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Lead Isotopic Compositions of Common Arsenical Pesticides Used in New England

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Abstract

The three most important arsenical pesticides and herbicides that were extensively used on apple, blueberry, and potato crops in New England from mid-1800s to recent times are lead arsenate, calcium arsenate, and sodium arsenate. Lead arsenate was probably the most heavily used of the arsenical pesticides until it was banned in 1988. Other metal-arsenic pesticides were also used but in lesser amounts. A recent report identified areas in New England where arsenical pesticides were used extensively (Robinson and Ayuso, 2004). On the basis of factor analysis of metal concentrations in stream sediment samples, a positive correlation with pesticide use was shown in regions having stream sediment sample populations that contained concentrations of high arsenic and lead. Lead isotope compositions of stream sediments from areas with heavy use of the pesticides could not be entirely explained by lead originating from rock sulfides and their weathering products. An industrial lead contribution (mostly from atmospheric deposition of lead) was suggested in general to explain the lead isotopic distributions of the stream sediments that could not be accounted for by the natural lead in the environment. We concluded that when agricultural land previously contaminated with arsenical pesticides is urbanized, pesticide residues in the soils and stream sediments could be released into the groundwater. No lead isotopic data characterizing the compositions of pesticides were available for comparison.

We have determined the lead isotopic compositions of commonly used pesticides in New England, such as lead arsenate, sodium metaarsenite, and calcium arsenate, in order to assist in future isotopic comparisons and to better establish anthropogenic sources of Pb and As. New data are also presented for copper acetoarsenite (or Paris green), methyl arsonic acid and methane arsonic acid, as well as for arsanilic acid, all of which are used as feed additives to promote swine and poultry growth. The new data characterize these anthropogenic sources. The data show that the arsenical pesticides have similar compositions: $^{208}Pb/^{207}Pb$ = 2.3839-2.4721, $^{206}Pb/^{207}Pb$ = 1.1035-1.2010, and $^{206}Pb/^{204}Pb$ = 17.070-18.759 and, more importantly, that the pesticides overlap the composition of the stream sediments that represent the areas with the most extensive agricultural use. Copper acetoarsenite (Paris green), arsenic oxide, methyl arsonic acid, methane arsonic acid, and arsanilic acid were also analyzed and have lead isotope compositions that range widely. An important source of arsenic and metals to most of the stream sediment samples in New England appears to be weathering products from rocks and industrial lead, but the extensive use of arsenical pesticides and herbicides up to about the 1960s can also be a significant anthropogenic source in agricultural regions.

Introduction

Extensive application of arsenical pesticides and herbicides on apple, blueberry, and potato crops in New England may have contributed significant amounts of arsenic, lead, and other metals to the surface environment. The pesticides and herbicides were used as recently as the early 1970s (D'Angelo and others, 1996) and represent important potential sources of arsenic, lead, and other metals in soils and sediments that can ultimately influence the composition of ground water. Lead arsenate, calcium arsenate, and sodium arsenate were the most important pesticides and herbicides used in New England. Among the three, lead arsenate was the most extensively used arsenical pesticide (Peryea, 1998). Lead arsenate was intensely used in apple orchards, and together with calcium arsenate, and sodium arsenate, was also applied to blueberry and potato crops (D'Angelo and others, 1996). Copper acetoarsenite (Paris Green) was also reportedly used throughout the region (Shepard, 1939; Veneman and others, 1983; Peryea, 1998).

Anomalously high contents of arsenic, lead, and other metals in soils from orchards have been attributed to the application of arsenical pesticides (Veneman and others, 1983; Chormann, 1985). Soils that have not been greatly disturbed retain arsenic and lead near the top of the soil horizon, suggesting that metal migration is not significant (Veneman and others, 1983; Peryea, 1998). Robinson and Ayuso (2004) used statistical tests and lead isotopic tracers to evaluate the degree to which elevated levels of arsenic and other metals in stream sediments in New England are associated with former agricultural areas inferred to have used arsenical pesticides. Agricultural census data were evaluated to define an agricultural index that identified areas that used arsenical pesticides extensively. Lead isotope compositions of stream sediments from a range of agricultural-index settings mostly overlapped the isotopic range of rock sulfides and their weathering products. A few of the sediments representing high agricultural-index settings were more radiogenic than the geologic background values and were attributed to lead from industrial uses (atmospheric deposition). No lead isotope data were available for herbicides and pesticides for comparison. Robinson and Ayuso (2004) concluded that the extensive application of arsenical pesticides and herbicides in New England could represent a major anthropogenic source of arsenic and other metals to the surface environment and particularly in agricultural areas. This report provides lead isotopic data for compounds that have been used as pesticides (10 samples) and feed additives (two samples) in an effort to better distinguish among the possible anthropogenic sources of arsenic.

