgments .....	16
References.....	16

## Figures

1 Topographic map of study area .....	2
2 Plot showing acid-leach and residue fractions of soils and tills. ....	11
3 Summary plot showing all leach and residue data for soil and till profiles. ....	12
4 Plot showing isotopic compositions of soil and till profiles, and average isotopic composition of Penobscot Formation.....	13
5a Average compositions and ranges of total carbon, total sulfur, pH, lead, and arsenic for bulk fractions of the soil and till profiles, shown as a function of depth.....	14
5b Average compositions and ranges of lead and arsenic for leach fractions of soil and till profiles shown as a function of depth.....	14
6 Plot showing isotopic compositions of soil and till profiles, field of iron-hydroxides, average composition of galena and the field of most commonly used pesticides in New England. ....	16

## Tables

1 Range of lead isotope compositions and contents of lead and arsenic in soil profiles.....	5
2 Average and range in major- and trace-element compositions of Penobscot Formation. ....	6
3 Average and range of trace-element compositions of leach fractions and total carbon, total sulfur, and pH of bulk fractions of soil profiles. ....	7

# Lead Isotopic Compositions of Soil and Near-Surface Till Profiles from a Watershed Containing Arsenic-Enriched Groundwater in Coastal Maine

By Robert Ayuso, Nora Foley, Gregory Wandless, Jeremy Dillingham, and Anna Colvin

## Abstract

Lead isotope compositions of soils and near-surface tills from an area of coastal Maine known to have groundwater with anomalously high arsenic contents were measured in order to determine the source of the lead and, by inference, possible sources of arsenic. Five soil and till sites were selected for detailed chemical and isotopic analysis. To construct profiles of the soil and till horizons, five samples were collected at 10-cm intervals from the surface to the base of each horizon. Total lead and arsenic concentrations and lead isotopic compositions were measured for 48 leaches and bulk residues. The soils and tills are underlain by sulfidic schists of the Penobscot Formation. Several generations of minerals containing arsenic and lead exist in the regional bedrock, including rock-forming silicates (feldspar and micas), sulfide minerals formed during diagenesis (for example, arsenic-rich pyrite), and sulfide and oxide minerals that formed as a result of Silurian metamorphic and igneous events (for example, arsenopyrite, galena, iron-oxides, and arsenic-sulfides). A young group of secondary minerals (for example, iron-hydroxides, arsenic-hydroxides, lead-sulfate, and arsenic-jarosite) formed from recent weathering and pedogenic processes.

Acid-leach compositions of the soils and tills represent lead that is adsorbed to mineral surfaces or held in soluble minerals (iron- and manganese-hydroxides, carbonate, and some micaceous minerals), whereas residue compositions may reflect bedrock. Labile lead (acid-leach fractions) from the soils and tills shows a moderate range in values of  $^{206}\text{Pb}/^{207}\text{Pb} = 1.1870$  to  $1.2069$ ,  $^{208}\text{Pb}/^{207}\text{Pb} = 2.4519$  to  $2.4876$ , and  $^{206}\text{Pb}/^{204}\text{Pb} = 18.583$  to  $18.836$ ; values vary as a function of depth. Residues, which range in  $^{206}\text{Pb}/^{207}\text{Pb} = 1.2056$  to  $1.2328$ ,  $^{208}\text{Pb}/^{207}\text{Pb} = 2.4661$  to  $2.5000$ , and  $^{206}\text{Pb}/^{204}\text{Pb} = 18.831$  to  $19.303$ , are distinctly more radiogenic than the leach fractions. The profiles display an isotopic stratigraphy with no sharp isotopic discontinuities. Generally, the lowest  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios in the leach fractions are in the uppermost horizons (the surface soil layer) compared to horizons deeper in the profiles (50 cm). The highest  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios are in the surface soil layers. Average lead contents of the leach fractions decrease

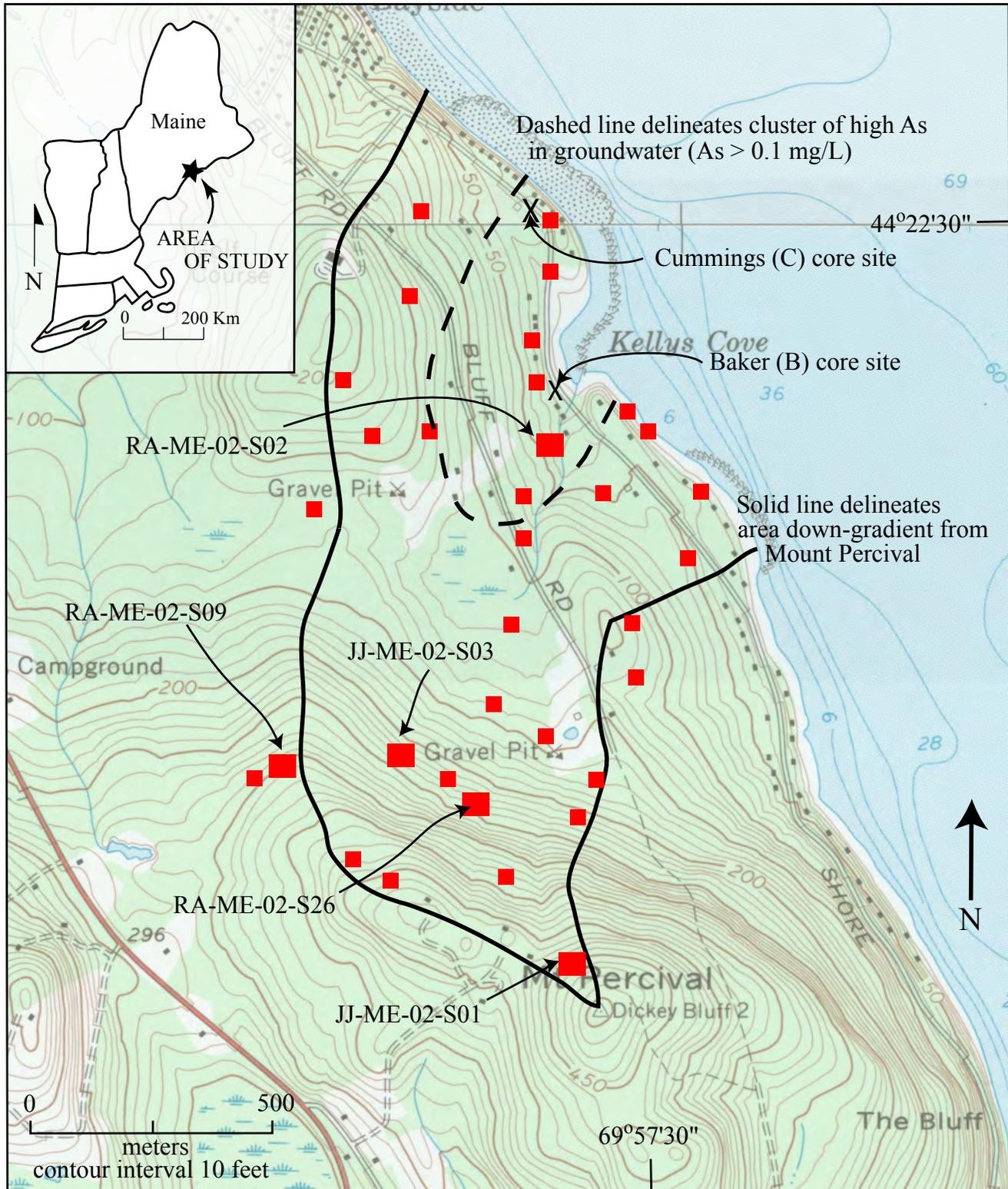
with depth (from 252 ppb in the surface soil layer to 17 ppb in the bottom interval). Average arsenic contents show no clear trend with depth (from 985 to 716 ppb). The profiles show that the average values of  $C_{\text{total}}$  (surface soil layer 6.17 wt percent, bottom of pit 1.73 wt percent) and pH vary as a function of depth (surface layer 4.55, bottom of pit 5.11). The values of  $S_{\text{total}}$  show no clear trend (surface soil layer 0.03, bottom of pit 0.02).

The range in lead isotope values in the soil and till profiles is generally consistent with multiple sources that include both natural and anthropogenic lead. The most likely geologic sources of lead (and, by inference, of arsenic) contributing to the surface soil layer and to most tills in the watershed are (1) the breakdown of arsenic-bearing sulfides in the Penobscot Formation during glaciation and (2) weathering. The lead isotope compositions of the profiles overlap values of U.S. aerosols (from burning of fossil fuels), and also values of pesticides used historically and extensively in New England. The leach fractions at the top of the profiles (horizons where organic matter is abundant) closely overlap lead isotope values for recent aerosols (1997-1999). A multicomponent mixing scheme that included lead from young aerosols (1997-1999) derived from combustion of fossil fuels, lead from the iron-hydroxides (reflecting an assortment of natural and anthropogenic sources), and lead from the local parent rock (Penobscot Formation) could account for lead isotope variations in the soil profiles. Our results show that, although a genetic bond likely exists between the soil and till profiles and the local country rocks, lead isotope variations and lead contents cannot be conclusively related to the arsenic contents. Solubility differences for lead and arsenic in the surface soil layers, together with the effects of elemental redistribution during weathering and soil formation may best explain decoupling of lead and arsenic.

## Introduction

The predominant source of lead and arsenic in soils and near-surface tills is often thought to be local rocks, although substantial input from non-local rocks and other metal sources

2 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine



**Figure 1.** Topographic map of study area showing locations of 34 sites selected for soil and till profiles and boreholes for water and core samples (C, Cummings site; B, Baker site). Large squares identify locations of five soil and till profile sites used for the lead isotope study; smaller squares are locations of other soil and till profiles used in the larger geochemical study (R. Ayuso, unpublished data, 2004). Dashed line encloses an area containing groundwater with high measured arsenic contents ( $As > 0.1 \text{ mg/L}$ ) (Lipfert and Reeve, 2004). Solid line encloses area of the watershed.

generated as a result of human-induced activities may also be present. Anthropogenic metal sources are related to industrial and urban activities (for example, burning of fossil fuels, mining and metal alloy industries, smelting, manufacturing, wood preservation, glass and ceramics industries, sewage, and so on), as well as agricultural activities (for example, pesticide and herbicide use). In areas containing groundwater with anomalously high arsenic concentrations, a critical step toward establishing the ultimate source of arsenic depends on properly evaluating the relative contributions from natural and anthropogenic sources.

Several areas in New England have groundwater wells supplied by bedrock aquifers that are anomalously rich in arsenic (Marvinney and others, 1994; Peters and others, 1999; Ayotte and others, 2003). This preliminary study is focused on a small watershed in the Northport area in coastal Maine (fig. 1). This watershed is the focus of extensive geological studies to determine the processes leading to arsenic mobilization and groundwater enrichment (Ayuso and Foley, 2002; Foley and others, 2004a). Detailed sampling of rocks, stream sediments, and areas containing abundant sulfide minerals have been used to establish the geochemical characteristics of the natural background (Ayuso and Foley, 2004). Samples were obtained from drill core to characterize the bedrock, as well as soils and near-surface tills (summary in this study; R. Ayuso, unpublished data, 2004) and to obtain information relating to groundwater chemistry (Lipfert and Reeve, 2004).

