CHAPTER 7
Source Attribution for Lead Contamination at Superfund Sites

7.1 Introduction

7.1.1 Purpose

This chapter provides information for assessments at lead sites where source attribution techniques may be needed to better inform site management decisions. It is relevant to a variety of lead sites where multiple sources of lead in the environment complicate site decisions under Superfund authorities. This chapter will provide information to support site decisions at lead-contaminated sites using a consistent analytical or scientific framework, acknowledging that a flexible, site-specific approach may be needed for characterization, risk assessment, and risk management. The source attribution techniques in this Handbook promote best practices for assessing and managing risks associated with lead-contaminated residential sites being addressed under Superfund authority.

7.1.2 Sources of Lead and Environmental Distribution

Lead is a widespread, naturally occurring element that occurs in the Earth's crust and geological formations (*e.g.*, rocks, sediment, etc.). Lead is the 38th most abundant element with an average crustal abundance of 14 milligrams per kilogram (mg/kg) (Krauskopf and Bird 1995). Lead can be dispersed by natural processes such as wind and soil erosion, or by intentional transport such as human activities like mining and the inclusion of lead in consumer products (*e.g.*, LBP). In some situations, mine waste has been used as construction fill, roadbed materials, and building materials. Furthermore, sediment-associated lead can be reintroduced into river sediment from a contaminated riverbank or dispersed via airborne transport. In many urban environments, soil mixed with other materials from the as-built environment is used to modify site elevation to facilitate property development. Urban fill material is a soil matrix that can include brick, cement, wood, wood ash, coal, coal ash, boiler ash, clinkers, asphalt, glass, plastics, metal, ceramics, demolition debris, roadside ditch materials, slag, and other waste materials. Many of these fill components can be sources of lead.

7.1.3 Urban Environments

The distribution and anthropogenic concentrations of lead in the environment is the most widely studied legacy metal in industrial cities (Maxim et al. 2022). The sources of lead are predominantly from historical use of leaded gasoline, LBP, coal burning, and industry. These widespread anthropogenic sources make determining the background levels of lead more

complicated. Knowing the background level of lead is an important part of the process necessary to accurately attribute lead to specific sources. This information is also useful in determining if the release of lead can be addressed using Superfund authority.

7.1.4 Source Attribution Overview

A wide array of techniques has been used to determine the relative contributions of lead from natural and anthropogenic sources in soils, sediments, water, and air. The EPA has used several methods in Superfund site investigations, including site history, spatial deposition, elemental concentrations and ratios, isotopic analysis, and other soil-metal characterization (NAS 2017). Also, combinations of these methods may be used in a weight-of-evidence approach.

7.1.4.1 What is Source Attribution?

Source attribution involves identifying unique physical or chemical characteristics associated with suspected sources of lead in the environment, and comparing those characteristics with lead in samples of soil, sediment, water, and air collected from a site to determine its origin (NAS 2017). Various physical and geochemical fingerprinting strategies are available for each of the different environmental media at a site; selection of the appropriate one(s) to implement depends on site-specific variables uncovered during site characterization and researching site history. The general assumption behind fingerprinting is that the physical or chemical composition of a sample is a function of the characteristics or composition of the lead sources and the relative amount of each source that contributes to it. The characterization tools that are most used for lead source attribution include lead concentrations with spatial analysis, lead isotope ratio analysis, solid-phase speciation analysis using spectroscopy, microscopy, and sequential extraction techniques, and element correlation using multi-variate statistical methods.

7.1.4.2 Why is Source Attribution Important?

As part of the Superfund program, the EPA conducts site investigations, determines whether a site needs to be remediated, and identifies the parties that may be responsible for the contamination. Given that lead is a naturally-occurring metal and has been used in a variety of consumer products known to cause environmental contamination, parsing out the source of lead contamination at a site is critical to identifying potentially responsible parties (PRPs). If lead is discovered to be a result of nonpoint anthropogenic background sources, federal and local stakeholders may collaborate as appropriate to evaluate whether lead is present at concentrations above risk thresholds. If lead is found to be a result of one or more CERCLA

sources of concern, EPA will first look to PRPs to clean up the lead that is present above risk thresholds in site-impacted media.

Similarly, EPA will look first to PRPs to bear the costs for investigation and remediation at Superfund sites. At Superfund sites associated with lead-mining districts, cleanup costs can range from hundreds of millions to billions of dollars. As such, source attribution is a useful tool to establish PRP liability for the cleanup costs.

7.1.4.3 When to Consider Using Attribution Techniques

Urban sites and mining sites can be complex and problematic when identifying contaminant sources. This is due to the multiple possible natural and anthropogenic sources of contamination, and is further complicated at mining sites due to their sheer size, and at urban sites which may have multiple potential point sources of contamination (*e.g.*, manufacturing plants, processing facilities, and landfills) within a relatively small geographic area.

Source attribution is typically more successful for sites with concentrated waste materials. It can be more challenging at sites with large amounts of low-concentration wastes, such as landfills and mining sites. Source attribution can also be more diffcult in areas with high concentrations of lead that are due to either local geology, anthropogenic background, or multiple nonpoint sources.