Lead Isotope Geochemistry

The isotope ratios of lead are useful to investigate the mobility of metals because biological, physical and chemical processes in the near surface environment do not disturb the isotopic signatures and because natural and anthropogenic point sources commonly can be uniquely distinguished. This suggests that the isotope ratios can be used to evaluate the contributions of lead from geological background (rocks, minerals, soils) and from human activities (agricultural, industrial, and urban). An important objective of this study is to determine whether pesticides have distinct lead isotope signatures.

Lead has a short residence time in water (Jaffe and Hites, 1986) and in sediments within a watershed; lead is thought to originate generally from regional bedrock (including aeolian

sediments and recycled soils), and as a result of land use (from rural and agricultural to urban settings). A variety of anthropogenic sources of lead have been proposed, all of which may have distinct isotopic compositions, and which also contribute other metals (e.g., As, Sb, Zn, Cd). As a result of gasoline and coal combustion, industrial plant emissions, ore smelting (Graney and others, 1995; Dunlap and others, 1999; Ayuso and others, 2001; Tarzia and others, 2002), urbanization (sewage, domestic and industrial debris, waste incineration, etc.) and other activities emitting metals into the atmosphere, the natural geochemical cycle of lead in the near surface environment has been severely disturbed. Extensive use of pesticides on agricultural lands can increase the amount of anthropogenic lead in ponds, lakes and streams as a result of the interaction of surface water runoff (e.g., Erel and Patterson, 1994; Kober and others, 1999) with lead-contaminated soils. Various lead contributions from natural, atmospheric and industrial point sources should be retained in lake and stream sediments (e.g., Hopper and others, 1991; De Vivo and others, 2001).

Lead Isotope Techniques

The pesticides were prepared for analysis using standard techniques at the U.S. Geological Survey, Reston. The pesticides were dissolved in dilute HNO_3 and this solution was passed through Pb columns using normal elution protocols (Ayuso and others, 2003). Isotopic compositions were measured using a Finnigan-MAT 262 thermal ionization mass spectrometer (TIMS). Mass fractionation was monitored by periodic analysis of 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 atomic mass unit of about 0.1% was applied to all samples. Maximum analytical uncertainties for ± 2 standard error of the mean are as follows: $^{206}Pb/^{204}Pb < 0.002$, $^{206}Pb/^{207}Pb < 0.00003$, and for $^{208}Pb/^{207}Pb < 0.00004$).