The objectives of this study are to examine the distributions of the isotopic compositions in the watershed, to determine whether the soil and near-surface till profiles in the Northport area (fig. 1) have distinct lead isotope signatures as a function of depth, and, most importantly, to test whether there is compelling genetic evidence establishing the source of lead and arsenic in soils and tills. Petrogenetic links between lead and arsenic in the soil and till profiles and in the Lower Ordovician Penobscot Formation (bedrock underlying the till in the area) or between the soils and tills and anthropogenic sources will help to identify the source of metals and metalloids in the near-surface environment. Assessing the influence of lead (and related elements) from outside sources depends on establishing analytically distinguishable lead isotope differences between the natural background materials (for example, bedrock, sulfide mines, and mineral occurrences) and other sources resulting from human activities (for example, gasoline and pesticide use). This report summarizes the geochemical features of leach fractions of soils and tills from different depth intervals at five sites as well as the average major- and trace-element compositions of the Penobscot Formation obtained from outcrop and drill core.

## The Penobscot Formation

### Bedrock in the Northport area

Rusty-weathering iron-sulfide-rich rocks of the Lower Ordovician Penobscot Formation constitute the regional bed-

rock in the Northport area (Stewart and Tucker, 1998). Pelitic beds (with sandy siltstone layers) are abundant in the upper part of the formation. Limestone and calcareous sandstone are rare. Diorite dikes and muscovite granite pods and dikes are found locally. Regional metamorphism of the Penobscot Formation produced coarse-grained andalusite in the pelitic beds (Stewart and Tucker, 1998). Ridges and higher elevations in the Northport area have outcrops of the Penobscot Formation covered by a layer of glacial sediments (till) that had been scavenged from the underlying rocks by the Late Wisconsinan Laurentide ice sheet (Hunter and Smith, 2001). In the coastal lowlands of eastern Maine, glaciomarine sediments were deposited as ice withdrew at about 14,000 and 12,200 yr B.P. (Dorion and others, 2001). The till deposits, which predominate in the watershed, characteristically lack bedding and consist of a jumbled assortment of clay, silt, sand, cobbles, and boulders.

### Previous work

A major conclusion of previous investigations by Ayuso and Foley (2002) and Foley and others (2004a) is that several generations of metal sulfides and secondary minerals containing arsenic and lead exist in the Penobscot Formation. In addition to the oldest generation of sulfide minerals (including arsenic-rich pyrite and pyrrhotite), which likely formed by diagenesis, there is a distinct sulfide and oxide mineral population (including galena, pyrite, arsenopyrite, iron-oxide minerals, and arsenic-sulfides) that formed as a result of Silurian metamorphic and igneous events affecting the Penobscot Formation (Foley and others, 2004a, b). Moreover, secondary oxide and sulfate minerals (for example, iron-hydroxides, anglesite, arsenic-hydroxides, and arsenic-jarosite) have also formed from recent weathering of the till and from pedogenic processes. We have suggested that low-temperature oxidation and decarbonation reactions involving the young group of arsenic-bearing minerals in contact with local groundwater are likely to account for the bulk of the arsenic contributed to the regional groundwater (Foley and others, 2004a).

### Near-surface soil profiles in the Northport area

The major protolith of the soils in this portion of Waldo County is glacial till, but marine and lacustrine sediments can also be locally important. The predominant soil type in the watershed belongs to the Peru-Marlow-Brayton association, which is found along the coast and consists of deep, nearly level to steep soils that range from well drained to poorly drained; the soils developed in predominantly moderately coarse-textured compact glacial till (Hedstrom and Popp, 1981). Another soil type in the watershed—one that is somewhat less extensively developed—belongs to the deep, nearly

#### 4 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine

level to steep soils of the Boothbay-Swanville-Lyman association (Hedstrom and Popp, 1981), generally found landward from the predominant Peru-Marlow-Brayton soil association. The Boothbay-Swanville-Lyman soil association differs from the Peru-Marlow-Brayton association mainly in that some of the soils are moderately well drained to poorly drained and that they formed in marine and lacustrine sediments. The Boothbay-Swanville-Lyman soil association also includes excessively drained soils in moderately coarse textured glacial till (Hedstrom and Popp, 1981). Thus, the dominant soils in the watershed developed on glacial till and were derived mostly from the gneiss and schist local bedrock, perhaps with contributions from nearby granitic rocks. Glaciofluvial sediments, organic material, and alluvium may also constitute significant components in the soils.

The profiles typically contained unstratified clay to boulder-sized constituents (generally up to about 10 cm and infrequently up to 20 cm). The soil, till, and other near-surface materials generally make up a relatively thin (< 1.5 m thick) layer that overlies bedrock. A predominantly local provenance for the glacial till in the watershed appears likely, on the basis of the types and amounts of pebbles and cobbles in the profiles. Organic-rich and irregularly bedded layers (decomposing forest litter: roots, leaves, twigs, and other organic debris) dominate the top of the profiles, extending generally to about 8 to 12 cm. Intensely weathered, saprolitized, and disaggregated, rusty-sulfidic schistose bedrock was encountered at many sites at the bottom of the profiles, starting at about 60 cm. The large pebbles and boulders in the intermediate depth intervals were predominantly rusty-sulfidic schist, in addition to minor granite, mafic rocks, and quartzite.

Abrupt color changes were occasionally found in the depth profiles, and color variations in the dominant soil association in the watershed generally are characterized by a surface layer of dark brown soils with fine sandy loam at the top (~10-15 cm thick), overlying a layer of gray to orange-brown fine sandy loam (~4-7 cm). Deeper in the profiles, the subsoils ranged from dark orange-brown silty to sandy loam to gray and green-brown pebbly to sandy loam (~25-35 cm). The profiles were usually dug shallower than about 1 m and ended below the subsoils in a dense layer (substratum) of disaggregated schist and gneiss fragments or intensely weathered bedrock. Locations dug at higher elevations (Mt. Percival area) (fig. 1) were characterized by abundant outcrop and consisted of soils and tills shallowly underlain by bedrock. In the predominant soils, permeability above the substratum and bedrock is moderate. In the spring, the water table is commonly perched above the substratum and bedrock (Hedstrom and Popp, 1981).

The profiles of the Northport area contain various silicate, carbonate, oxide, and rare sulfide minerals identified by petrography, X-ray diffraction, and electron microprobe analysis. The tills also have abundant organic constituents at the top of the profiles. The soils display several horizons that characteristically reflect the general incorporation of organic material and the effects of weathering. Leaching of the topmost layer,

breakdown of organic material, and removal of soluble ions enhance the acidity of the soils and result in the dissolution of oxides, reduction of iron, and formation of soluble metal-organic complexes (Hedstrom and Popp, 1981). The metal complexes migrate lower in the profile, and many precipitate as a result of chemical and biological reactions as hydroxides of iron, aluminum, and manganese. The silicate mineralogy is dominated by quartz, feldspar, and mica, including sericite and chlorite, all of which are distributed throughout the depth profiles. Our studies suggest that iron-hydroxides are the predominant secondary minerals in the profiles and underlying bedrock (Ayuso and Foley, 2002; Foley and others, 2004a, b; N. Foley, unpublished data, 2005). The tills contain goethite, lepidocrocite, and a variety of iron-manganese-hydroxide minerals. In general, the iron and manganese-iron oxyhydroxide minerals occur throughout the till profiles, although they are most abundant in the upper depth intervals, particularly below the organic layer. Rare sulfide minerals in some near-surface tills include pyrrhotite, greigite, sphalerite, galena, djurite, and arsenopyrite. Carbonate (calcite, manganian siderite) and iron-bearing phosphate minerals also were identified in some of the depth intervals.

### Analytical Techniques

Profiles were obtained at five sites and represent a subset of 34 sites (fig. 1) that have been investigated for a geochemical study in progress. Pits approximately 30 to 40 cm in diameter were hand dug in the midsummer to expose profiles from the ground (free of forest litter) to at least 60 cm. Five or six samples (about 150-500 g) were obtained approximately 10 cm apart in order to select representatives of the morphological variations in the soils and tills. For example, the samples from the tops of the profiles are from the uppermost surface layers of the soils, as characterized by color (for example, most are dark brown), particle size, and morphology (silt or sandy loam). Most soils in the area exhibited contrasting color and compositional features distinguishing the soils, subsoils, and lower horizons. The surface layer was clearly evident in the watershed (mostly representative of the A1 horizon, and in some cases the Ap soil horizon) (Hedstrom and Popp, 1981). This topmost layer, which is at or near the surface, consists of humified organic matter and minerals and may include a plowed surface horizon that was part of the underlying mineral horizon (B). Often, bedrock was encountered at depths of less than 60 cm. The samples were air dried and prepared using 50 to 100 mg of the <0.2-mm-sized fraction following established techniques for lead isotope analysis at the U.S. Geological Survey, Reston (Ayuso and others, 2004b).

Analysis of the secondary minerals in soils and tills provides a means to establish the composition of labile lead and a way to distinguish labile lead from lead inherited from the parent rocks and the original rock-forming minerals (silicates, oxides, sulfides). Although hot and prolonged leaching of min-

erals using acid mixtures (HCl and HNO<sub>3</sub>) is a standard dissolution procedure for secondary minerals (Tessier and others, 1979), such leaching also attacks the original rock-forming minerals, especially sulfide constituents. The resulting acid solution mixes lead from secondary minerals and from original minerals. Thus, the standard leach method was unsuitable for our study. In order to attack only the secondary minerals, we devised a cool and mild acid leach (1.5N HCl+3N HNO<sub>3</sub>). This solution was passed through lead columns by means of established elution protocols (Ayuso and others, 2004b). The acid leach aliquots represent anthropogenic and labile lead (Erel and others, 1997) trapped in the iron-hydroxide, carbonate, or organic materials or lead from other secondary minerals and organic material likely available for rock/fluid reactions (such as clay minerals). These minerals are the constituents that may have been important metal point sources to groundwater. They can also contain lead and arsenic (and other metals) derived from outside of the watershed.

Mixed solutions of HF-HNO<sub>3</sub> were used for final dissolution of the residual fractions. All isotopic compositions were measured by using a Finnigan-MAT 262 thermal ionization mass spectrometer (TIMS). Mass fractionation was monitored by frequent analysis of the NIST-SRM 981 standard. Lead blanks during the course of the study were less than 50 nanograms and thus are not significant compared to the lead abundances in the samples. A mass fractionation correction per amu of about 0.1 percent was applied to all samples. Maximum analytical uncertainties for  $\pm 2$  standard error of the mean are as follows:  $^{206}\text{Pb}/^{204}\text{Pb} < 0.002$ ,  $^{206}\text{Pb}/^{207}\text{Pb} < 0.00003$ , and for  $^{208}\text{Pb}/^{207}\text{Pb} < 0.00004$ . Table 1 summarizes the lead isotope data.

