

Coupling Meteorology, Metal Concentrations, and Pb Isotopes for Source Attribution in Archived Precipitation Samples

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Abstract

A technique that couples lead (Pb) isotopes and multi-element concentrations with meteorological analysis was used to assess source contributions to precipitation samples at the Bondville, Illinois USA National Trends Network (NTN) site. Precipitation samples collected over a 16 month period (July 1994 - October 1995) at Bondville were parsed into six unique meteorological flow regimes using a minimum variance clustering technique on back trajectory endpoints. Pb isotope ratios and multi-element concentrations were measured using high resolution inductively coupled plasma – sector field mass spectrometry (ICP-SFMS) on the archived precipitation samples. Bondville is located in central Illinois, ~ 250 km downwind from Pb smelters in southeast Missouri. The Mississippi Valley Type ore deposits in Missouri provided a unique multi-element and Pb isotope fingerprint for smelter emissions which could be contrasted to industrial emissions from the Chicago and Indianapolis urban areas (~ 125 km north and east, of Bondville respectively); and regional emissions from electric utility facilities. Significant differences in Pb isotopes and element concentrations in precipitation varied according to the meteorological clusters. Industrial sources from urban areas, and thorogenic Pb from coal use, could be differentiated from smelter emissions from Missouri by coupling Pb isotope ratios with multi-element concentrations in precipitation. Using a three endmember mixing model based on Pb isotope ratio differences, industrial processes in urban airsheds contributed 56 ± 19 %, smelters in southeast Missouri 26 ± 13 %, and coal combustion 18 ± 7 %, of the Pb in precipitation collected in Bondville in the mid-1990s.

Keywords: lead isotopes, metal sources, smelters, precipitation, toxic release inventory

1. Introduction

Emissions of metals to the environment and their potential health impacts continue to be of concern on local, regional and global scales (Nriagu and Pacyna, 1988; Morishita et al., 2011a, b). Methods to identify and track metals from integrated source, transport and deposition processes continue to be developed (Keeler et al., 2006; Pancras et al., 2006). Based upon study goals, metal concentration(s) as well as isotope ratios are included in some source attribution efforts. Lead (Pb) is often a metal selected for such process-based studies because of its health concerns from neurotoxicity, and because differences in Pb concentrations and isotope ratios often reflect variability in natural and anthropogenic source terms (Ault et al., 1970; Komarek et al., 2008).

In ideal cases, Pb emission sources provide unique elemental and isotopic fingerprints for environmental forensic studies. Pb has four main isotopes, ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%), and ^{208}Pb (52.4%). ^{208}Pb is formed from the radioactive decay of ^{232}Th , ^{207}Pb from ^{235}U , and ^{206}Pb from ^{238}U . ^{204}Pb is referred to as common Pb and has no radioactive parent. The uranium and thorium parents have differing decay rates resulting in predictable changes in Pb isotope ratios that reflect the timing when the Pb was incorporated into host materials (Faure, 1986). Common anthropogenic emission sources of Pb and other elements to the atmosphere include high temperature processes such as gasoline combustion, smelting, coal combustion, and oil refining (Nriagu and Pacyna, 1988, Graney et al., 1995). Following emission, Pb isotope ratios are not believed to be significantly altered by subsequent physical or chemical processes in the atmosphere (Ault et al., 1970; Komarek et al., 2008).

The use of Pb isotope ratios as a means to fingerprint emission sources has included studies of aerosols as well as wet and dry deposition samples. Some of the pioneering efforts focused on differences in Pb isotopes from gasoline consumption related sources on the North American continent (Sturges and Barrie, 1987, 1989) and the northern Atlantic Ocean (Church et al., 1990; Hamelin et al., 1989; Veron et al., 1992; Veron and Church, 1997). Identifying global scale differences in sources of Pb to the atmosphere were subsequently documented using this Pb isotope approach (Bollhofer and Rosman, 2001, 2002). Studies at sites on the North American continent that have coupled metal concentrations and Pb isotope ratios as a means to assess longer term metal deposition and source budgets from atmospheric transport processes have included ice cores (Rosman et al., 1994), snow pack (Simonetti et al., 2000a), lichens (Carignan and Gariépy, 1995; Carignan et al., 2002; Simonetti et al., 2003), peat (Kylander et al., 2009; Shotyk et al., 2010) and lake and estuary sediments (Graney et al., 1995; Gobeil et al., 1995). Shorter term temporal and smaller scale spatial resolution may be needed to document the importance of location specific source impacts such as emissions from smelters or other point sources (Aznar et al. 2008; Gallon et al., 2006; Rabinovitz, 2005; Simonetti et al., 2004; Telmer et al., 2004). The use of wet deposition (precipitation samples) would be ideal for such studies, and several groups have explored this possibility at sites in North America (Simonetti et al., 2000b, c; DesJardins et al., 2004). To date, such efforts have been limited because of logistical challenges in collecting samples on an event basis and because of the low Pb concentrations in the samples. In contrast to the sample collection challenges, rapid advances in analytical methods such as high resolution inductively coupled plasma – sector field mass spectrometry (ICP-SFMS)