Results

Lead isotopic compositions of pesticides and herbicides are in Table 1 and Figure 1. The table also shows compositions of widely used feed additives marketed to promote swine and poultry growth. The pesticides and herbicides display an extensive range in values of $^{206}Pb/^{207}Pb = 1.1035-1.2010$, $^{208}Pb/^{207}Pb = 2.3839-2.4721$, and $^{206}Pb/^{204}Pb = 17.070-18.759$ (Fig. 1). Isotopic compositions of galena from sulfide mines and bedrock, and their secondary alteration products (predominantly Fe- and Mn-oxyhydroxides) in coastal New England are shown for comparison in Figure 2 (Ayuso and Foley, 2002; 2004; Foley and others, 2004). The isotopic compositions of the sulfides and secondary minerals overlap. The secondary minerals are slightly more radiogenic (Fig. 2) and indicate that they include a lead contribution from sources more radiogenic than the primary sulfides. The stream sediments representative of a wide range of agricultural index values (inferred to reflect variations in pesticide application) from Robinson and Ayuso (2004) also have a wide range in values of $^{206}Pb/^{207}Pb = 1.1645-1.2233$, and $^{208}Pb/^{207}Pb = 2.4317-2.4717$ (Fig. 3). Lead isotope compositions of the pesticides and herbicides in some cases show large differences even for similar compounds. For example, lead arsenate (acid form) ($^{206}Pb/^{204}Pb = 18.395$) is significantly more radiogenic than lead arsenate (basic form) ($^{206}Pb/^{204}Pb = 17.070$). These variations are consistent with a different source of lead in its manufacture.
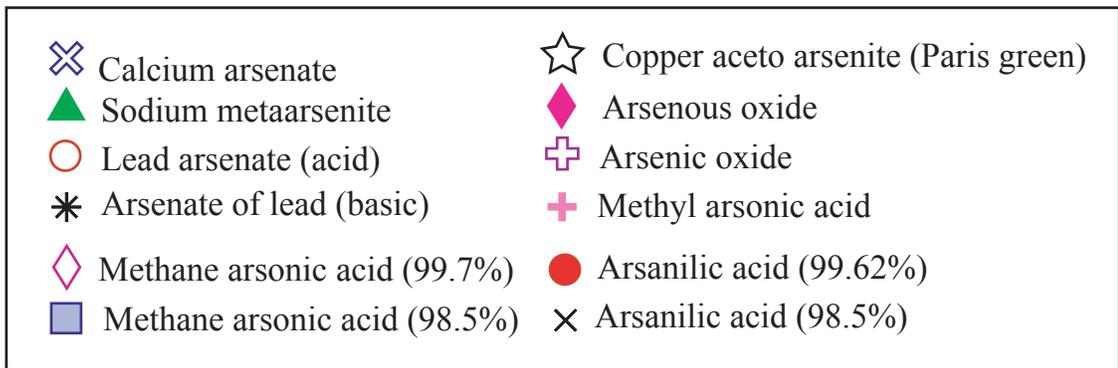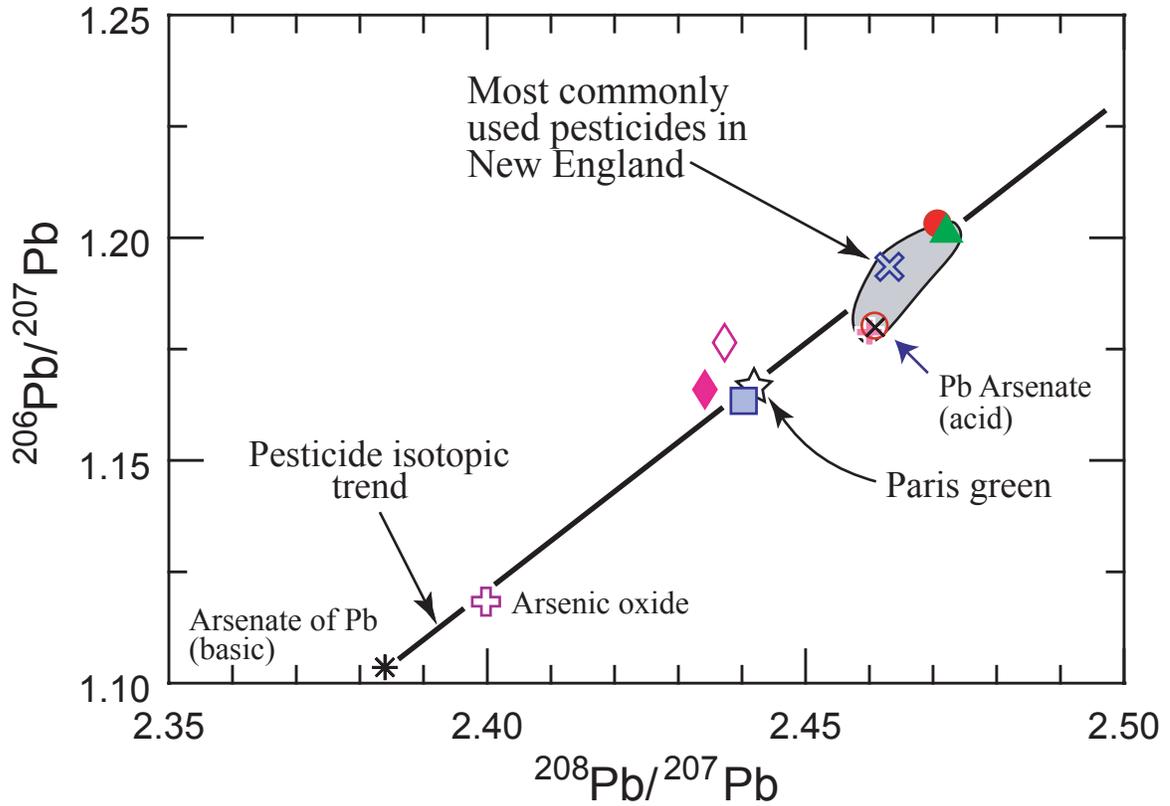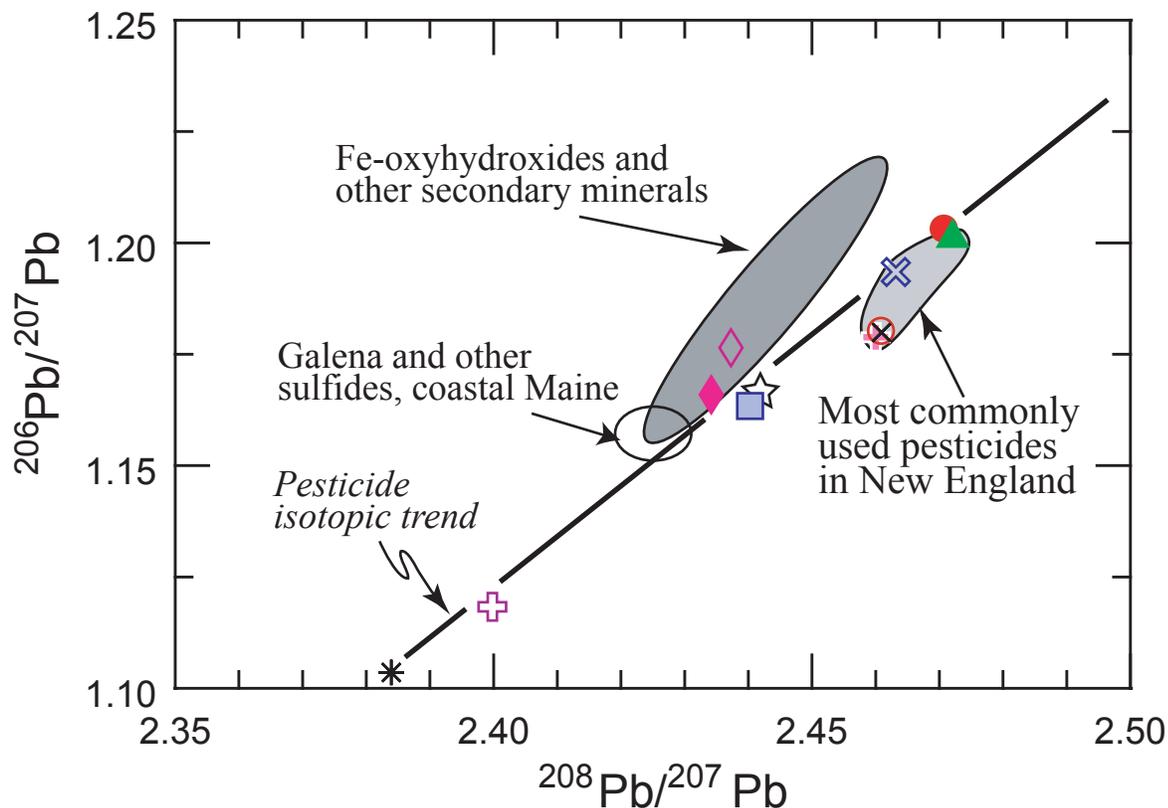
Figure 1. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plot showing the compositions of arsenical pesticides, herbicides and feed additives. (See Table 1 for sample descriptions.)