Major- and trace-element compositions and mineralogy of the Penobscot Formation and material from the near-surface till depth intervals in the watershed were obtained by various analytical techniques including XRD, XRF, ICP-MS, and INAA. Table 2 summarizes the major- and trace-element data for samples from outcrops and rocks obtained from drill core. Table 3 is a summary of the trace-element data for the leach aliquots obtained on the soils and tills used in the lead isotope study.

## Results

### Lead isotope data

A summary of lead isotope compositions of a total of 48 leach and residues from five soil and subsoil (mostly till and, in some cases, marine and lacustrine sediments) profiles is given in table 1 and figures 2 and 3. Fields showing the isotopic compositions of galena from sulfide mines and bedrock (Penobscot Formation) (fig. 4), lead and arsenic contents (fig. 5), and the isotopic compositions of secondary mineral alteration products (predominantly iron-hydroxides) are also shown for comparison (fig. 6) (Ayuso and Foley, 2002, 2004; Foley and others, 2004a, b). The minerals and rocks represent lead that would be available to the groundwater directly from the sulfide-rich Penobscot Formation bedrock and from galena associated with sulfide-mineralized mines and occurrences.

**Table 1.** Range of lead isotope compositions and contents of lead and arsenic in the soil profiles, Northport area, coastal Maine

Depth Profile Leach	Average (range) content (in ppb)		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
	Pb	As			
0-10 cm horizon	296 (86.5-606)	1221 (70.5-3960)	18.601-18.751	1.19046-1.20111	2.45188-2.46186
10-20 cm horizon	42.3 (20.4-29.8)	638 (17.6-2030)	18.603-18.774	1.19351-1.20252	2.46314-2.47236
20-30 cm horizon	26.4 (11.9-47.4)	874 (47.1-2150)	18.583-18.836	1.18703-1.20355	2.47327-2.48761
30-40 cm horizon	29.1 (9.6-65.9)	843 (34.1-1860)	18.731-18.822	1.19147-1.20685	2.46895-2.47630
40-50 cm horizon	16.9 (12.2-19.7)	716 (48.9-1780)	18.733-18.810	1.19128-1.23280	2.46994-2.49296
Depth Profile Residue (bulk)	Average (range) content (in ppm)		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
	Pb	As			
0-10 cm horizon	35.9 (23.7-59.6)	176 (37.9-517)	18.831-18.976	1.20560-1.21375	2.46654-2.48104
10-20 cm horizon	18.7 (15.0-22.1)	172 (13.0-606)	18.925-19.303	1.21182-1.23280	2.47863-2.49296
20-30 cm horizon	21.8 (16.6-24.3)	221 (62.0-657)	18.893-19.267	1.21042-1.23151	2.48156-2.50001
30-40 cm horizon	21.9 (20.5-23.2)	203 (55.0-616)	18.937-19.041	1.21163-1.21884	2.48024-2.49473
40-50 cm horizon	18.9 (8.9-28.0)	225 (59.0-640)	18.905-19.026	1.20992-1.21774	2.48008-2.49028

## 6 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine

**Table 2.** Average and range in major- and trace-element compositions of the Penobscot Formation, Northport area, Maine

[nd, not determined]

	Outcrops (in wt percent)			Core samples (in wt percent)		
	Average (n=9)	Minimum	Maximum	Average (n=19)	Minimum	Maximum
SiO <sub>2</sub>	61.25	46.94	75.75	61.53	45.55	83.91
Al <sub>2</sub> O <sub>3</sub>	19.90	13.47	28.69	18.49	7.16	27.57
Fe <sub>2</sub> O <sub>3</sub>	5.55	1.08	8.26	6.95	2.63	9.73
MnO	0.06	0.01	0.12	0.07	0.03	0.27
MgO	1.37	0.06	2.31	2.17	0.66	6.92
CaO	0.73	0.02	3.78	0.89	0.1	6.98
Na <sub>2</sub> O	1.97	0.43	4.59	1.32	0.34	3.82
K <sub>2</sub> O	4.28	0.99	7.36	3.37	0.3	6.93
TiO <sub>2</sub>	0.90	0.03	1.63	0.93	0.48	1.42
P <sub>2</sub> O <sub>5</sub>	0.09	0.06	0.16	0.11	0.04	0.20
LOI	3.53	0.64	5.82	3.57	1.34	5.81
As <sup>1</sup>	28.3	7.7	65.0	82.6	0.7	730
Pb	28.8	9.7	52.7	17.2	7.5	42
Ba	850	52	1620	696	106	1330
Rb	166	56	288	177	41	320
Sr	141	26	294	144	67	449
Y	25	2	43	40	26	60
Cs	10	1	16	28	5	98
La	29.45	4.35	44.22	62	26	138
Ce	59.75	9.78	90.27	132.68	58.69	312.43
Pr	6.40	1.03	9.90	14.19	5.84	33.58
Nd	24.75	3.42	38.48	50.89	20.71	121.31
Sm	5.03	0.66	8.21	9.64	4.05	22.38
Eu	1.40	0.14	2.54	2.19	1.03	5.25
Gd	4.64	0.54	7.82	2.19	1.03	5.25
Tb	0.79	0.09	1.31	1.21	0.74	2.26
Dy	4.52	0.48	7.25	6.65	4.33	11.13
Ho	0.95	0.09	1.49	1.30	0.83	1.90
Er	3.02	0.26	4.61	3.60	2.25	5.16
Tm	0.47	0.04	0.70	0.53	0.32	0.80
Yb	2.94	0.27	4.38	3.39	2.05	5.04
Lu	0.46	0.04	0.68	0.50	0.29	0.72
Zr	153.1	30.3	279.2	206.7	95.7	276.5
Hf	4.7	1.3	8.3	5.32	2.53	7.23
Nb	17.3	5.6	24.9	17.1	8.1	25.5
Ta	1.4	0.1	2.3	1.3	0.3	2.6
Th	10.4	0.6	18.6	15.2	6.3	21.35
U	3.9	0.9	6.1	4.8	1.7	11.3
Be	3.4	2.0	5.0	nd	nd	nd
Sb	0.4	0.2	0.6	0.5	0.1	1.3

**Table 2.** Average and range in major- and trace-element compositions of the Penobscot Formation, Northport area, Maine—Continued

{nd, not determined}

	Outcrops (in wt percent)			Core samples (in wt percent)		
	Average (n=9)	Minimum	Maximum	Average (n=19)	Minimum	Maximum
Hg	9.3	5.0	14.3	nd	nd	nd
Bi	0.3	0.1	0.8	0.4	0.1	1.1
Se	0.6	0.1	1.2	0.7	0.2	3
Tl	1.5	0.6	2.9	1.3	0.2	2.7

	Outcrops (in ppm)			Core samples (in ppm)		
	Average (n=9)	Minimum	Maximum	Average (n=19)	Minimum	Maximum
Sc	18.3	0.7	32.2	18.9	7.6	32.7
V	178.8	15.9	516.6	115.0	30.2	212.8
Ni	39.9	26.7	63.8	576.1	24.7	4220
Co	8.8	2.0	31.0	24.9	8.0	54.0
Cr	98.8	27.0	179.0	2404	83.0	20800
Ga	26.9	17.4	40.4	25	8.2	40.1
Ge	2.3	1.2	3.1	1.9	0.9	3.1
Cu	29.9	17.7	55.4	30.8	10.6	70.9
Zn	105.5	66.9	127.9	119.8	36.0	198.2
Mo	5.4	2.9	12.3	5.8	2.6	14.3
Sn	3.6	2.3	4.8	8.7	1.9	67.1
W	1.6	0.7	3.5	4.5	0.7	20.7
Au <sup>2</sup>	2.7	0.8	10.0	0.6	0.2	1.4
Ag	2.5	0.2	8.8	nd	nd	nd
Hg <sup>2</sup>	9.3	5.0	14.3	nd	nd	nd

<sup>1</sup> Arsenic content in sulfide-rich band; maximum content away from sulfide-rich bands is 120 ppm.<sup>2</sup> Gold and mercury content in ppb.**Table 3.** Average and range of trace-element compositions of the leach fractions and C<sub>total</sub>, S, and pH of the bulk fractions of the soil profiles

[bdl, below detection limit]

Leach	0-10 cm (in ppb)			10-20 cm (in ppb)			20-30 cm (in ppb)		
	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum
As	985	40.3	3960	639	17.6	2030	702	14.2	2150
Pb	252	76.0	606	42.3	20.4	112	25.9	11.9	47.4
Ba	779	229	1970	2504	255	7430	2737	512	7700
Rb	174	28.1	676	229	25.0	499	200	52.8	343
Sr	949	58.7	4150	733	55	3750	643	107	3140
Y	120	36.4	295	91.2	18.7	511	126	35.1	613
Cs	3.05	0.16	26.70	4.80	0.34	29.00	8.20	0.90	59.90
La	72.0	36.9	123.0	49.6	15.7	129.0	59.1	28.3	134.5
Ce	120.9	76.1	211.0	108.8	31.1	348.0	118.2	44.2	438.5
Pr	22.1	8.8	41.2	16.9	4.1	72.8	23.6	7.9	85.6
Nd	96.0	35.6	205.0	78.5	16.9	429.0	116.2	32.8	515.5

## 8 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine

**Table 3.** Average and range of trace-element compositions of the leach fractions and  $C_{total}$ , S, and pH of the bulk fractions of the soil profiles [bdl, below detection limit]—Continued