7.2 Issues for Consideration

The Superfund program was primarily established to address human health and environmental risks posed by hazardous waste sites. CERCLA gives the EPA the resources and authority to remediate sites and seek reimbursement from PRPs. Sites may be addressed using removal authorities to mitigate immediate threats. For complex sites, the first phase of the Superfund process is the Site Assessment; from there, steps in the Superfund assessment process may include NPL listing, site characterization (the RI/FS), the ROD, remedial design and remedial action, construction and post-construction completion, NPL deletion, and reuse (U.S. EPA 2023d). While source attribution may be used during the removal process, two of these steps (Site Assessment and Risk Assessment, which occurs as part of the RI/FS) are discussed below in relation to source attribution of lead at Superfund sites.

7.2.1 CERCLA Authority

CERCLA gives EPA the authority to clean up sites and seek reimbursement from PRPs. Given that lead is both a naturally occurring element and widespread in the environment due to its

legacy use in gasoline and paint, determining both natural and anthropogenic background is important. This allows the EPA to separate lead due to the contaminated site (evaluated under Superfund) from lead present at background levels that would not generally be addressed under CERCLA.

7.2.2 Geologic Confounding

A variety of geologic processes can cause natural lead enrichment; natural processes that occur at or near the earth's surface, such as volcanic emissions, forest fires, and erosion, can concentrate lead or disperse it into the environment. In most rock, lead occurs at low concentrations; when present at high concentrations, lead forms discrete lead-rich minerals, the most common of which are lead sulfide (galena), lead carbonate (cerussite), and lead sulfate (anglesite). Four categories of mineral deposits might be encountered at a mining Superfund site:

1. Primary lead deposits in which lead is the primary or sole commodity motivating mining;
2. Mineral deposits in which lead minerals are part of the ore body and an essential part of the economics, but production of other metals is also essential;
3. Mineral deposits in which lead is recovered as a byproduct because it is economically profitable to do so, but not necessary for profitability; and
4. Mineral deposits where lead at lower concentrations (*e.g.*, <0.5%) is mined with the ore but is not recovered.

Distinguishing lead from natural (background) sources and lead from local mining materials or waste is much more challenging in contaminated soil. Natural or mined materials from the same region will typically contain lead with similar lead isotopic composition, making fingerprinting a less useful source attribution technique. The same is true for non-mining sites that have high naturally-occurring lead in soils.

7.2.2.1 Potential Past Impacts

Historical review of public records at a site can be used, along with onsite observations, to determine whether a predominant source of lead contamination exists, even when other nearby sources may be present, or whether there are several point sources of lead at the site. Examples of past site use that may affect site characterization and source attribution techniques include whether there are or were buildings onsite constructed before the 1980s that could have been painted with LBP; whether there are obvious atmospheric point sources of lead nearby, such as a smelter or mine; whether mine-waste material containing lead has

been deposited onsite as backfill or used as roadway material; and whether lead-acid batteries were stored or disposed of onsite.