The three most commonly used compounds in New England (lead arsenate-acid form, calcium arsenate, and sodium arsenate) have similar isotopic compositions and are generally more radiogenic than the rest of the pesticides (Figs. 1-2). Arsenous oxide and arsenic oxide manufactured by different companies have contrasting isotopic values that are less radiogenic than the most commonly used compounds in New England (Fig. 1). Both methyl arsonic acid and methane arsonic acid (and copper acetoarsenite or Paris green) have intermediate isotopic compositions between lead arsenate and arsenous oxide. Preliminary isotopic data for commonly used feed additives used to promote swine and poultry growth have a similar range as that of the most commonly used arsenical pesticide and herbicide compounds in New England.

Table 1. Lead isotopic compositions of pesticides, herbicides, and feed additives (Ayuso and others, 2004).

Compound name as labeled and purity (if known)	Formula	Manufacturer and date (if known)	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Most commonly pesticides and herbicides used in New England					
Calcium arsenate	$Ca_3(AsO_4)_2$	Pfaltz and Bauer Inc., 1981	18.617	1.19345	2.46316
Sodium metaarsenite (98.0%)	$NaAsO_2$	Aldrich Chemical Co.	18.759	1.20102	2.47212
Lead arsenate (acid) (91.6%)	$PbHAsO_4$	Pfaltz and Bauer Inc., 1976	18.395	1.18026	2.46083
Acme arsenate of lead (basic)	$Pb_5OH_9(AsO_4)_3$	PBI/Gordon Corp., Acme Quality Paints (from H. Evans, USGS), 1950?	17.070	1.10352	2.38394
Copper acetoarsenite (90.0%)	$C_4H_6As_6Cu_4O_{16}$	Sherwin-Williams Co., Paris green, 1985	18.153	1.16649	2.44191
Other pesticides and herbicides					
Arsenous oxide	As_2O_3	Union Mechling Co. (from J. Ayotte, USGS)	18.153	1.16587	2.43421
Arsenic oxide (99.95%)	As_2O_3	Aldrich Chemical Co.	17.342	1.11826	2.39982
Methyl arsonic acid (99.9%)	CH_5AsO_3	Ricerca Inc., 1993	18.381	1.17881	2.46001
Methane arsonic acid (99.7%)	CH_5AsO_3	Vineland Chemical Co., 1978	18.333	1.17644	2.43727
Methane arsonic acid (98.5%)	CH_5AsO_3	Vineland Chemical Co., 1982	18.042	1.16337	2.44030
Feed additives (poultry and swine growth)					
Arsanilic acid (99.62%)	$C_6H_8AsNO_3$	Fleming Labs Inc., 1990	18.754	1.20321	2.47068
Arsanilic acid (99.86%)	$C_6H_8AsNO_3$	Fleming Labs Inc., 1990	18.411	1.17985	2.46093

Figure 2. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plot showing the field of arsenical pesticides and herbicides, galena and other sulfide minerals from mineralized and unmineralized areas in coastal Maine and New Hampshire, sulfides at various stages of weathering, and of secondary Fe- and Mn oxy-hydroxides (representative of the natural background compositions) (Ayuso and Foley, 2002). Symbols are given in figure 1.

Discussion

Prior to 1914, most metallic arsenic was imported from Germany (e.g., Smith, 1945). From 1914 to about 1930 the bulk of the arsenic production (marketed for commercial applications as As_2O_3, arsenic trioxide, or white arsenic) in the U.S. was derived as a metallurgical by-product of the smelting of copper or lead by American Smelting and Refining Co., ASARCO (both copper and lead smelting in several domestic plants), Anaconda Copper Co. (copper smelting), U.S. Smelting Co. (lead smelting), and others. Table 1 also shows two analyses of As_2O_3 or arsenic trioxide produced by two different companies (labeled as arsenous oxide and arsenic oxide) that show