Leach	0-10 cm (in ppb)			10-20 cm (in ppb)			20-30 cm (in ppb)		
	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum
Sm	25.1	7.7	62.7	20.9	4.0	140.0	31.5	7.8	158.5
Eu	6.2	2.2	15.8	5.5	1.5	35.3	7.9	2.5	39.2
Gd	22.8	6.9	58.8	19.2	3.7	134.0	29.2	7.1	154.0
Tb	4.5	1.3	11.3	3.6	0.7	25.6	5.4	1.3	28.9
Dy	23.9	7.5	61.1	20.0	4.2	137.0	28.9	7.3	152.0
Ho	4.5	1.2	11.4	3.9	0.8	25.0	5.5	1.5	28.7
Er	11.7	3.7	29.0	10.6	2.3	60.6	14.8	4.1	70.4
Tm	1.6	0.5	4.1	1.4	0.3	6.2	1.9	0.6	7.5
Yb	9.6	3.0	25.5	9.1	1.9	34.8	12.3	3.5	50.6
Lu	1.5	0.4	3.8	1.3	0.3	4.9	1.7	0.5	7.5
Zr	98.7	20.8	268	124	23.9	879	158	34.9	1060
Hf	3.0	0.8	7.9	3.7	1.0	24.7	4.7	1.1	31.9
Nb	15.6	5.1	40.8	7.3	2.9	17.5	6.3	2.9	17.4
Ta	2.8	0.7	15.1	0.4	0.1	0.9	0.3	0.1	1.1
Th	58.4	18.6	115.0	51.6	11.4	181.0	50.0	13.3	167.5
U	7.1	2.7	28.8	16.8	4.1	114.0	17.2	7.2	46.1
Be	12.0	4.6	27.2	17.4	3.4	39.7	22.7	2.9	49.9
Sb	10.3	3.3	20.8	7.0	1.5	15.5	5.3	1.5	16.0
Hg	bdl	bdl	bdl	1.2	1.2	1.2	1.1	1.1	1.1
Bi	bdl	bdl	bdl	bdl	bdl	bdl	0.8	0.1	1.3
Se	42.2	29.9	68.9	65.4	30.9	166.0	29.0	11.0	59.8
Tl	1.6	0.2	6.4	2.2	0.4	5.2	2.0	0.3	4.4
Cd	18.9	7.4	28.2	17.6	6.9	34.3	16.4	5.1	32.8
Sc	bdl	bdl	bdl	bdl	bdl	bdl	138.5	138.5	138.5
V	307.9	150.0	826.0	294.4	87.1	631.0	270.2	102.0	751.0
Ni	261.3	117.0	564.0	235.8	137.0	497.0	63.6	13.0	162.5
Co	463.4	28.7	2230.0	632.1	53.8	2370.0	1031.0	67.5	3500.0
Cr	130.9	53.0	285.0	167.3	59.1	428.0	151.2	82.0	284.0
Ga	18.0	5.7	63.8	12.4	4.0	35.0	10.4	4.1	24.2
Ge	1.4	0.5	2.2	1.7	0.7	4.3	1.2	0.5	3.8
Cu	24.5	5.8	153	17.1	5.23	89.7	24.2	3.49	69.9
Zn	934	233	1780	832	67	2350	865	68.2	1950
Mo	10.0	1.23	34.6	6.4	1.06	33.7	4.16	1.01	16.9
Sn	4.88	1.08	18.4	3.36	1.17	10.7	2.66	2.66	2.66
W	10.4	1.5	63.4	11.1	1.19	79	12.38	1.225	77.3
Br	2143	662	4140	2586	542	5020	2464	446	4430
I	2215	581	3920	4864	665	11800	5971	525	17900

**Table 3.** Average and range of trace-element compositions of the leach fractions and C<sub>total</sub>, S, and pH of the bulk fractions of the soil profiles [bdl, below detection limit]—Continued

Bulk	0-10 cm (in wt percent)			10-20cm (in wt percent)			20-30 cm (in wt percent)		
	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum
C <sub>total</sub>	6.17	2.85	7.25(16.45)	4.18	1.78	8.15	3.13	0.47	6.85
S	0.03			0.03			0.02		
pH	4.55	3.09	5.88	4.69	3.88	5.96	4.86	4.28	5.83
Leach	30-40 cm (in ppb)			40-50 cm (in ppb)					
	Average	Minimum	Maximum	Average	Minimum	Maximum			
As	678	16.0	1860	577	17.8	1780			
Pb	27.7	9.6	65.9	19.0	12.2	27.5			
Ba	2401	532	5530	2115	297	5210			
Rb	200	45.9	361	256	46.2	410			
Sr	717	82	3380	1225	92	4220			
Y	132	25.5	575	174	31.7	733			
Cs	8.66	1.16	59.25	6.65	1.21	26.30			
La	70.3	26.7	148.5	83.0	31.2	150.0			
Ce	111.1	37.8	299.0	174.8	67.6	540.0			
Pr	25.1	7.0	69.9	33.0	10.8	86.6			
Nd	113.8	28.9	412.0	148.7	36.1	437.0			
Sm	30.4	6.4	146.5	38.2	8.0	126.0			
Eu	7.6	1.9	36.2	8.9	2.0	29.1			
Gd	28.4	5.9	143.0	36.9	7.6	131.0			
Tb	5.5	1.1	29.1	6.4	1.3	22.7			
Dy	30.1	6.2	161.5	35.1	7.3	127.0			
Ho	5.8	1.0	30.7	6.8	1.1	25.1			
Er	16.2	2.8	84.0	18.9	3.2	69.7			
Tm	2.2	0.4	11.3	2.6	0.5	9.3			
Yb	15.1	2.5	76.9	16.7	3.1	59.8			
Lu	2.2	0.3	11.7	2.5	0.4	9.5			
Zr	166	33.1	1150	251	34.2	1090			
Hf	4.9	1.1	33.1	7.7	1.3	32.0			
Nb	6.3	2.7	14.0	7.2	3.1	11.4			
Ta	0.3	0.1	0.9	0.4	0.2	0.8			
Th	42.6	13.3	83.4	49.2	19.4	168.0			
U	21.5	7.2	44.4	25.1	10.0	62.3			
Be	23.1	3.4	40.8	20.5	2.4	38.4			
Sb	5.4	1.5	19.7	6.3	1.6	26.0			
Hg	bdl	bdl	bdl	bdl	bdl	bdl			
Bi	0.8	0.0	1.4	0.9	0.9	1.0			
Se	24.0	11.9	43.6	17.0	6.3	37.5			

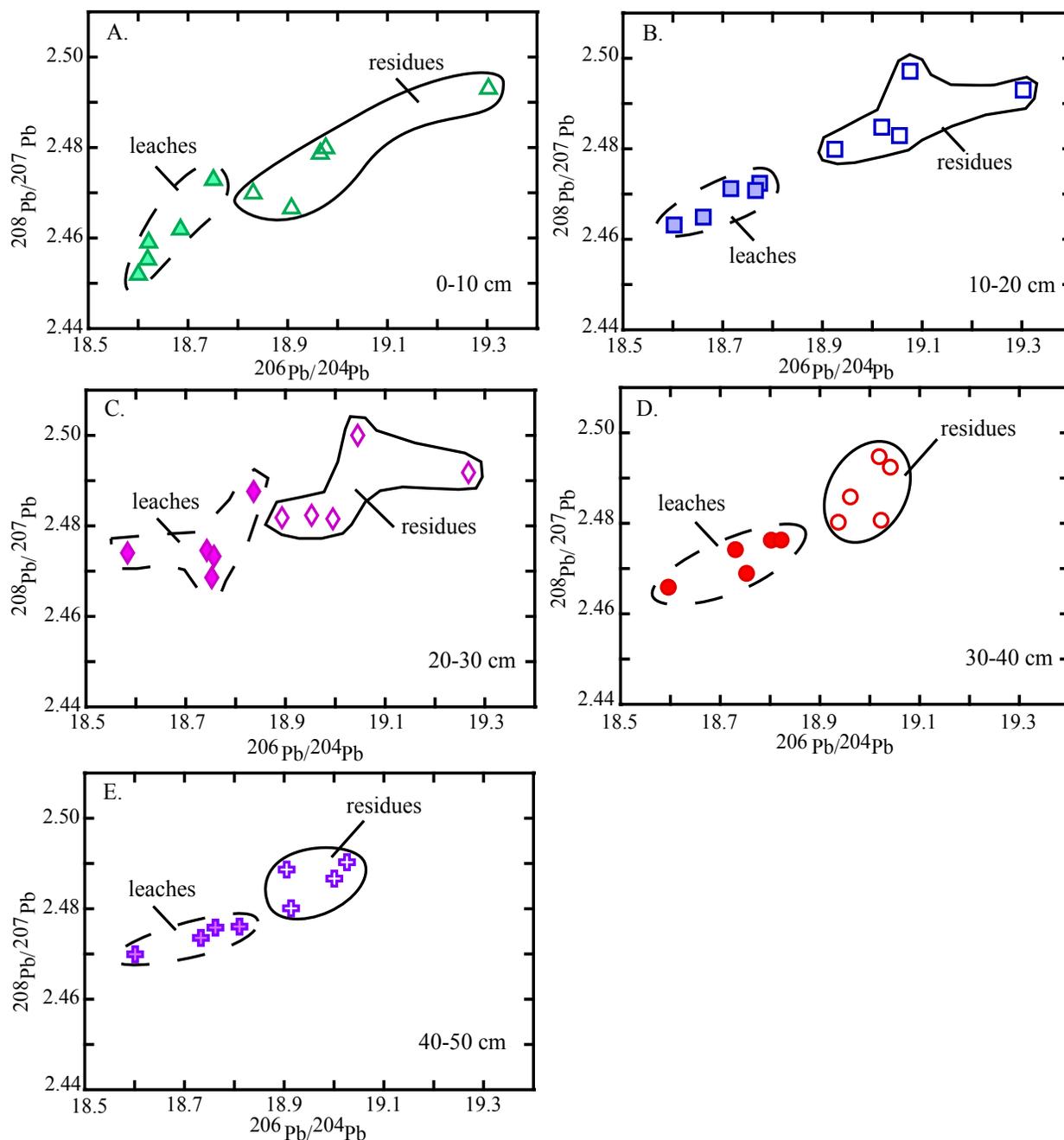
## 10 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine

**Table 3.** Average and range of trace-element compositions of the leach fractions and  $C_{total}$ , S, and pH of the bulk fractions of the soil profiles [bdl, below detection limit]—Continued

Leach	30-40 cm (in ppb)			40-50 cm (in ppb)		
	Average	Minimum	Maximum	Average	Minimum	Maximum
Tl	2.2	0.2	5.3	2.0	0.3	8.0
Cd	16.3	3.0	32.5	13.5	3.7	28.5
Sc	118.8	117.5	120.0	132.0	109.0	172.0
V	256.2	77.0	830.5	243.9	108.0	590.0
Ni	79.5	6.5	329.5	325.5	129.0	1460.0
Co	1337.8	66.4	3230.0	1354.9	74.7	4830.0
Cr	134.7	68.9	240.5	88.2	46.5	154.0
Ga	13.0	4.5	30.2	11.4	6.3	20.0
Ge	1.1	0.0	1.8	1.6	0.8	2.4
Cu	16.1	0.08	56.7	13.2	3.44	31.7
Zn	734	34.7	1900	644	169	1670
Mo	4.17	1.36	11.4	4.75	1.07	12.4
Sn	2.98	2.98	2.98	1.54	0.932	3.48
W	9.3	1.23	61.8	5.4	1.2	45
Br	2478	311	5220	1876	219	4080
I	6472	826	17900	3186	383	5930
Bulk	30-40 cm (in wt percent)			40-50 cm (in wt percent)		
	Average	Minimum	Maximum	Average	Minimum	Maximum
$C_{total}$	2.44	0.39	5.95	1.73	0.94	4.9
S	0.02			0.02		
pH	4.95	4.27	6.00	5.12	4.40	6.27