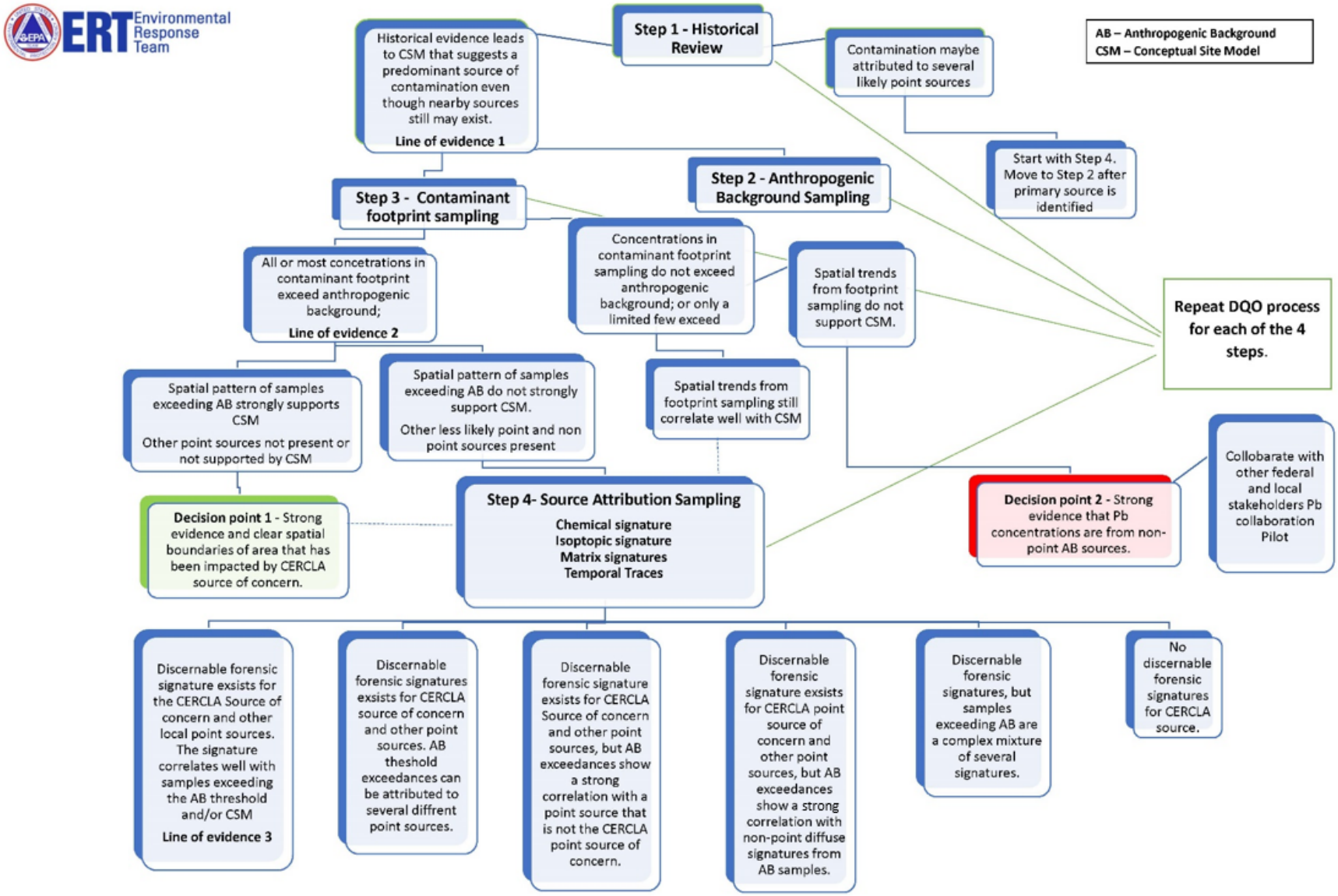
7.2.2.1.1 *Transport Mechanisms*

Lead can be dispersed in the environment by natural processes and through intentional (human-caused) transport. Lead attached to suspended sediment particles or to riverbank soils, or from commercial sources such as paint and other consumer products, can be transported in natural waters and by overland runoff. Airborne transport of lead in surface soils or dust, or attached to particulate emissions, can disperse lead great distances depending on prevailing weather patterns. Intentional transport of mining materials and waste (*e.g.*, rock, tailings, slag, chat) or other consumer products can be an important mechanism of lead dispersal in the environment. These transport mechanisms should be considered when tracking lead from sources to affected areas.

7.2.2.2 Anthropogenic Background

Anthropogenic background sampling and contaminant footprint sampling can be used at a site to determine lead concentrations within the site boundary and lead concentrations attributable to anthropogenic background. If lead concentrations in the contaminant footprint do not exceed anthropogenic background, and spatial analysis of trends in site lead concentrations do not appear to support the current CSM, then the CSM may require updating, or lead concentrations are from nonpoint anthropogenic background sources. If lead concentrations in the contaminant footprint exceed anthropogenic background and the spatial pattern of concentrations appears to support the current CSM, there is strong evidence and clear spatial boundaries of an area that has been impacted by the CERCLA source of concern. This is shown as a decision tree in Figure 7-1.

Figure 7-1. Lead Source Attribution Decision Tree (from OSC Readiness [U.S. EPA 2022c])



The primary goal of CERCLA is to protect human health and the environment from current and potential threats posed by uncontrolled releases of hazardous substances. Contamination at Superfund sites may originate from releases attributable to the site itself, as well as contamination from other sources, including natural and/or anthropogenic sources. In some cases, the same contaminant associated with the hazardous release at the site is also a constituent of background. Contaminants of potential concern (COPCs) with both site release-related and background-related sources should be included in the risk assessment (U.S. EPA 2002a).

In cases where background soils naturally contain high levels of lead, or where there are nonpoint sources contributing to anthropogenic background, concentrations of lead in soil outside the site boundary may be above screening levels. In these cases, lead should be included in the risk assessment and discussed qualitatively in the risk characterization for areas outside the site boundary. Background information is important to risk managers because the CERCLA program generally does not clean up to concentrations below natural or anthropogenic background levels (U.S. EPA 2002a, 2002c).

7.2.2.3 EPA Authority for Cleanup

Under Superfund, EPA can only address media where it has the authority to perform the cleanup. The Superfund program includes community involvement, the goal of which is to advocate and strengthen community participation during Superfund cleanups. Many Superfund sites, particularly those that are more complex, have CAGs associated with them (see Section 4.4). CAGs are made up of representatives of diverse community interest and are designed to serve as the focal point for exchanging information among the local community and EPA, the State regulatory agency, and other pertinent federal agencies involved at the site. The CAG provides a public forum for community members to present and discuss their needs and concerns, and can assist EPA in making better decisions on how to clean up a site by offering EPA an opportunity to hear and consider community preferences for site cleanup and remediation. CAGs are most useful at Superfund sites in communities where there is a high level of interest and concern about site activities.

In situations where lead concentrations do not exceed anthropogenic background, and spatial trends from contaminant footprint sampling do not appear to support the current CSM, it may be necessary to collaborate with other federal, state, and local stakeholders and partners to address lead concentrations present above screening levels.

7.3 Methods for Lead Source Attribution

Numerous methods have been proposed for use to determine the specific sources of lead that contribute to the contamination of a site (Table 7-1). A more detailed description of the methods, examples of their application (see Appendix D), and a more detailed discussion of the strengths and weaknesses are provided in the following sections.