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substantial isotopic differences. From 1974 to 1986 the domestic supply of arsenic was controlled by ASARCO, and since 1986 by imports from various countries (Sweden, France, Chile, Canada, Mexico, China, and others) (Kirk-Othmer Encyclopedia of Chemical Technology, 1992).
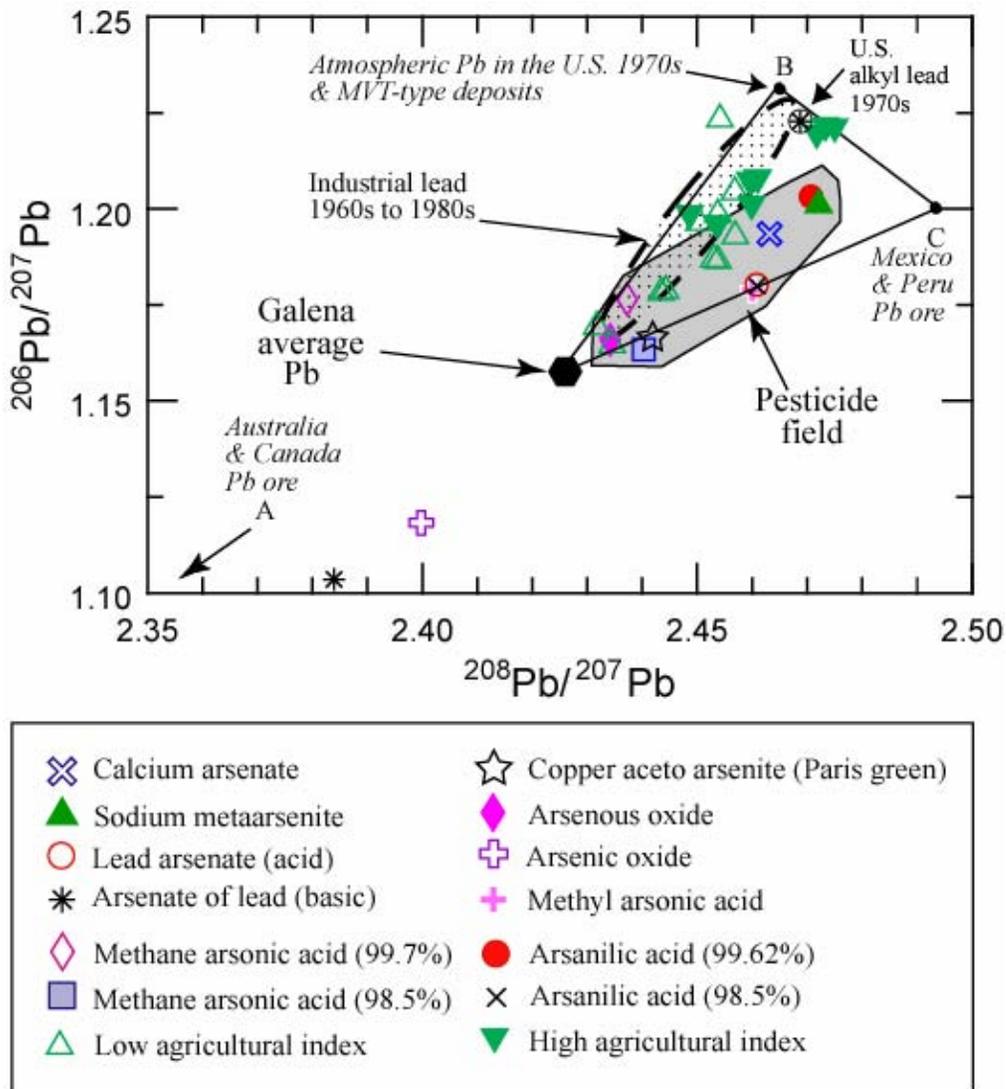