Labile lead obtained from the leach fractions shows a moderate range in values of  $^{208}\text{Pb}/^{207}\text{Pb} = 2.4519$  to  $2.4876$  and  $^{206}\text{Pb}/^{204}\text{Pb} = 18.583$  to  $18.836$  (figs. 2, 3) and  $^{206}\text{Pb}/^{207}\text{Pb} = 1.1870$  to  $1.2069$  (fig. 4). In every site, the leach fractions are lowest for  $^{208}\text{Pb}/^{207}\text{Pb}$  in the uppermost soils (surface layers within 10 cm from the surface), in contrast to the values obtained deeper in the profiles (up to about 50 cm from the surface). Considering all of the sites in the Northport watershed, as a group the leach fractions of the surface layers of the soils have the least radiogenic values, and in general, the profiles display an isotopic stratigraphy (fig. 3). Ratios of  $^{206}\text{Pb}/^{207}\text{Pb}$  are also higher in the uppermost soil horizons (table 1). Moreover, samples from approximately equivalent horizons and representing the different sites in the watershed have a narrow range in isotope compositions (figs. 2, 3). For example, the uppermost soil surface layers have a limited range in values of  $^{206}\text{Pb}/^{204}\text{Pb} = 18.619$ - $18.751$  (~ 0.7 percent), except for the middle depth interval (representative of 20-30 cm), where the values of  $^{206}\text{Pb}/^{204}\text{Pb}$  range from  $18.583$  to  $18.836$  (~ 1.3 percent). In this portion of the profiles (20-30 cm), soil and glacial processes controlling the dis-

solution and re-precipitation of the secondary minerals did not homogenize the labile lead isotope compositions (see similar results obtained on temperate forest near-surface tills by Emmanuel and Erel, 2002). Compositions of the residues range in  $^{206}\text{Pb}/^{207}\text{Pb} = 1.2056$  to  $1.2328$ ,  $^{208}\text{Pb}/^{207}\text{Pb} = 2.4661$  to  $2.5000$ , and  $^{206}\text{Pb}/^{204}\text{Pb} = 18.831$  to  $19.303$  and are distinctly more radiogenic than the leach fractions (table 1, fig. 2). Notably, the leach and the residue fractions are not aligned along a tight systematic trend but scatter about a broad band. The residue fractions have isotope compositions that overlap the Penobscot Formation (fig. 4). Sulfide minerals (galena) from massive sulfide deposits in coastal Maine and from other regional mineral occurrences are distinct from the iron-hydroxides in the Penobscot Formation, being much lower in  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  (fig. 6). The mineral deposits do not appear to have been involved as direct sources of the lead in the till from the Northport area, although the relatively unradiogenic nature of compositions of the leach fractions (fig. 6) may be attributed to lead redistribution emanating from mineral deposits and occurrences in the area (Foley and others, 2004b).

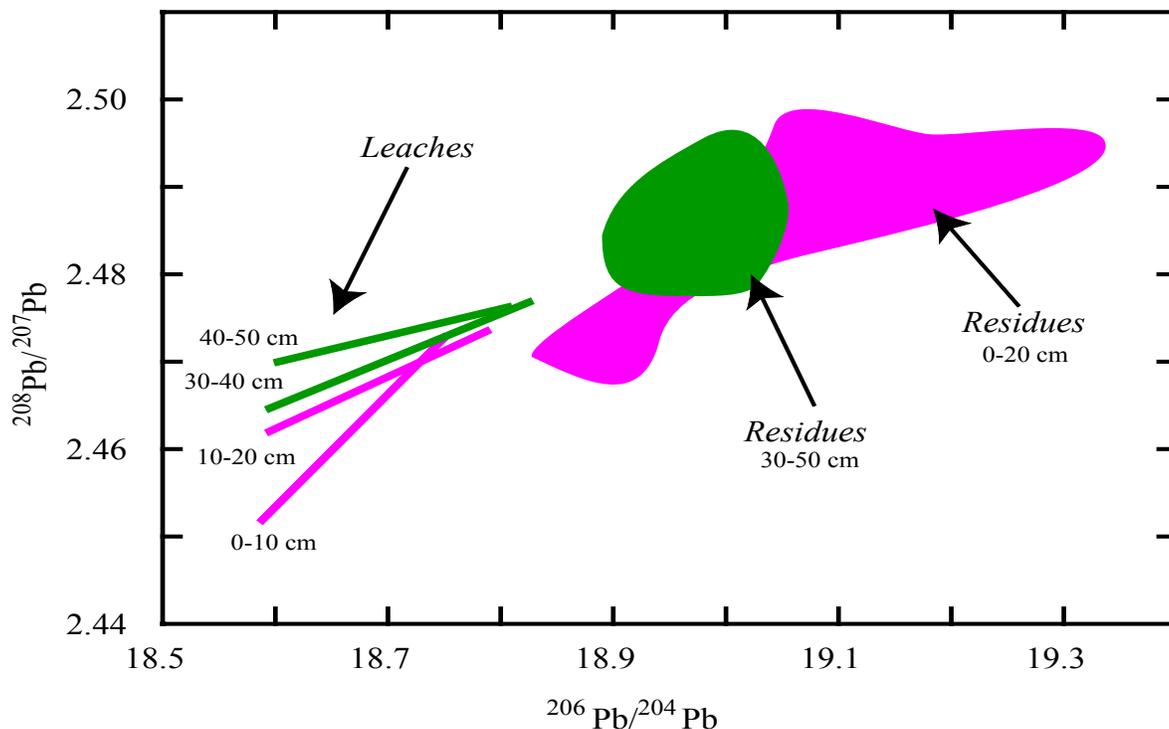


**Figure 2.**  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  plot showing the acid-leach (solid symbols) and the residue (open symbols) fractions of the soils and tills at successive depth intervals. (A) 0-10 cm. (B) 10-20 cm. (C) 20-30 cm. (D) 30-40 cm. (E) 40-50 cm. Note that data for near-surface till profiles at 20 to 30 cm show more scatter than other depth intervals. Analytical error is less than symbol size

## Major and trace element contents: Penobscot Formation

The major- and trace-element variations of the sulfidic Penobscot Formation are consistent with its overall diversity, which ranges from pelite dominated to sandy silts containing wide variations in contents of sulfide mineral and which includes andesitic to dioritic dikes and felsic granitic pods

and dikes (table 2). Calcareous rocks are not abundant in the Penobscot Formation but are locally distributed. A wide range in the contents of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$ , for example, can be attributed to the various relative proportions of iron-rich sulfides, pelitic rocks, and calcareous rocks. Outcrop and drill core samples of the Penobscot Formation have equivalent contents and ranges of the major and trace elements in general but can exhibit significant contrast in their arsenic content (table 2). Drill core whole-rock samples are somewhat depleted in



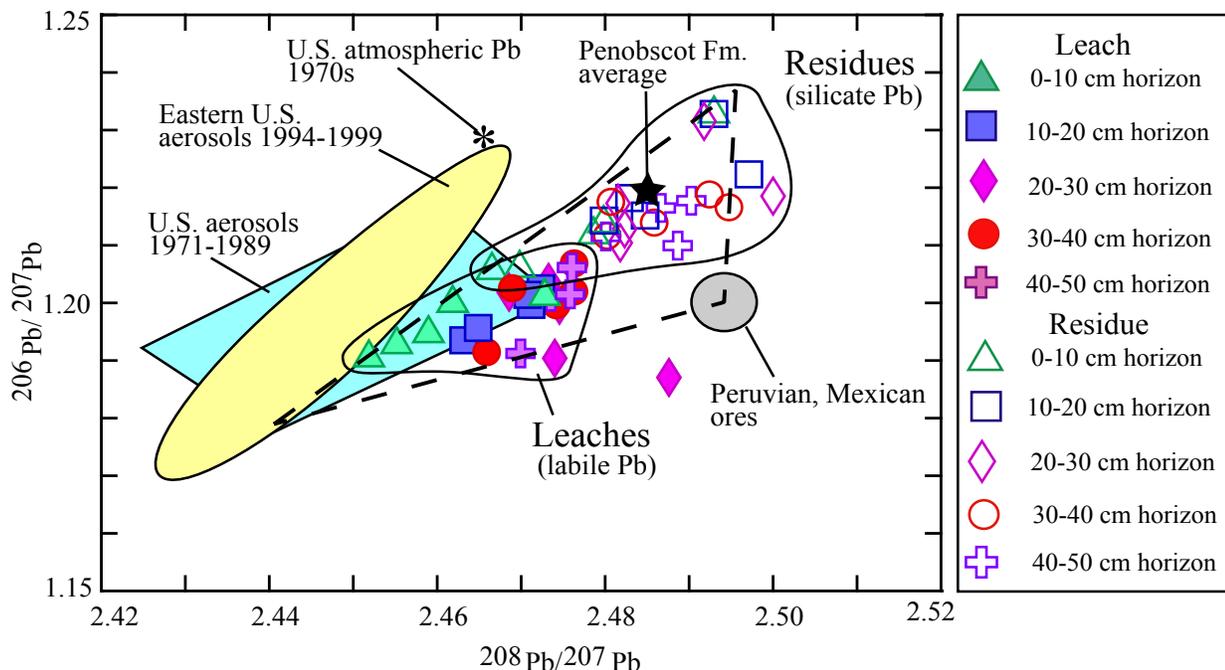
**Figure 3.**  $^{208}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  summary plot showing all leach and residue data for the soil and till profiles. Generalized trends of leach fractions for each depth from the five sites are plotted from the surface (0-10 cm) to the bottom of the profile (40-50 cm). (The 20- to 30-cm interval is omitted because the data show significant scatter.) The leach fractions, which correspond to labile lead, are represented by lines of decreasing slope as a function of depth. The residue fractions, which represent silicate lead, are grouped into shallow (0-20 cm) and deep (30-50 cm) sets. The data show that the residues deeper than 30 cm are more homogeneous than the residues higher in the profile.

lead (average  $\sim 17$  ppm) and enriched in arsenic (average = 83 ppm; up to 730 ppm in a sulfide mineral rich layer), compared to the outcrop samples (average lead  $\sim 29$  ppm; average arsenic  $\sim 28$  ppm) (table 2).