Table 7-1. Available Methods for Use for Determining Lead Source Attribution at Superfund Sites

Source Attribution Method	Strengths	Weaknesses
Site characterization and history	Used to build CSM; can guide investigations towards likely lead sources; collects information on previous land use and likely presence of LBP and other anthropogenic sources.	Not quantitative in nature; if multiple potential sources are found, additional attribution techniques will be needed.
Lead concentrations – spatial and depth sampling analysis (chemical signature)	Spatial distribution of lead at a site is often a clue to its source; sampling and analysis laterally and at depth may help identify the lead concentration both in soil parent material and in layers that have been enriched by human activities. Often used in combination with an analysis of prevailing wind diagrams and land use patterns.	Natural, alluvial, or aerially deposited material may show similar spatial patterns of lead that require further analysis; interpreting lead concentrations as a function of depth can be complicated by weathering (lead can be more concentrated near the surface as more soluble materials are removed).
Lead-isotope ratios (isotopic signature)	If the isotopic signature is unique, lead isotopic composition can potentially identify a lead source: stable lead isotopes can be measured with a high degree of precision and accuracy; lead is unreactive and immobile over a wide range of environmental conditions; fractionation of lead isotopes by physical, chemical, and biologic processes is minimal. The isotopic concentration of lead does not change appreciably as it is dispersed through the environment.	If lead isotopic compositions of the source and non-source materials are similar, or overlap, this method cannot be used on its own to assess lead sources. Available data for non-CERCLA sources (*e.g.*, paint, gasoline, coal) can be quite limited and can also vary greatly causing a fair amount of overlap. The expertise and mass spectrometry instrumentation required for measurement of lead isotope ratios are not widely available at commercial laboratories and may be challenging or expensive to access.

Table 7-1. Available Methods for Use for Determining Lead Source Attribution at Superfund Sites

Source Attribution Method	Strengths	Weaknesses
Mineralogic analysis and particle morphology of bulk sample or separated fractions	Minerals unique to specific sources (*e.g.*, galena) can help with source attribution. Lead concentrations tend to depend on particle size in material deposited as dust, with larger particles deposited closer to the source; particle-size analyses can help to determine source.	As lead disperses through the environment, soil concentrations typically decrease with increased distance from the source, and lead is more likely to be adsorbed to other soil minerals, rendering this technique inconclusive on its own.
Lead chemical speciation	Can provide additional means for understanding sources, contaminant distribution, and associations with other metals.	Lead can be dispersed or poorly crystallized, or be associated with small particles, making speciation difficult; weathering, alteration, and dissolution of primary lead compounds can change lead speciation.
Source-associated tracers, including ratios of lead concentrations to concentrations of other metals (matrix signature), and looking at stable isotopes other than lead	Can be used to determine the contribution of lead from multiple sources on the basis of the composition of the geologic materials with which lead is associated, or the ratios of lead to other metals specific to a certain process (*e.g.*, smelter emissions).	Methods have not been extensively applied to the specific problem of lead-source attribution.

7.3.1 Elemental Concentration Ratios

Spatial distribution of lead at a site is often a clue to its source. Lead is well-suited for tracing of its source by spatial distribution; its low chemical mobility means that lead typically remains where it is deposited and most movement would be associated with mass movement physical processes (*e.g.*, erosion). Spatial deposition analysis can be used in combination with an analysis of prevailing wind diagrams and land use patterns. Sampling and analysis laterally and at depth may help identify the lead concentration both in soil parent material and in layers that have been enriched by human activities (Nazarpour et al. 2019). A study of surface soil lead concentrations in the urban center of Durham, North Carolina used spatial lead distribution to great effect for attributing lead paint and gasoline sources (Wade et al. 2021). The highest lead concentrations were found within 1 mile of pre-1978 residential foundations and inversely correlated with building age. The streetside soil concentrations were correlated with traffic flow. Spatial distribution of lead along the Big River, Missouri gave contributing evidence for source attribution of lead from a waste chat pile adjacent to the riverbank (Noerpel et al. 2020). Upstream of the pile, lead concentrations in stream sediments are near background, increase

significantly near the waste pile, and steadily decrease with downstream distance from the pile, indicating fluvial transport and dilution effects.

There are, however, a few limitations to using spatial distribution of lead for attribution. Natural, alluvial, or aerially deposited material may show similar spatial patterns of lead that require further analysis. Interpreting lead concentrations as a function of depth can be complicated by weathering or pedogenic processes, which can lower surface lead concentration over time via burial (Wade et al. 2021). Additionally, lateral translocation of lead by erosion, runoff, or active land use can also complicate interpretation.

Elemental ratio analysis has been utilized in some cases but methods have not been extensively applied specifically to lead source attribution and are typically used as a complementary analysis. Utilizing elemental ratios involves trace metal co-contaminants present in the lead source(s), which could be used as a source-associated tracer, including ratios of lead concentrations to the co-contaminants. Gathering total concentration data on soils from a contaminated site is a common and routine method for baseline site characterization, so additional utility may be gained by this additional elemental ratio analysis. In one study, the zinc/cadmium and lead/cadmium ratios in soils and plants were used to distinguish between top and bottom ash from a smelting operation source (Bi et al. 2009). More commonly, total elemental ratios have been employed to support more established and validated methods (*e.g.*, lead isotopic ratio analysis) (Wang et al. 2015, Graney and Landis 2013). However, the limitations of utilizing elemental ratios for source attribution are similar to those of the lead isotope ratio method; it depends on knowledge of all potential sources to the site, having total elemental concentrations of all sources, and unique ratios of elements between sources.