and Multi-Collector ICP-SFMS now allow high precision measurement of Pb isotope ratios in low concentration samples (Krachler, 2007; Yip et al., 2008).

Following the phase out in use of alkyl-lead additives in gasoline (Nriagu, 1990), the predominant sources of Pb to the atmosphere in the United States and Canada have become more varied. According to recent EPA Toxic Release Inventory estimates, primary metal mining (smelting), electrical utilities (coal-fired power plants in particular), and secondary metal processing (e.g., battery recycling) are now major point sources of Pb emissions to the atmosphere. The contributions of individual point sources of Pb emissions can be quantified if the Pb isotopes and elemental fingerprints from distinct sources can be determined. Previous studies have successfully documented spatial variations in Pb isotope ratios reflecting smelting sources near smelting sites (Rabinovitz, 2005; Gallon et al., 2006; Prapaipong et al., 2008) and this approach might be adapted to determine impacts from smelters processing ores from similar suites (and ages) of ore deposits at downwind receptor sites.

Such an opportunity was hypothesized for precipitation samples collected in the mid-1990s for the Lake Michigan Mass Balance study (LMMB study, Landis et al., 2002). One of the sample collection sites used in that study, the Bondville, Illinois USA National Trends Network (NTN) site (40.05°N, 88.37°W), is located in a rural region with flat terrain ~ 250 km downwind from three Pb smelters in southeast Missouri located in Herculaneum (38.26°N, 90.37°W), Buick (37.71°N, 91.20°W) and Glover (37.48°N, 90.69°W). The Pb isotope composition of the Mississippi Valley Type (MVT) ore deposits that are mined in southeast Missouri was compiled from several sources (Graney et al., 1995; Goldhaber et al., 1995). Compared to other ore deposits, as well as coal deposits, the Missouri MVT Pb occupies a unique field in Pb isotope space (Fig. 1). The Missouri MVT Pb should provide a unique isotopic fingerprint that might be coupled with element concentrations to determine source contributions at downwind sites.

Landis et al. (2002) described how a minimum variance clustering technique was used for analysis of HY-SPLIT 24 hour sigma-layer back trajectory endpoints to identify six unique meteorological transport regimes of event precipitation samples to the Bondville site (Fig. 2): west (W), east-northeast (NE), southeast – slow (SE), southeast – rapid (SE-R) south-southwest rapid (SW-R) and southwest (SW). The back trajectories represent the most probable path of the advected air parcels for the 24 hours preceding each precipitation event. We hypothesized that coupling elemental concentrations and Pb isotope ratios with the previously defined meteorological clusters could be used as a means to apportion Pb in precipitation from the smelters in southeast Missouri at Bondville (SW cluster), to industrial emissions from the Chicago and Indianapolis urban airsheds (~ 125 km north and east, of Bondville respectively) from the NE cluster, and regional emissions from electric utility facilities from the SE and SE-R clusters. To achieve this objective, this paper will describe measurements of Pb isotope ratios and multi-element concentrations in archived precipitation samples using ICP-SFMS for source attribution in wet deposition over a 16 month period at Bondville.

2. Methods

A total of 82 wet deposition samples were collected between July 1, 1994 and October 31, 1995 at Bondville. The precipitation samples included rain as well as a few rain/snow events and

spanned all seasons. The samples were collected on an event basis using an automated wet-only sample collection system described in Landis and Keeler (1997). Following sample collection, the samples were acidified with ultra-pure nitric acid (to a 0.2% v/v nitric acid concentration). Multi-element concentrations were measured in these samples in 1995 and 1996 using a Perkin Elmer Elan 5000 inductively coupled plasma - quadrupole mass spectrometer (ICP-QMS). This ICP-QMS was used to determine Pb isotope ratios on a subset of the samples in 1998 (Fig. 3a). The use of this instrument indicated isotopic differences between samples, but the precision of the method was not sufficient for robust source attribution efforts.