### Lead and arsenic contents: Soils and near-surface till profiles

Baseline concentrations of arsenic in U.S. near-surface till are  $\sim 7.4$  mg kg $^{-1}$  (Shacklette and others, 1971). Locally, arsenic concentrations can vary widely because of the content of sulfide minerals (for example, sulfide-rich shales, sulfide-rich hydrothermal veins, and so on) and redox conditions. Pyrite oxidation in black-shale parent rock results in acid-sulfate soils, for example, that can be enriched in arsenic (Smedley and Kinniburgh, 2002). In the Northport area, the average contents of the bulk fractions of the soils and tills used in this study show a wide range of lead and arsenic contents (fig. 5, table 1) and closely parallel the variations found for data representing all of the sites in the Northport area (R. Ayuso, unpublished data, 2004). In the bulk fractions of the profiles, the content of lead is highest in the surface layer (average  $\sim 34$  ppm). The content of arsenic shows no systematic trend with depth in the soil profiles ( $\sim 144$  ppm at the top;  $\sim 225$  ppm at

the bottom). High contents of arsenic in all the depth intervals of sample RA-ME-02-S26 account for the wide range and overall enrichment of arsenic in the average compositions of the sites used for the isotope study. As a group, the sites used for the isotope study (tables 1, 3), compared to all of the sites in the geochemical study of the Northport watershed, appear to contain about twice as much arsenic (average arsenic 62 ppm at 0-10 cm, 73 ppm at 40-50 cm) (R. Ayuso, unpublished data, 2004). Variations in the contents of lead and arsenic in the leach fractions of the depth intervals (fig. 5) also closely parallel the variations found when the data for all of the sites in the Northport area are considered. Again, sample RA-ME-02-S26 accounts for the highest contents of lead in the leach fractions (tables 1, 3). Lead contents decrease with depth (from an average of 252 ppb in the surface soil to an average of 19 ppb in the bottom horizon). Average arsenic contents, however, show no clear trend with depth (an average of 985 ppb in the uppermost soil surface layer and 577 ppb in the bottom horizon). The leach fractions are also most variable for lead and arsenic in the soil surface layer (lead  $\sim 76$  ppb to  $\sim 606$  ppb; arsenic  $\sim 40$  ppb to  $\sim 3900$  ppb). Other elemental contents, which are the subject of a detailed study in preparation, vary as a function of depth: for example, Cd, Zn, and V contents decrease from the top to the bottom of the profiles, and Zr, Hf, U, and Co increase (table 3). The average contents of  $C_{\text{total}}$



**Figure 4.**  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  plot showing the isotopic compositions of the soil and till profiles and the average isotopic composition of the Penobscot Formation (representing bedrock in the area and the likely parent rock of the till). Compositions of U.S. aerosols evolved from  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.15$  in the mid-1960s (dominated by Mississippi Valley type lead from United States and lead imports from Mexico (Mississippi Valley type lead data from Doe and Delevaux, 1972) to  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.23$  in the 1970s and early 1980s (as a result of predominant use of Mississippi Valley-type lead) and then decreased to  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.20$  in the early 1990s (Rosman and others, 1994; Erel and others, 1997; Bollhöfer and Rosman, 2001). Also shown for reference: the range of U.S. aerosols for 1971-1989, eastern U.S. aerosols 1997-1999 (Rosman and others, 1994; Erel and others, 1997; Bollhöfer and Rosman, 2000; 2001), U.S. atmospheric lead in the 1970s (Chow and others, 1975), and lead ore from Mexico and Peru (Chow and others, 1975). See text for additional explanation and references.

(surface soil 6.17 wt percent, bottom horizon 1.73 wt percent) and pH (surface soil 4.55, bottom horizon 5.11) show consistent differences as a function of depth (table 3). The values for S, however, show no clear trend along the profiles (surface soil 0.03 percent, bottom horizon 0.02 percent) (table 3).

## Discussion

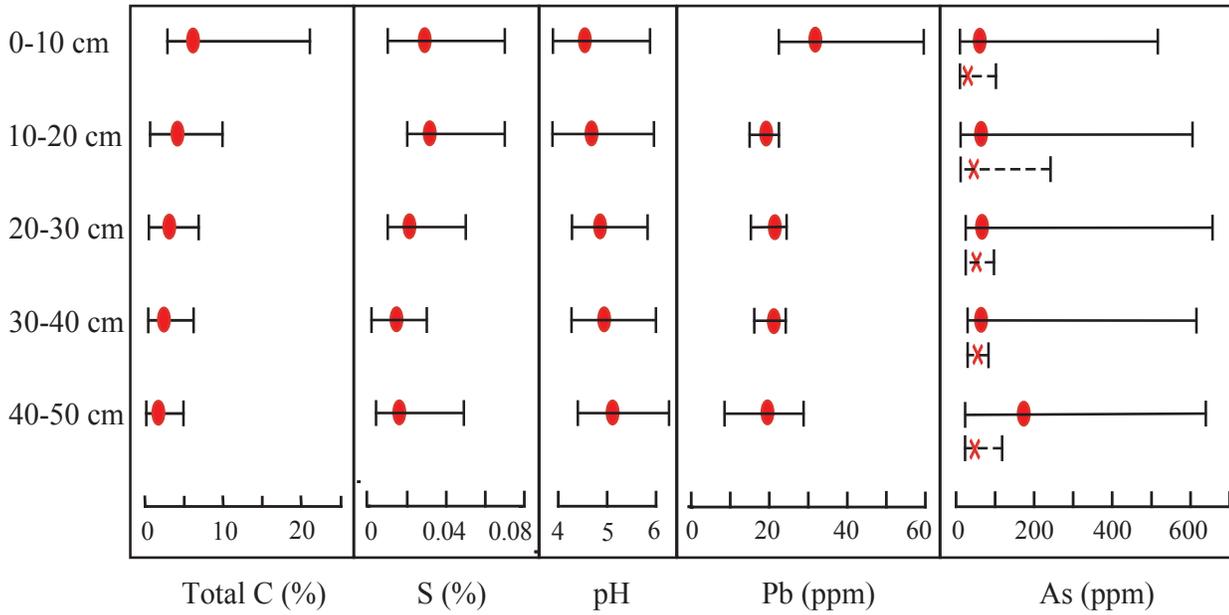
Lead isotope ratios are useful for investigating metal mobility because biological, physical, and chemical processes in the near-surface environment do not disturb the isotopic signatures. Natural and anthropogenic point sources frequently can be distinguished. The isotope signatures can be used to evaluate the contributions of lead from geological background materials (rocks, minerals, near-surface tills, and so on) and lead originating from human activities. Sources providing lead may also be the same as those providing other metals.

In temperate forest soils similar to those found throughout most of New England, the affinity for lead is greatest in the iron-hydroxides, followed by organic matter and by silicate

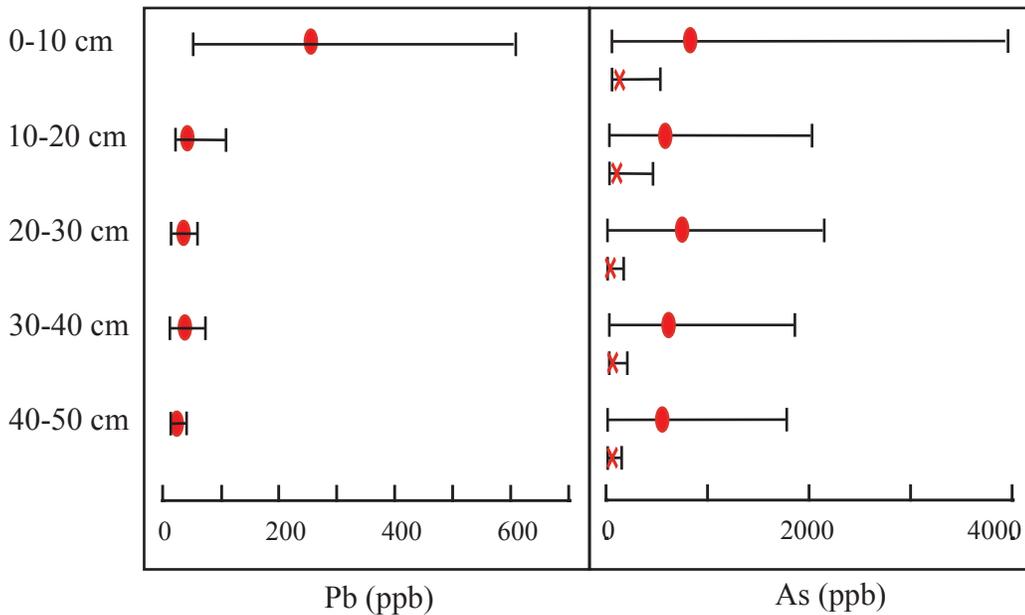
minerals (Emmanuel and Erel, 2002). Arsenic, like lead, has a strong preference for residing in the iron-hydroxides under surface conditions (Korte and Fernando, 1991). The abundance of newly formed secondary minerals that can accept metals and metalloids that are potentially harmful to human health results in a very short residence in water (for example, lead, Jaffe and Hites, 1986; arsenic, Smedley and Kinniburgh, 2002). Moreover, lead residence in a temperate forest floor is also thought to be short, probably less than 80 yr (Miller and Friedland, 1994; Erel and others, 1997).

The dominant source of anthropogenic lead in the near surface environment is generally from industrial emissions involving combustion of alkyl-lead gasoline additives (Chow and others, 1975). The most important domestic sources of lead ore used for industrial applications in the United States (for example, gasoline additives) were Mississippi Valley type deposits. As the supply of lead shifted from domestic to foreign sources, values of  $^{206}\text{Pb}/^{207}\text{Pb}$  in aerosols and gasoline became more variable (fig. 4). By the 1970s, the lead isotopic composition of U.S. alkyl lead (fig. 4) nearly matched that of atmospheric lead ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.23$  and  $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.46$ ) (Chow and others, 1975; Bollhöfer and Rosman, 2000). From

14 Lead Isotopic Compositions of Soil and Near-Surface Till Profiles in Coastal Maine



**Figure 5a.** Average compositions (red ovals) and ranges (solid lines) of total carbon, total sulfur, pH, lead, and arsenic for bulk fractions of the soil and till profiles are shown as a function of depth. For arsenic, ranges (dashed lines) and averages (red x) are also shown for depth profile, omitting two sites in the watershed that contain much higher values of arsenic.



**Figure 5b.** Average compositions (red ovals) and ranges (solid lines) of lead and arsenic for leach fractions of the soil and till profiles are shown as a function of depth. For arsenic, ranges (lines) and averages (red x) are also shown for depth profile, omitting two sites in the watershed that contain much higher values of arsenic.

1982 to 1984, the lead isotopic compositions of industrial emissions in the eastern United States had values of  $^{206}\text{Pb}/^{207}\text{Pb}$  equal to 1.213 (Sturges and Barrie, 1987). By 1997 to 1999 (fig. 4), aerosols in the eastern United States were less radiogenic (Bollhöfer and Rosman, 2001) than those measured in alkyl lead in the 1970s (Chow and others, 1975).

Emissions from fossil fuel combustion are extensively distributed through long-range atmospheric transport (Nriagu and Pacyna, 1988), resulting in heavily polluted soils enriched in lead and, notably, in near-surface materials that are also associated with enrichments in arsenic, zinc, and cadmium (Steinnes, and others, 1989). In addition to the effects of fossil fuel combustion, the natural geochemical cycle of lead also has been greatly disturbed by emissions from industrial plants and ore smelters (Graney and others, 1995; Dunlap and others, 1999; Ayuso and others, 2001; Tarzia and others, 2002), the effects of urbanization (Hopper and others, 1991; Erel and others, 1997; Hansmann and Koppel, 2000; Teutsch and others, 2001), and other human activities that emit metals (arsenic, antimony, cadmium, selenium, mercury, and so on) into the atmosphere and surface environment (Steinnes and others, 1992). Other studies have shown that water reactions with metal-contaminated soils and runoff into ponds, lakes, and streams can enhance the effects of anthropogenic activities (Erel and Patterson, 1994; Kober and others., 1999; DeVivo and others, 2001). Atmospheric precipitation, however, is thought to contribute very little arsenic to surface and ground-water bodies unless there is a significant and local source of contamination (Smedley and Kinniburgh, 2002).