7.3.1.1 Lead Speciation

The chemical speciation of lead in soils can provide additional information on source attribution. Positively identifying a chemical form of lead present in soils that originated from a previous release would provide evidence that the source contributed to the soil contamination. For example, if galena (lead sulfide) is associated with mining activities, and galena is present in a soil sample, that would provide a line of evidence that the soil lead may have originated from the mining activity. However, several challenges may arise as many primary lead compounds are not stable in soil environments. Weathering, alteration, and dissolution of primary lead compounds can alter lead chemical speciation and may result in adsorption of lead on mineral or organic-matter surfaces or its substitution as a minor element in newly precipitated phases obscuring the results.

Selective extractions have been used to assess the chemical speciation of lead.[99] Most series of selective extractions are based on a method developed by Tessier (Tessier et al. 1979). Various methods are reviewed and summarized by Ure (Ure et al. 1993). One potential issue is that while the extracting medium may target lead associated with specific materials (*e.g.*, organic matter, carbonates, or iron or manganese oxide), it might also capture other materials, resulting in a partial separation. Combined with the problem with changes in the lead species, this leads to imprecision in the method. However, despite the limitations, selective extractions are useful for assessing relative reactivity of lead in different soil fractions that can then be compared with other soil layers or other sources and should be confirmed by other methods.

For example, at the Klondyke State Superfund site, a six-step sequential chemical extraction was coupled with x-ray absorption spectroscopy (XAS) and XRF to study lead speciation in mine tailings to correlate lead-containing particle size that may dominate the dispersion in arid or semi-arid landscapes (Hayes et al. 2012). This information may be useful in site characterization to inform the potential risk to surrounding communities that lends to remedy selection (*e.g.*, capping or phytostabilization) of mine tailings.

7.3.2 Isotopic Analysis

Stable lead isotope data are useful for source attribution studies because isotopic compositions are conserved as lead moves through the environment (*i.e.*, lead does not change its isotopic composition or fractionate through typical weathering and transport processes). Four stable lead isotopes occur in geologic materials (*i.e.*, ore bodies, coals, and uncontaminated background rocks and soils). ^{204}Pb is "primordial," or original, in geologic materials, ^{206}Pb and ^{207}Pb are the endpoints in the decay chains of ^{238}Uranium (^{238}U) and ^{235}U, respectively, and ^{208}Pb is the end of the decay chain for ^{232}Thorium (^{232}Th) (Komárek et al. 2008, Cheng and Hu 2010, Tuccillo et al. 2023). Therefore, lead isotope ratios within the uranium decay chain are a function of the concentrations of uranium (U) and thorium (Th) present in a system. There are also >40 unstable isotopes of lead. For example, ^{210}Pb is a short-lived naturally occurring isotope with a half-life of 22.6 years; ^{210}Pb is commonly used for dating recent sediments and peat deposits but is not typically used for source attribution.

A graphical approach is often used to examine isotopic data and draw inferences about potential sources of lead. The isotopic ratios of samples may be plotted against the inverse lead concentration (*e.g.*, ^{206}Pb/^{204}Pb vs. 1/Pb). This approach can reveal high-concentration "source"

[99] Selective extraction is an analytical process where lead is leached from a sample with a solution to recover only a specific form of lead.

material and low-concentration background samples, as well as samples that fall along the mixing continuum. Three-isotope graphs that plot two ratios (*e.g.*, $^{206}Pb/^{207}Pb$ vs. $^{206}Pb/^{204}Pb$) often produce a more useful data representation when lead concentrations are heterogeneous. In a simple binary system, samples will plot along a mixing line connecting two sources with known isotopic signatures (Brugam et al. 2012, Ellam 2010).

Isotopic data provide an additional level of sample information that supplements lead concentration data and spatial analysis. The isotopic composition can potentially identify a lead source if the isotopic signature is unique. The effectiveness of isotopic fingerprinting is related to several factors: uniqueness of the stable isotope signature of lead source(s), the fact that lead is generally immobile and unreactive over a range of geochemical conditions, and because fractionation of lead isotopes by physical, chemical, and biological processes is minimal. Thus, the lead isotopic composition of natural and anthropogenic sources (including ore deposits) does not change appreciably as it is dispersed through the environment. Observed differences in isotopic composition of soil lead can be attributed to mixing of multiple sources (Cheng and Hu 2010). Lead isotopic composition of ore deposits on a global scale is highly variable (Bird 2011, Miller et al. 2007) and lead derived from ore deposits can differ from lead found in non-ore rocks and soils (Hopper et al. 1991 as cited by NAS 2017).