64 of the archived samples contained sufficient volume for subsequent measurement of Pb isotope ratios and multi-element concentrations using a newer generation of ICP-MS instrumentation, a ThermoFinnigan (Bremen, Germany) Element2, high resolution ICP-magnetic sector field MS (ICP-SFMS) in 2006. The samples accounted for 97.2 % of the total precipitation volume and 97.5 % of the total Pb in the 82 precipitation samples collected from July 1994 through October 1995 at Bondville.

A method to optimize direct measurement of Pb isotope ratios from precipitation samples using ICP-SFMS without performing any additional pre-concentration or purification steps was developed for this study following suggestions provided in Krachler et al. (2004). Using the fast scanning speed operation mode, the instrument specific detector dead time was determined to be 35 nanoseconds. A narrow mass width window (10%) while scanning in the low mass resolution mode at a high scanning rate produced the flat topped peak shapes needed for optimal Pb isotope ratio measurement. Signal stability was maximized by using self-aspiration sample introduction through a cyclonic spray chamber using a sample uptake rate of $150 \mu\text{l min}^{-1}$. Detector related isotope ratio measurement inefficiencies were determined through analysis of National Bureau of Standards Standard Reference Material 981 (NBS SRM 981) and occurred when Pb concentrations were greater than 2 ppb. All precipitation samples with Pb concentrations greater than 2 ppb were diluted to 1.5 ppb during subsequent isotope ratio analysis.

To optimize the accuracy of the Pb isotope ratios measured from the precipitation samples, the NBS SRM 981 standard was analyzed before and after every precipitation sample. The average of the Pb isotope ratios from the bracketing NBS SRM 981 sample results was used to correct the Pb isotope ratios from the precipitation sample for mass bias (Krachler et al., 2004; Yip et al., 2008). The measurement of the Pb isotope ratios from each precipitation sample was repeated four times between the NBS SRM 981 runs. Each replicate included three minutes of data acquisition, resulting in a total sample consumption of 2 ml. The relative standard error from each of the four sets of measurements was averaged to determine the relative precision of the isotope ratio measurements. All isotope ratio results using the ICP-SFMS are reported with two sigma relative error bars in this study. Optimal ICP-SFMS Pb isotope ratio precision was obtained on samples with concentrations between 1.0 and 1.5 ppb, high precision results from samples with concentrations as low as 0.10 ppb were possible. Fig. 3b contrasts the results obtained with the ICP-SFMS compared to samples previously analyzed with the ICP-QMS instrument (Fig. 3a). We found this ICP-SFMS technique provided precision sufficient for a robust source apportionment analysis.

Data processing and statistical analyses were performed using SAS v.9.2 (SAS Institute, Cary, NC). The following parametric procedures were applied where appropriate to the multi-element and Pb isotope ratio results: (i) t-test for independent samples, and (ii) one-way analysis of variance (ANOVA). Two-sided tests were used unless otherwise stated. A level of significance of $\alpha=0.05$ was used for the statistical procedures.

3. Results and Discussion

3.1 Long Term Stability of Metal Concentrations in Archived Precipitation Samples

In this paper we will focus on metals and metalloids (As, Cd, Cr, Cu, Mo, Ni, Pb, S, Sb, Se, V, Zn) that can provide fingerprints for anthropogenic emission sources (Nriagu and Pacyna, 1988) in the Bondville precipitation samples. The first issue addressed was long term sample stability to determine whether samples could be archived for ten years without altering element concentrations. This concern was first assessed by analysis of bottle blanks. Following collection and acidification to $\text{pH}<2$, the original samples (bottle blanks and precipitation samples) had been archived in their original collection bottle (1 liter polypropylene) and stored in a cold room. After 10 additional years of leaching, the bottle blank concentrations of Pb (and most other elements) measured in 2006 were equivalent to the concentrations that were measured in 1996. This indicates that the bottles used to store the samples were cleaned properly (Landis and Keeler, 1997) and there was no significant long term leaching contribution of Pb (and most other elements) from the bottle to its contents. The exception was zinc (Zn). The median bottle blanks for Zn ($n=6$) in 2006 were 20% of the median precipitation sample concentrations. The source of the Zn in the bottle blanks is believed to be from the coloring agents and plasticizers used during production of the polypropylene containers.