Figure 3. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ plot showing the arsenical pesticide field (except for arsenic oxide and arsenate of lead-basic), average composition of galena (representative of the natural background compositions) (Ayuso and Foley, 2002; 2004; Foley and others, 2004), and acid-leach compositions of stream sediments representing various intensities of agricultural use shown as open triangles (low agricultural intensity) and upside down solid triangles (high agricultural intensity) (Robinson and Ayuso, 2004). All other symbols are as in figures 1 and 2. Also plotted are the generalized range of isotopic compositions of industrial lead from the 1960s to the 1980s (Erel and Patterson, 1994), alkyl lead in the U.S. in the 1970s (Chow and others, 1975), Mississippi Valley type (MVT) ore deposits (Doe and Delevaux, 1972), Pb ore from Mexico and Peru (Chow and others, 1975), Pb ore from Australia and Canada (Cumming and Richards, 1975). In the period from 1982 to 1984 the lead isotopic compositions of industrial emissions in the eastern U.S. had values of $^{206}Pb/^{207}Pb$ = 1.213 (Sturges and Barrie, 1987). By 1997 to 1999, U.S. aerosols in the Eastern U.S. were less radiogenic (Bollhöfer and Rosman, 2001) than values measured in alkalyl-lead in the 1970s (Chow and others, 1975). Points labeled A (Australian Broken Hill Pb), B (atmospheric Pb in the U.S. in the 1970s and Mississippi Valley-type deposits), and C (Pb ore from Mexico and Peru) are from Bollhöfer and Rosman (2001). Maximum analytical uncertainties are smaller than the size of the symbols (e.g., ± 2 standard error of the mean for $^{206}Pb/^{204}Pb$ < 0.002, $^{206}Pb/^{207}Pb$ < 0.00003, and for $^{208}Pb/^{207}Pb$ < 0.00004).

The most important domestic source of lead ore used for industrial applications in the U.S. and for gasoline additives is from Mississippi Valley type (MVT) ore deposits (Fig. 3). However, from about 1930 to 1970 lead ore produced from MVT deposits decreased as the main domestic source in the U.S., as lead recycling and imports increased (Graney and others, 1995). Foreign sources of lead to the United States have included mines from Australia, Canada, Mexico, and Peru. The foreign sources of lead are substantially different in their isotope compositions compared to the MVT deposits (Fig. 3). By the 1970s the lead isotopic composition of alkyl lead in the U.S. nearly matched the isotopic composition of atmospheric lead and that of MVT deposits (Chow and others, 1975). In the period from 1930 to 1970, coinciding with the most intensive applications of pesticides in New England, anthropogenic lead throughout the U.S. was primarily derived from combustion of alkyl-lead gasoline additives and input of lead to the atmosphere (Chow and others, 1975). Lead is extensively distributed and transported, mainly by the atmosphere (e.g., Nriagu and Pacyna, 1988), effectively mixing local and regional airborne sources.

An important feature of the production of arsenical pesticides is that they all share arsenic trioxide (As_2O_3) as the starting material (Ullman's Encyclopedia, 1998). This indicates that the lead isotopic composition of the arsenic trioxide produced by the various manufacturers will depend on the lead isotope compositions of the raw materials (e.g., arsenian sulfides such as arsenopyrite associated with copper and lead ore), and lead acquired during the manufacturing process. As a consequence of this variability, the lead isotopic compositions of the pesticides will also be variable, and more importantly, the lead ratios can be used as isotopic tracers of the different pesticide contributions in near surface inorganic and organic materials.

Because of the intrinsic isotopic variability of the natural materials used during the manufacture of the arsenical pesticides, however, in order to precisely assess the relative contributions of pesticides and herbicides in a given area it is important to focus on the specific arsenian compounds that were applied in the area. For example, it would be important to establish the type and dates of pesticide applications, as well as the manufacturer, type of raw materials used for the arsenic trioxide and the approximate date of production. An additional complication in assessing the input of arsenical pesticides is that isotopic variability in near-surface materials may also reflect sequential application of various pesticides on individual tracts in diverse proportions and with potentially distinct isotopic compositions.

Our survey of lead isotopic compositions of the pesticides shows that significant differences in lead isotopic signatures do exist. However, an inventory describing in detail the pesticide types and amounts applied in New England over the last half-century can not be assembled because such records either do not exist or are incomplete. The exact dates of manufacture of the pesticides used in this study are also unknown, but in general they range from 1950 (?) to 1985. As a group, the compounds do not have a distinctive signature that can be uniquely traced to any of the major foreign or domestic industrial lead suppliers in the U.S. The pesticides plot along a trend in isotope diagrams (Fig. 1), for example, for values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$. The pesticide isotope trend, in addition, cannot be explained as a simple binary mixture involving industrial lead suppliers. It is significant to note that in lead isotope diagrams most pesticides plot within a field bound by the compositions of lead from domestic (e.g., MVT deposits) and foreign sources (Mexico and Peru), and lead from the natural environment (here represented by sulfide mines and from unmineralized areas in Coastal Maine) (Figs. 2-3).