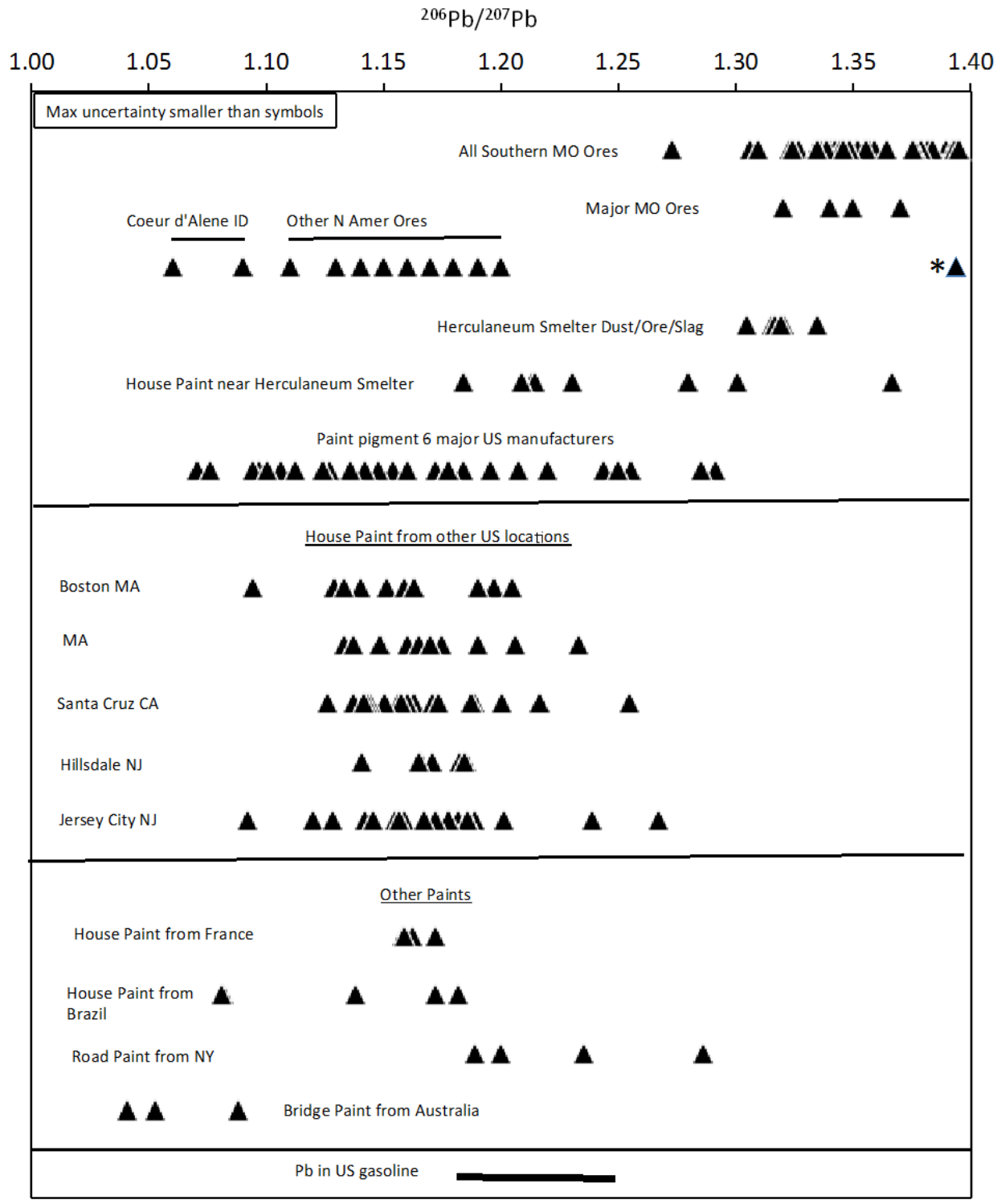
Lead isotopes can be effective in determining lead sources if the isotopic values of the source materials are unique (*e.g.*, Pribil et al. 2014, Ma et al. 2014, MacKinnon et al. 2011, Prapaipong et al. 2008, Clark et al. 2006, Steinnes et al. 2005, Gulson et al. 1981, Rabinowitz and Wetherill 1972). Analyzing the depth distribution and isotopic signatures of lead in soil may allow source determination (Wang et al. 2022, MacKinnon et al. 2011, Prapaipong et al. 2008, Steinnes et al. 2005). If the isotopic character of the lead in soil is different from the parent rock/material, then it is likely that the lead originated from a different source. Numerous studies have used lead-isotope ratios to distinguish between potential sources of lead in soils and atmospheric and household dust (*e.g.*, Wang et al. 2022, Kelepertzis et al. 2020, Graney et al. 1995, Gulson et al. 1981; see Figure 7-2). Changing lead concentration isotope patterns with depth in a soil profile can reveal aerial deposition of lead in shallow horizons and geogenic lead in deeper horizons. This approach has been used to identify lead deposition from coal burning (Ma et al. 2014), lead smelters (Prapaipong et al. 2008), and leaded gasoline (MacKinnon et al. 2011, Graney et al. 1995). Studies have shown that if the lead isotopic compositions of potential sources are unique and known, and if the lead isotopic values in samples of concern fall within the range of the source materials, then the contribution of each source of lead contamination can be determined. However, if the lead isotope compositions of potential source materials

overlap or if there is uncertainty about potential source materials, then the isotopic method cannot be completely determinative of the source of lead and additional techniques should be used (Tuccillo et al. 2023).