Because the precipitation samples were archived in their original form (not filtered), there is also potential that some elements may continue to leach from the aerosols that were incorporated into the bottles during the precipitation process (e.g., particles captured during below cloud washout processes). This possibility was tested by contrasting the results from samples analyzed in 1996 and again in 2006. Based on a comparison of the analytical results, there was no significant difference between the volume weighted (vw) Pb concentrations measured in 1996 and 2006 (the ratio of the vw Pb concentrations in 2006 compared to 1996 was 1.02). This result suggests most of the Pb (and many of the other elements) in the precipitation samples were in readily soluble forms in 1996 and stayed in solution during storage. Based on results from leaching studies from aerosols collected during the LMMB study, elements from anthropogenic sources from this region are in readily soluble forms because they were either initially in dissolved form in the precipitation, desorbed from the surfaces of particulate material, or were present in particles that are readily soluble in a weak acid ($\text{pH}<2$) solution (Karajaberlian, 2001).

3.2 Metal Concentrations in Precipitation, Estimated versus Measured Fingerprints

The EPA Toxic Release Inventory (TRI) emission databases provide a means to compare emission estimates to those measured in aerosol and precipitation studies. Based on EPA TRI records, the Herculaneum, Glover and Buick smelters (all located in southeast Missouri) were major sources of stack air Pb emissions in Missouri in the 1990s. In addition to Pb, estimates of

emissions of other metals from these operations including As, Cd, Cu, Sb and Zn are available from the TRI database. Yearly emissions from stack air from Herculaneum, Glover, and Buick were composited and the results are displayed in Fig. 4a. Based on the EPA TRI records, the emissions of Pb and other metals from the smelters in Missouri were similar in the years prior to, during, and after precipitation collection in the 1990s.

Smelters are not the only point sources of metal emissions from Missouri that might be captured in precipitation samples at Bondville, Illinois. For example, the St. Louis metropolitan area contains other sources including iron and steel production and electric utility power plants (Wang et al., 2011). In some cases, emissions from these sources would likely mix with the smelter emissions prior to deposition in precipitation at the Bondville site. The EPA TRI database was used to produce a composite of stack air emissions from all point sources in Missouri (Fig. 4b). Similarly a composite profile for all stack air emissions in the United States was compiled to produce Fig. 4c. It should be noted that the EPA changed its reporting requirements in 1998. Prior to that time, emissions from the electric utility sector were not reported. This accounts for the significant increase in As and Zn emissions from 1998 onward in Fig. 4b and 4c.

To compare the predicted fingerprint to those present in precipitation, the results from measuring the concentrations of elements in the individual precipitation samples were used to calculate volume weighted (vw) precipitation concentrations on a per cluster basis (Table 1). Then these results were used to calculate the average amount of the elements in nanograms (ng) per precipitation event from each cluster (Fig. 5 a, b). This measured fingerprint includes the same suite of metals obtained from the TRI estimates (Fig. 5a) as well as other elements associated with anthropogenic processes (Fig. 5b).

The relative ranking of the elements from the US composite stack air TRI estimates is Zn>Cu>Pb>As>Sb>Cd (Fig. 4c) whereas the precipitation results are Zn>Pb>Cu>As>Sb>Cd (Fig. 5a) for five of the six clusters (the SW cluster was the exception, where Cd was greater than Sb). The higher Pb concentrations than anticipated in the precipitation samples suggests additional Pb from transportation and other non-point sources (which are not part of the TRI emissions database) contributed to rainfall concentrations (USEPA, 2000).

The smelting source fingerprint predicted by the TRI database should be reflected in enhanced contributions of Pb and Cd to the SW cluster events compared to the other clusters (Fig. 4a). To assess this possibility and better visualize the relationship between element mass per precipitation event on a per cluster basis, relative mass factors (RMF) were calculated (Fig 5 c, d). The RMF is the quotient of the element mass per event for an individual cluster and the element mass per event for all of the Bondville precipitation events minus one. Any RMF greater than zero from an individual cluster indicates an element is elevated relative to the results for all precipitation events. In this paper we will refer to RMF values greater than 0.25 as being enhanced. Based on the RMF results, the Pb and Cd mass in the SW cluster was found to be enhanced compared to other clusters (Fig. 5c), reflecting contributions from smelters in southeast Missouri.