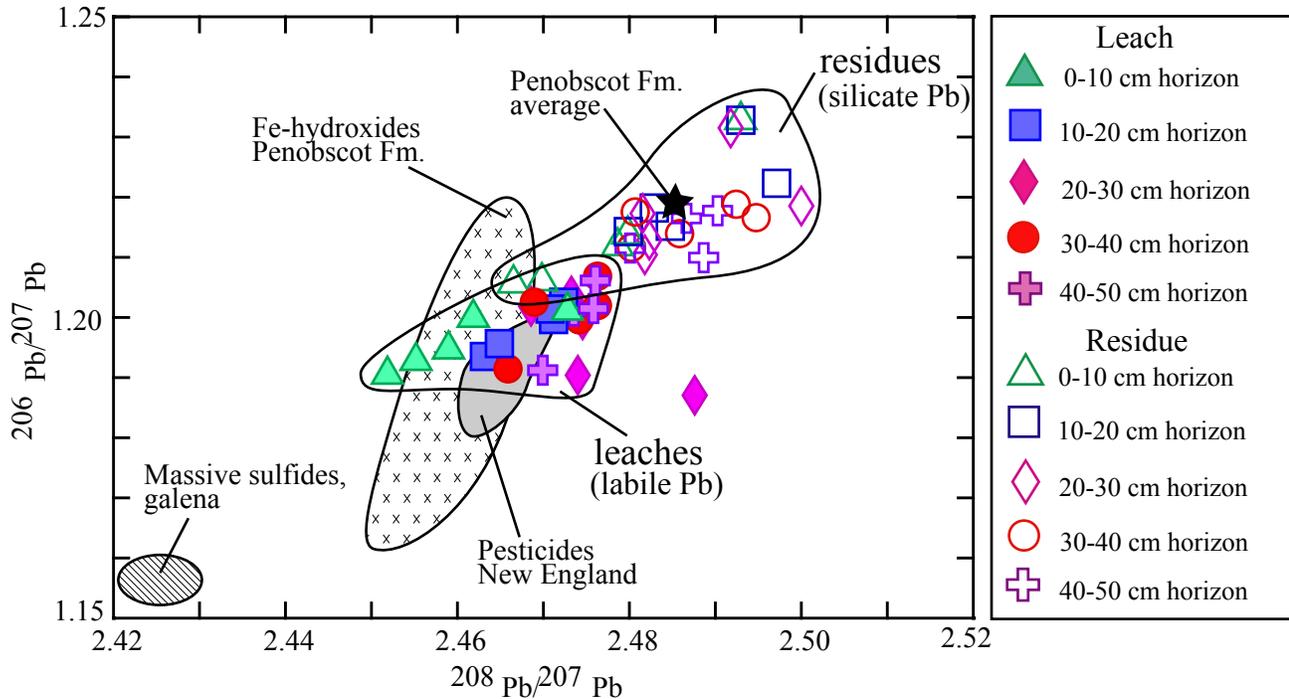
The most important natural source of lead (and, by inference, of arsenic) to the surface soil layer and to most tills in the watershed is likely the breakdown of sulfide-bearing parent rocks during glaciation and subsequent weathering of the oxidation zone overlying the groundwater (Ayuso and Foley, 2002, 2004; Foley and others, 2004a). The lead isotope compositions of the profiles overlap the iron-hydroxides from the local bedrock, the average Penobscot Formation, and the established fields of U.S. aerosols and pesticides that had been extensively used in New England (Ayuso and others, 2004a) (figs. 4, 6). Decomposition of the sulfide minerals as a result of fluid migration would have leached and oxidized bedrock and soils, producing iron-hydroxides and other secondary minerals (carbonates, sulfates, sulfides, oxides). Arsenic- and lead-bearing iron-sulfides, such as pyrite, would have been converted to limonite, goethite, and other secondary iron oxyhydroxide minerals. Generally, the bulk of the lead (and, by inference, of arsenic) in the original sulfide minerals may have been captured by the secondary minerals. Subsequent reduction of such iron-hydroxide minerals is thought to release metals (for example, arsenic) into the groundwater (Matisoff and others, 1982; Stuben and others, 2003).

Although the soil and till profiles show some lead isotopic variations from top to bottom (leach fractions are lowest in  $^{208}\text{Pb}/^{207}\text{Pb}$  in the surface soil layer, 10 cm from the surface), there is no obvious discontinuity that can be used

to distinguish a boundary for the possible effects of near-surface contaminants (such as industrial lead from atmospheric deposition) and lead derived from weathered parent rock. The trend from top to bottom of the profiles shows that the lead-isotope compositions of U.S. aerosols overlap the values of the leach fractions of the surface soil layers (fig. 4). Lead isotope contributions from the youngest aerosols (1997-1999) appear to decrease or be absent in a trend from the top, where organic matter is most abundant, toward the leach compositions of the deeper till fractions. The field of the iron-hydroxides also overlaps the compositions of the leach fractions at the top of the profiles (fig. 6). Deeper leach fractions in the profiles (> 10 cm) are shifted from the field of aerosols and gasoline (1997-1999) and the field of the iron-hydroxides toward somewhat higher values of  $^{208}\text{Pb}/^{207}\text{Pb}$  and the field of the arsenical pesticides (figs. 4, 6). The lead isotope field for the 1997-1999 aerosols is extensive, and is almost as large as the field for all of the U.S. aerosols and gasoline produced since the 1960s (for example,  $^{206}\text{Pb}/^{207}\text{Pb}$  as low as ~1.15 according to Rosman and others, 1994).

Considered as a group, results for labile lead in the soil and till profiles suggest the involvement and mixing of at least three components: (1) lead from eastern U.S. aerosols (1997-1999), perhaps preferentially concentrated at the top of the profiles, (2) lead from the iron-hydroxides (representing a rough average of various natural and anthropogenic sources), and (3) lead from the parent rock (Penobscot Formation) (figs. 4, 5). Values of  $^{208}\text{Pb}/^{207}\text{Pb}$  higher than those of the iron-hydroxides and pesticides in the deeper profiles may indicate a more prominent role for foreign lead sources (Peruvian and Mexican lead ores) or perhaps a natural source that has not been identified (figs. 4, 6). However, no evidence has been documented for such foreign lead ores in the region; moreover, local bedrock with the appropriate high values of  $^{208}\text{Pb}/^{207}\text{Pb}$  is unknown. The arsenical pesticides do not have a distinctive lead isotope range (Ayuso and others, 2004a) that would allow for an exact evaluation of their contribution to the labile lead, separate from that of the iron-hydroxides (fig. 6).

This study was carried out as a test of whether the lead isotopes in the soils and tills can be linked to the likely parental rocks (Penobscot Formation) and to investigate whether additional constraints on relative metal contributions from natural and anthropogenic sources are possible on the basis of these data. Although our data show that a general link between the soil and till profiles and the local country rocks is feasible, a conclusive interpretation of results that directly relate the lead contents and lead isotope variations to the arsenic contents must remain equivocal. At this time, it seems that the contrasting solubilities of lead (low solubility at high soil pH) and arsenic (complexing and solubility contrasts with pH) in the near-surface layers, and the various effects of mechanical disturbance (tillage, and digging) near the surface redistributed lead deeper into the soil, subsoil, and till (Peryea, 1998, 1999) and, more importantly, effectively decoupled lead from arsenic.



**Figure 6.**  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{208}\text{Pb}/^{207}\text{Pb}$  plot showing the isotopic compositions of the soil and till profiles, the field of iron-hydroxides (representing a mixture dominated by rock lead but containing anthropogenic lead from industrial sources), average composition of galena (representative of the natural background compositions from the massive sulfide deposits in the area) (Ayuso and Foley, 2002; 2004; Foley and others, 2004a), and the field of the most commonly used pesticides in New England (Ayuso and others, 2004a; Robinson and Ayuso, 2004). The pesticides include lead arsenate, calcium arsenate, and sodium arsenate, which were applied to apple, blueberry, and potato crops (D'Angelo and others, 1996; Chormann, 1985), and are historically important for the development of arsenical near-surface tills (Veneman and others, 1983; Peryea, 1998). Owing to widespread application, the arsenical pesticides can be considered as a local but potentially significant anthropogenic source of arsenic and lead.

## Conclusions

Lead isotope compositions of near-surface soil and till profiles were measured in an area known to have groundwater with anomalously high arsenic contents to determine the source of the lead and, by inference, to provide constraints on possible sources of arsenic. Labile lead from the soils and tills shows a moderate range in isotope values, distinctly less radiogenic than the residue fractions. Leach fractions are lowest in values of  $^{208}\text{Pb}/^{207}\text{Pb}$  in the soil surface layers. Acid-leach compositions represent lead that is loosely bound in minerals (iron- and manganese-hydroxides, carbonate, and micaceous minerals) and likely approximate the composition of lead available to the regional groundwater. The profiles show that average lead (34 ppm) and arsenic (144 ppm) contents are generally highest in the surface soil layer. Contents of major and trace elements vary widely in the till parent rock, primarily variably sulfidic schists of the Penobscot Formation. Samples of drill core extracted from the Penobscot Formation show wide ranges in their arsenic content. Overall, core samples are depleted in lead (average 17 ppm) and enriched in arsenic (average 83 ppm), compared to outcrop samples (average lead 29 ppm; average arsenic 28 ppm). Our lead isotope and other geochemical data show that a connection exists between the

soil and till profiles and the local Penobscot Formation, but a common source for lead and arsenic cannot be conclusively identified at this time.

## Acknowledgments

We thank William C. Cannon and Bruce R. Doe for constructive comments.

## References

- Ayotte, J.D., Montgomery, D.L., Flanagan, S.M., and Robinson, K.W., 2003, Arsenic in groundwater in eastern New England: Occurrence, controls, and human health implications: *Environmental Science and Technology*, v. 37, p. 2075-2083.
- Ayuso, R.A., Callender, E., and VanMetre, P., 2001, Pb isotopes of lake sediments and effects of human activities on water quality, in Cidu, R. ed., *Proceedings of the Tenth International Symposium on Water Rock Interaction WRI-10*, v. 2: New York, Balkema, p. 1473-1475.