Lead isotope ratios in geological materials vary because lead isotopes are produced by the radioactive decay of uranium and thorium over geologic timescales. Lead-isotope ratios are often reported as $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, and plots of these ratios give the most complete differentiation between ore deposits and between sources of environmental lead. Other isotope ratios such as $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ are commonly reported and can be calculated from the ^{204}Pb-normalized values. Lead isotope ratios are measured using mass spectrometry, either with thermal ionization (TI-MS) or with ICP-MS as the ion source. The ICP-MS instruments include those with quadrupole-based (ICP-QMS), time-of-flight-based (ICP-TOF-MS), and sector-based (or sector field) (ICP-SFMS) mass analyzers, equipped with single or multiple collector detection. These techniques all have their unique advantages and limitations in analyzing lead isotope ratios in environmental samples (Gulson et al. 2018, Bird 2011, Komárek et al. 2008). A single method or a combination of these methods can be used to optimize the data acquisition process, depending on the required analytical precision, sample load, and instrument availability (Komárek et al. 2008). A standard reference material (*e.g.*, NIST Standard Reference Material [SRM]-981) is necessary to calibrate analytical instruments and to correct for mass bias (Yuan et al. 2016).

Other metals that are co-contaminants with lead also have isotopic variability that can be used in source apportionment studies (for example, cadmium [$^{114}Cd/^{110}Cd$; Zhang et al. 2020], mercury [$^{202}Hg/^{198}Hg$; Estrade et al. 2010], copper [$^{65}Cu/^{63}Cu$; Gonzalez et al. 2016], and zinc [$^{66}Zn/^{64}Zn$; Gonzalez et al. 2016]). These other non-traditional isotopes are increasingly being studied and, in some cases, combined with lead isotope compositions (*e.g.*, Schleicher et al. 2020). These isotope systems require the multi-collector ICP-MS technique for high resolution discrimination of isotope ratios. It is anticipated that source apportionment studies using isotope tracers at impacted sites will increasingly take advantage of multiple isotopic elements.

Figure 7-2. Compilation of $^{206}Pb/^{207}Pb$ Ratios in North America Ore Deposits, Gasoline, and Paint Samples



Note: the asterisked triangle represents the average $^{206}Pb/^{207}Pb$ ratios in ores from the Upper Mississippi Valley District (source: NAS 2017).

7.3.3 Additional Soil-Metal Characterization

7.3.3.1 X-ray Absorption Spectroscopy (Spectroscopic Speciation)

XAS is an element-specific technique that may be used to chemically speciate elements (*e.g.*, lead) in soils and other environmental samples. Advantages of XAS include the ability to conduct *in situ* measurements with little to no pretreatment of a soil/environmental sample. XAS is suitable for distinguishing multiple phases that may be present in a sample enabling the identification of both primary and secondary phases. Determining lead chemical speciation is also possible at lower concentrations in soils (<20 mg/kg) depending upon sample matrix. Crystallinity is not a requisite for sample analysis as XAS spectra is independent of the chemical phase and may be used to identify amorphous phases, organo-metallic complexes, adsorbed phases, and species in solution. Disadvantages of XAS sample anaysis are related to instrument access. At this time, XAS is primarily a synchrotron-based technique. Beamtime at these facilities is usually awarded through a competitive proposal process. The most commonly used XAS analysis technique with environmental samples is Linear Combination Fitting (LCF) of the energy region near the x-ray absorption near edge structure (XANES). In this process, the pattern created by the unknown sample is compared algebraically against a library of known standards to determine the major species composition.

Other lab-based methods exist for determining speciation, though they have significant limitations. The accuracy of a series of selective extractions has been assessed by comparing them with direct spectroscopic analyses, such as XAS, x-ray fluorescence, Raman spectroscopy, and other advanced methods (Hayes et al. 2012, 2009, Scheckel et al. 2005), that provide information on chemical bonding. For example, in a study of mine tailings from Leadville, Colorado, coupling of direct characterization of lead speciation that used XAS with a series of selective extractions revealed discrepancies between lead fractions targeted in extractions and lead speciation determined spectroscopically, and demonstrated substantial redistribution of lead after extraction treatment (Ostergren et al. 1999).

Generally, XAS can be used only as a secondary line of evidence when determining source attribution. This is because in most cases, the species of lead can change in the environment. These changes often take place in a predictable manner which can non-conclusively point to a potential source. This was the case in the Big River in Missouri where the lead from tailings piles near the river had a substantial amount of primary lead ore species (galena) present in the piles and the relative abundance of galena decreased with distance from the river as secondary oxidation products (Cerussite, Anglesite, and adsorbed lead) became more prevalent. Direct access to a potential source, however, led to isotopic analysis being the main line of evidence in

that study (Noerpel et al. 2020). XAS speciation could be used as a main line of evidence only if the suspected source produced an environmentally stable and uncommon lead species (*e.g.*, leaded glass).