When RMF results from other elements are examined (Fig. 5c, d), the Zn, Cu, Sb, Cr and Mo mass per precipitation event is enhanced in the NE cluster. The NE cluster corresponds to air parcels from the Chicago and Indianapolis urban corridors. Emissions from iron/steel foundries and other industrial sources including metal fabricating and plating facilities (Keeler et al., 2006, Morishita et al., 2011a, b) located in these urban areas would enhance the contributions of this group of elements to precipitation from the NE cluster. The S, Se and As mass from the SE-R cluster is enhanced compared to the other clusters, and likely reflects contributions from coal combustion sources (Keeler et al., 2006; Morishita et al., 2011a, b); whereas the enhanced V and Ni mass from the SE-R cluster could reflect contributions from oil refineries and oil-fired power plants (Keeler et al., 2006, Pancras et al., 2006) located in the Gulf Coast region of the United States. The W cluster typically contains the lowest RMF results for many elements, reflecting few upwind anthropogenic emission sources.

The predicted and measured multi-element fingerprints provided valuable insights for source attribution purposes. Pb isotope ratios may help to further refine smelting source fingerprints and better define the other sources on an event and cluster basis.

3.3 Using Pb Isotope Ratios in Precipitation to Aid in Source Attribution

There are several methods to present results from Pb isotope ratio measurements. In this paper $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios (y-axis) versus either $^{207}\text{Pb}/^{206}\text{Pb}$ or $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios (x-axis) will be used. A linear trend (or triangular field) on these plots is commonly obtained. Individual datum from coal or ore deposits often reflects the age of the Pb that was incorporated into the host material. On a $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope plot, older Pb will be found in the upper right quadrant of the diagram, and younger Pb in the lower left quadrant (Fig. 1). The decrease in $^{207}\text{Pb}/^{206}\text{Pb}$ ratios from old to young Pb reflects the difference in decay rate of the parent ^{235}U and ^{238}U isotopes. The difference in $^{208}\text{Pb}/^{206}\text{Pb}$ can reflect differences in the amount of parent ^{232}Th and ^{238}U . More thorogenic source materials generate higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. The Pb in ore deposits from Missouri (and most of the other MVT ore deposits in the United States) yields lower $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ than ore deposits from other locations. This feature yields a unique Pb isotope ratio fingerprint for processes that use MVT ore from Missouri.

When the $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ results from the Bondville precipitation are portrayed a linear trend is apparent (Fig. 6a) with the lowest ratios likely reflecting contributions from the Missouri MVT Pb source. This relation is more revealing when the isotope ratios are coded to match their meteorological cluster (Fig. 6c). Many (but not all) of the low $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios are associated with the SW flow regime.

When $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ results are examined, additional information about differences in Pb sources in individual samples and cluster groups is indicated (Fig. 6b, d). Use of the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio provides greater offset between individual data points, but this observation is tempered to some extent by lesser precision of $^{208}\text{Pb}/^{207}\text{Pb}$ ratios when compared to $^{207}\text{Pb}/^{206}\text{Pb}$ results. Nonetheless, the use of plots with $^{208}\text{Pb}/^{207}\text{Pb}$ ratios suggests several additional sources may be impacting the Bondville site during different precipitation events.

Specifically, the NE cluster precipitation samples now seem to be characterized by lower $^{208}\text{Pb}/^{207}\text{Pb}$ ratios than samples from other clusters.

Additional information to assess event based differences in contributions from sources to precipitation samples can be found by examining element ratios on an event and cluster basis versus the Pb isotope ratios (Fig. 6e and f). The lowest As/Cd and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are typically found in SW cluster samples (Fig. 6e) as anticipated for samples that contain contributions from smelters in Missouri. Higher As/Cd and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios might be expected when impacts from coal fired power plants are substantial, this seems to be reflected in several samples from the SE cluster. In Fig. 6f, V/Mo versus $^{208}\text{Pb}/^{207}\text{Pb}$ ratios are depicted. Low V/Mo and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios seem to characterize many of the samples from the NE cluster, where metal fabricating and plating industries are common. Several samples from the SW-R cluster contain elevated V/Mo and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios that could reflect the signature of long range transport of emissions from oil refining facilities. In summary, combining elemental ratios and Pb isotopes provided more information on emission source signatures than either method alone.