- Ayuso, R.A., and Foley, N.K., 2002, Arsenic in New England: Mineralogical and geochemical studies of sources and enrichment pathways: U.S. Geological Survey Open-File Report 02-454. [available online at URL <http://pubs.usgs.gov/of/2002/of02-454/>]
- Ayuso, R.A. and Foley, N.K. 2004, Geochemical and isotopic constraints on the sources of arsenic in groundwater from Coastal Maine, New England, in Wanty, R., and Seal, R., eds., Proceedings of the 11<sup>th</sup> International Symposium on Water Rock Interaction WRI-11, v. 1: New York, Balkema, p. 801-805.
- Ayuso, Robert, Foley, Nora, Robinson, Gilpin, Jr., Wandless, Gregory, and Dillingham, Jeremy, 2004a, Lead isotopic compositions of common arsenical pesticides used in New England: U.S. Geological Survey Open-File Report 2004-1432. [available online at URL <http://pubs.usgs.gov/of/2004/1432/>]
- Ayuso, R.A., Kelley, K.D., Leach, D.L., Young, L.E., Slack, J.F., Wandless, G. Lyon, A.M., and Dillingham, J.L., 2004b, Origin of the Red Dog Zn-Pb-Ag deposits, Brooks Range, Alaska: Evidence from regional Pb and Sr isotope sources: *Economic Geology*, v. 99, p. 1533-1554.
- Bollhöfer, A., and Rosman, K.J.R., 2000, Isotopic source signatures for atmospheric lead: The Southern Hemisphere: *Geochimica et Cosmochimica Acta*, v. 64 p. 3251-3262.
- Bollhöfer, A., and Rosman, K.J.R., 2001, Isotopic source signatures for atmospheric lead: The Northern Hemisphere: *Geochimica et Cosmochimica Acta*, v. 65 p. 1727-1740.
- Chormann, F.H., Jr., 1985, The occurrence of arsenic in near-surface tills and stream sediments, town of Hudson, New Hampshire: Durham, University of New Hampshire, unpublished M. Sci. thesis, 155 p.
- Chow, T.J., Snyder, C.B., and Earl, J.L., 1975, Isotope ratios of lead as pollutant source indicators, in Symposium on isotope ratios as pollutant source and behavior indicators, Vienna, Austria, Nov. 18-22, 1974: International Atomic Energy Agency Report STI/PUB/382, p. 95-108.
- D'Angelo, D., Norton, S.A., and Loiselle, M.C., 1996, Historical uses and fate of arsenic in Maine: Water Research Institute Completion Report 1986: Orono, University of Maine, 24 p.
- DeVivo, B., Somma, R., Ayuso, R.A., Calderoni, G., Lima, A., Pagliuca, S., and Sava, A., 2001, Pb isotopes and toxic metals in floodplain and stream sediments from the Volturno basin, Italy: *Environmental Geology*, v. 41, p. 101-112.
- Doe, B.R., and Delevaux, M., 1972, Source of lead in southeast Missouri galena ores: *Economic Geology*, v. 67, p. 409-425.
- Dorion, C.G., Balco, G.A., Kaplan, M.R., Kreutz, K.J., Wright, J.D., and Borns, H.W., Jr., 2001, Stratigraphy, paleoceanography, chronology, and environment during deglaciation of eastern Maine, in Weddle, T.K., and Retelle, M.J., eds., Deglacial history and relative sea-level changes, northern New England and adjacent Canada: Geological Society of America Special Paper 351, p. 215-242.
- Dunlap, E.C., Steinnes, E., and Flegal, R.A., 1999, A synthesis of lead isotopes in two millennia of European air: *Earth and Planetary Science Letters*, v. 167, p. 81-88.
- Emmanuel, S., and Erel, Y., 2002, Implications from concentrations and isotopic data for Pb partitioning processes in near-surface tills: *Geochimica et Cosmochimica Acta*, v. 66, p. 2517-2527.
- Erel, Y., and Patterson, C.R., 1994, Leakage of industrial lead into the hydrocycle: *Geochimica et Cosmochimica Acta*, v. 58, p. 3289-3296.
- Erel, Y., Veron, A., and Halicz, L., 1997, Tracing the transport of anthropogenic lead in the atmosphere and in near-surface tills using isotopic ratios: *Geochimica et Cosmochimica Acta*, v. 61, p. 4495-4505.
- Foley, N.K., Ayuso, R.A., West, N., Dillingham, J., and Marvinney, R.G., 2004a, Rock-water pathways for arsenic in weathering meta-shales: Mineralogical evidence of dominant processes, in Wanty, R., and Seal, R., eds., Proceedings of the 11<sup>th</sup> International Symposium on Water Rock Interaction WRI-11, v. 2: New York, Balkema, p. 1493-1499.
- Foley, N., Ayuso, R.A., Culbertson, C., Marvinney, R.G., and Beck, Fred, 2004b, Mining in downeast Maine: Progress toward a geoenvironmental model assessing consequences of mining metamorphosed massive sulfide deposits on the coast [abs]: Geological Society of America Abstracts with Programs, v. 36, no. 2, p. 82.
- Graney, J.R., Halliday, A.N., Keeler, G.J., Nriagu, J.A., Robbins, J.A., and Norton, S.S., 1995, Isotopic record of lead pollution in lake sediments from the northeastern United States: *Geochimica et Cosmochimica Acta*, v. 59, p. 1715-1728.
- Hansmann, W., and Koppel, V., 2000, Lead isotopes as tracers of pollutants in near-surface tills: *Chemical Geology*, v. 171, p. 123-144.
- Hedstrom, G.T., and Popp, D.J., 1981, Soil survey of Waldo County, Maine: Washington, D.C., United States Department of Agriculture Soil Conservation Service, 158 p.
- Hopper, J.F., Ross, H.B., Sturges, W.T., and Barrie, L.A., 1991, Regional source discrimination of atmospheric aerosols in Europe using the composition of lead: *Tellus*, v. 43B, p. 45-60.
- Hunter, L.E., and Smith, G.W., 2001, Morainal banks and the deglaciation of coastal Maine, in Weddle, T.K., and Retelle, M.J., eds., Deglacial history and relative sea-level changes, northern New England and adjacent Canada: Geological Society of America Special Paper 351, p. 151-170.
- Jaffe, R., and Hites, R.A., 1986, Fate of hazardous waste derived organic compounds in Lake Ontario: *Environmental Science and Technology*, v. 20, p. 267-274.
- Kober, B., Wessels, M., Bollhöfer, A., and Mangini, A., 1999, Pb isotopes in sediments of Lake Constance, central Europe constrain the heavy metal pathways and the pollution history of the catchment, the lake and the regional atmosphere: *Geochimica et Cosmochimica Acta*, v. 63, p. 1293-1303.

- Korte, N.E., and Fernando, Q., 1991, A review of arsenic (III) in groundwater: *Critical Reviews in Environmental Control* v. 21, no. 1, p. 39.
- Lipfert, G., and Reeve, A., 2004, Fracture-related geochemical controls on arsenic concentrations in ground-water, in Wanty, R., and Seal, R., eds., *Proceedings of the 11<sup>th</sup> International Symposium on Water Rock Interaction WRI-11*, v. 1: New York, Balkema, p. 431-434.
- Marvinney, R.G., Loiselle, M.C., Hopeck, J.T., and Braley, D., and Krueger, J.A., 1994, Arsenic in Maine groundwater: An example from Buxton, Maine, in *Focus Conference on Eastern Regional Ground Water Issues: Burlington, Vt.*, National Ground Water Association, p. 701-715.
- Matisoff, G., Khourey, C.J., Hall, J.F., Varnes, A.W., and Strain, W.H., 1982, The nature and source of arsenic in northeastern Ohio groundwater: *Ground Water*, v. 20, p. 446-456.
- Miller, E.K., and Friedland, A.J., 1994, Lead migration in forest near-surface tills: Response to changing atmospheric inputs: *Environmental Science and Technology*, v. 28, p. 662-669.
- Nriagu, J.O., and Pacyna, J.M., 1988, Quantitative assessment of worldwide contamination of air, water, and near-surface tills by trace metals: *Nature*, v. 333, p. 134-139.
- Peryea, F.J., 1998, Historical use of lead arsenate insecticides, resulting near-surface till contamination and implications for near-surface till remediation, in *Proceedings 16<sup>th</sup> World Congress of Near-Surface Till Science: Montpellier, France*, Science Reg. No. 274, Symposium 25, 8 p.
- Peryea, F.J., 1999, Gardening on lead- and arsenic-contaminated near-surface tills: *Washington State University Cooperative Extension Bulletin EB 1884*, 13 p. [available online at URL <http://cru.cahe.wsu.edu/CEPublications/eb1884/eb1884.pdf>]
- Peters, S.C., Blum, J.D., Klaue, B., and Karagas, M.R., 1999, Arsenic occurrence in New Hampshire groundwater: *Environmental Science and Technology*, v. 33, p. 1328-1333.
- Robinson, G.R., and Ayuso, R.A., 2004, Use of spatial statistics and isotopic tracers to measure the influence of arsenical near-surface tills use on stream sediment chemistry in New England, USA: *Applied Geochemistry*, v. 19, p. 1097-1110.
- Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P., and Hong, S., 1994, Isotopic evidence to account for changes in the concentration of lead in Greenland snow between 1960 and 1988: *Geochimica et Cosmochimica Acta*, v. 58, p. 3265-3269.
- Shacklette, H.T., Hamilton, J.C., Boerngen, J.G., and Bowles, J.M., 1971, Elemental composition of surficial materials in the conterminous United States: U.S. Geological Survey Professional Paper 574-D, p. D1-D71.
- Smedley, P.L., and Kinniburgh, D.G., 2002, A review of the source, behaviour and distribution of arsenic in natural waters: *Applied Geochemistry*, v. 17, p. 517-568.
- Steinnes, E., Solberg, W., Petersen, H.M., and Wren, C.D., 1989, Heavy metal pollution by long range atmospheric transport in natural soils of southern Norway: *Water, Air, and Soil Pollution*, v. 45, p. 207-218.
- Steinnes, E., Rambek, J.P., and Hanssen, J.E., 1992, Large-scale multi-element survey of atmospheric deposition using naturally growing moss as a biomonitor: *Chemosphere*, v. 25, p. 735-752.
- Stewart, D.B. and Tucker, R.D., 1998, *Geology of the northern Penobscot Bay, Maine*: U.S. Geological Survey Miscellaneous Investigations Series Map I-2551, 1 map, 1 datasheet.
- Stuben, D., Berner, Z., Chandrasekharan, D., and Karmakar, J., 2003, Arsenic enrichment in groundwater of West Bengal, India: Geochemical evidence for remobilization under reducing conditions: *Applied Geochemistry*, v. 18, p. 1417-1434.
- Sturges, W.T., and Barrie, L.A., 1987, Lead 206/207 isotope ratios in the atmosphere of North America: Tracers of American and Canadian emissions: *Nature*, v. 329, p. 144-146.
- Tarzia, M., De Vivo, B., Somma, R., Ayuso, R.A., McGill, R.A.R., and Parrish, R.R., 2002, Anthropogenic vs. natural pollution: An environmental study of an industrial site under remediation (Naples, Italy): *Geochemistry: Exploration, Environment, and Analysis*, v. 2, p. 45-56.
- Tessier, A., Campbell, P.G.C., and Bisson, M., 1979, Sequential extraction procedure for speciation of particulate trace metals: *Analytical Chemistry*, v. 51, p. 844-851.
- Teutsch, N., Erel, Y., Halicz, L., and Banin, A., 2001, Distribution of natural and anthropogenic lead in Mediterranean near-surface tills: *Geochimica et Cosmochimica Acta*, v. 65, p. 2853-2864.
- Veneman, P.L.M., Jr., Murray, J.R., and Baker, J.H., 1983, Spatial distribution of near-surface tills residues in a former apple orchard: *Journal of Environmental Quality*, v. 12, p. 101-104.