7.3.3.2 Scanning Electron Microscopy (SEM)-Energy Dispersive X-Ray (EDX)/Wave-Length Dispersive X-Ray (WDX)

The mineralogy and particle structure determined with optical microscopy and scanning electron microscopy (SEM) of sand particles has been used extensively on alluvial and dust deposits to track sediment sources (Cardona et al. 2005, Abu-Zeid et al. 2001, Arribas et al. 2000) and might serve to attribute lead sources in soil.

SEM coupled with elemental analysis, conducted with energy dispersive x-ray (EDX) spectroscopy or wave-length dispersive x-ray (WDX) spectroscopy, is an additional way of obtaining chemical information and information on particle structure. A description of the attributes and limitations of SEM and elemental analysis for identifying particle sources is provided in Pye (2004). SEM analysis of soils and sediments has been used extensively in attempt to speciate metals based on particle size, shape, and chemical composition (D'Amore et al. 2005 and references therein).

Specific elemental ratios and morphologic characteristics of particles can be used to infer mineral identity and combining mineralogy, particle size, and elemental composition has proved successful in source attribution (Sterling et al. 1998, de Boer and Crosby 1995). Linton et al. (1980) used specific particle structure and chemical composition to distinguish lead sources between automotive exhaust and paint chips. Sobanska et al. (1999) used spherical structure and elemental composition to identify lead originating from smelters. Demonstrative features such as spherical structure are indictive of high-temperature processing, such as smelting, whereas subtle etching of sand grains might provide important clues to particle source.

Transmission electron microscopy (TEM) coupled with EDX and electron diffraction may also be useful for determining source attribution. Examination of individual particles will provide insights into mineralogy and surface morphology for well crystalline materials (Buseck and Posfai 1999).

7.3.3.3 Electron Micro Probe Analysis (EMPA)

Electron Micro Probe Analysis (EMPA) has the same capabilities as SEM without the optical imaging optics (D'Amore et al. 2005). Coupling EMPA with WDX analysis, along with high beam current and long dwell times, provides increased elemental sensitivity compared to SEM/EDX

analysis (D'Amore et al. 2005). The application and use of EMPA for determining chemical speciation was a common technique during the 1980s and 1990s. However, advancement in other chemical speciation techniques have minimized use of the technique (D'Amore et al. 2005). A recent example of where EMPA has been used for assessing source attribution and chemical speciation was published by Taylor and Robertson (2009). EMPA was used to investigate road-deposited sediment where results demonstrated that lead was associated with two distinct phases: iron oxides and iron-rich glass slag grains. The identification of the glass slag phase had not been previously reported and was not included in the current extraction schemes.

7.3.1 Lines of Evidence Approach

Lead concentrations also tend to depend on particle size. Dividing particles into fine and course fractions can help to determine their source (*e.g.*, larger particles deposit closer to the source [NEPC 1998]).

Wire-mesh sieves are typically used for separating particles larger than 0.05 mm. Finer particles are measured by sediment rate separation, suspension density, or laser light scattering. For example, lead concentrations closer to a source such as a mining and smelting may be higher than in more distant soils (Taylor et al. 2010). Such geographic concentration data may be combined with dispersion models that predict downwind deposition and surface concentrations of atmospheric lead from known sources (Small et al. 1995).

The attribution of airborne lead and other metals to mining and smelting operations by using heavy minerals has generally been based on spatial variations in the quantity with which they are found in soils relative to the source and the area's predominant wind directions.

Source-associated tracers such as multi-elemental analysis and methods that involve stable isotopes other than lead have been used to determine the contribution of lead from multiple sources on the basis of the composition of the geologic materials with which lead is associated. For example, cadmium and zinc are commonly associated with and recovered during the processing of lead ores. As the ore is smelted, light isotopes of zinc and cadmium exit with the exhaust and the heavier isotopes are retained in the smelting residue. Therefore, the differences may be used to examine the deposition patterns of smelter products over a region by identifying zinc and cadmium isotopic composition of soils. In another example (Eckel et al. 2002), antimony/lead ratios were used to correlate soil lead contributions from smelting operations. Antimony was used in alloying processes at specific smelters.

Zinc, cadmium, and arsenic ratios have been used to identify lead sources from chat, whereas manganese has been used to identify uncontaminated soil. In another case, arsenic/lead ratios in soil were used to identify lead contaminated soils from pesticide application and lead/barium/zinc ratios were used to identify particles from paint sources.

Concerning attribution, OLEM supports using tools for source attribution where appropriate and when sufficient resources are available. In the past, there was much interest in attribution through speciation of lead in soil. Speciation can help only at sites where the forms of lead are distinctly different and the level of uncertainty often does not allow for confidence in source attribution. Once lead gets into soil, it will begin to transform to the equilibrium status of the soil. For example, if lead carbonate or hydroxycarbonate from LBP falls on an acidic soil, over time, it will convert to lead sulfate and be much different than the source material. This is very similar for lead in gasoline emissions, which change over time as well. In that situation, the key to identifying the source of lead would be finding mining ore still remaining in the soil. A better option for identifying the source is finding other element markers such as barium in LBP or using isotope techniques (if the original source material is still available and differs from other lead sources in the area).

At some sites, the use of multiple analytical tools can assist in identifying the source. As lead can weather and mix with the background over time, it is difficult for a single analytical method to constrain a source. However, the combination of two or more analytical methods has proven useful in complex source receptor studies.