The isotopic compositions of industrial lead in the 1960s to the 1980s, compared to the values of the pesticides, are shifted toward higher values of $^{206}Pb/^{207}Pb$ relative to $^{208}Pb/^{207}Pb$ (Fig. 3). One possible interpretation of the isotopic difference is that the industrial lead values reflect

lead sources dominated by MVT deposits and from foreign sources (Australia and Canada; points A and B in figure 3). In comparison, the pesticides would appear to indicate an additional contribution of lead from different foreign sources (e.g., Mexico and Peru, point C in figure 3), perhaps characterized by higher values of $^{208}Pb/^{207}Pb$.

Assuming that the analyzed pesticides are representative of those extensively used in New England, the following observations are offered as a way to explain the isotopic compositions of the acid-leach compositions of the stream sediments collected at sites that span various settings, from agricultural to urban. Although the isotopic composition of the stream sediments cannot be exactly characterized on the basis of the intensity of agricultural use as classified by Robinson and Ayuso (2004), sediments representing areas with more intense agricultural use were found to be somewhat more radiogenic (higher $^{208}Pb/^{207}Pb$ ratios) than most samples from areas with a lower intensity of agricultural use. Again, as a group, however, the stream sediments from areas classified from low to high agricultural intensity exhibit a range in compositions that overlaps the field of the pesticides, and significantly, a few of the more radiogenic sediments have values of $^{208}Pb/^{207}Pb$ that are closely equivalent to the composition of U.S. alkyl lead in the 1970s. It is important to note that the isotopic resemblance between the sediments and pesticides is not exact, as the sediments have higher values of $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{207}Pb$ than the pesticides (Table 1, Fig. 3).

The stream sediments cannot be conclusively shown to owe their isotopic compositions to a single source of lead. Our preferred interpretation is that the variability of isotopic compositions of the stream sediments allow for the contribution of the pesticides, in addition to lead derived from the natural background (e.g., as represented by the composition of galena), and lead from industrial uses (as represented by the field of industrial lead in the 1960s to 1980s and U.S. alkyl lead in the 1970s) (Fig. 3).

Conclusions

Although the predominant source of arsenic and metals to most soils and sediments in New England is likely derived from weathering of sulfide-rich rocks, the extensive application of arsenical pesticides and herbicides (lead arsenate, calcium arsenate, and sodium arsenate, and others) on apple, blueberry, and potato crops may have been a significant anthropogenic source of arsenic and lead.

Lead isotope compositions of pesticides and herbicides display an extensive range in values of $^{206}Pb/^{207}Pb$ = 1.1035-1.2010, $^{208}Pb/^{207}Pb$ = 2.3839-2.4721, and $^{206}Pb/^{204}Pb$ = 17.070-18.759. Lead isotopic compositions of pesticides have different signatures. They can be used as tracers to distinguish their input into near surface inorganic and organic materials. The pesticides plot along a trend in isotopic diagrams, for example, in values of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$. The pesticides do not have unique isotopic signatures that can be derived from single foreign or domestic industrial lead suppliers in the U.S. There is no simple binary mixture involving industrial lead suppliers that can explain the range of isotopic signatures.

The three most commonly used compounds in New England (lead arsenate-acid form, calcium arsenate, and sodium arsenate) have similar isotopic compositions. These compounds are more radiogenic than the rest of the pesticides and generally overlap the leach compositions of stream sediments representative of areas with the highest intensity of pesticide use. Most pesticides and herbicides plot within a three-component field bound by the compositions of lead from domestic (e.g., Mississippi Valley-type deposits) and foreign sources (Mexico, and Peru), and lead from the natural environment (sulfide mines and mineralized areas in Coastal Maine). The

pesticides, together with lead from the natural background and from industrial activities could explain the spectrum of compositions of the stream sediments. The extensive use of arsenical pesticides in New England up to about the 1960s may have been a significant anthropogenic source in agricultural regions.

Acknowledgements

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