To aid in source attribution estimates, the vw averages for the Pb isotope ratios on a per cluster basis (Table 1), were compared. Bonferroni *t* Tests were employed to identify clusters with significantly different isotope ratios. The highest average $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ isotope ratios are found in the SW-R, SE, and SE-R clusters and the ratios from these clusters overlap in isotopic composition, as do the W and NE cluster results, whereas the result for the SW cluster yields a distinct end member in Pb isotope ratio space (Fig. 7a). The use of $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ allows the SW-R, SE, and SE-R group to be distinguished from the NE group in Pb isotope space (Fig. 7b). The SE, SE-R and SW-R sectors have slightly higher $^{208}\text{Pb}/^{206}\text{Pb}$ than the NE cluster at equivalent $^{208}\text{Pb}/^{207}\text{Pb}$ ratios. The elevated $^{208}\text{Pb}/^{206}\text{Pb}$ could reflect Pb from thorogenic sources (^{208}Pb) sequestered during coal deposit formation. The Pb isotope based results can now be coupled with multi-element concentrations and elemental ratios to suggest precipitation at Bondville is dominated by Pb isotope contributions from three source groups. The dominant sources of Pb in the SE-R cluster are likely electric utility and oil refining facilities, as indicated by a combination of enhanced S, Se, As, V and Ni mass (Fig. 5c,d), high As/Cd and V/Mo ratios (Fig. 6e,f) and thorogenic ^{208}Pb . The Pb isotope ratios in consort with enhanced Pb and Cd mass (Fig. 5c) and low As/Cd ratios (Fig. 6e) from the SW cluster reflects southeast Missouri smelter contributions, and the Pb isotope ratios from the NE cluster in consort with enhanced Zn, Cu, Sb, Cr and Mo (Fig. 5c,d) and low V/Mo ratios (Fig. 6f) reflect contributions from metal fabricating and plating industries from the Chicago and Indianapolis urban areas.

3.4 Using Results from Other Pb Isotope Studies to aid in Source Attribution

Results from other Pb isotope studies can be used to help confirm contributions from (i) industrial processes in urban areas, (ii) electric utility sources, and (iii) smelters in southeast Missouri to Pb in precipitation from Bondville. The results of this study have been combined with Pb isotope ratios from coal deposits from the United States and Pb from MVT ore deposits in Missouri in Fig. 7c, d. The coal and Missouri MVT Pb occupy distinct areas in Pb isotope space, and some of the samples from Bondville fall on a mixing line between these two sources. This result suggests that coal and Missouri MVT Pb are contributors to the isotopic signatures

from the precipitation samples. However other data points from this study have lower $^{208}\text{Pb}/^{207}\text{Pb}$ than would be expected by a binary mixture of coal and Missouri MVT Pb. The other source of Pb, which would reflect ternary rather than binary mixing in the precipitation samples, is likely an urban airshed source signature.

To assess this possibility, Pb isotope ratios from aerosols collected in the Northern Hemisphere from the studies of Bollhofer and Rosman (2001 and 2002) are plotted in Fig. 7e,f. Aerosols from urban areas in Eurasia, Mexico, Canada and the United States plot in distinct fields. The Eurasia and Mexico fields reflect greater contributions of thorogenic Pb (^{208}Pb) than the aerosols from Canada and the United States. Most of the aerosol results from Canada and the United States plot on a binary mixing trend. The differences in aerosol composition in binary Pb isotope mixing space between the United States and Canada were previously noted in studies by Sturges and Barrie (1987, 1989). They suggested the binary mixing trend reflected differences in the ore deposit sources of Pb used in gasoline additives in the two countries. Emissions from Canada reflect a greater use of Pb from Canadian ore deposits, whereas those from the United States contain a contribution from Missouri MVT Pb (Fig. 1). Because many of these aerosols were collected in urban areas, this distribution between the US and Canada likely reflects homogenization processes in urban airsheds with numerous Pb emission sources. Most of the results from this study overlap with the Canada-United States aerosol field in Pb isotope space (Fig. 7 d,f), and the Pb isotopes in the precipitation samples from the NE cluster overlap with the urban aerosols from other studies (Fig. 7b,f). This urban endmember is associated with Pb emissions reflecting past and present use of Pb from ore deposit sources including emissions from transportation, incineration and recycling facilities (USEPA, 2000). Note that Pb from many of the coal deposits from the United States would plot on the mixing line between the Eurasia and Mexico field and the Missouri MVT Pb end member in Pb isotope space (Fig. 7d,f). That is, the coal deposits from the United States have more of a thorogenic (^{208}Pb) component than the signature typical of ore deposit lead from Canada and the United States.

3.5 Using Pb Isotope Mixing Models to Quantify Source Contributions

Based on multi-element fingerprints, and Pb isotope ratios measured in this and other studies, three sources: (i) industrial processes in urban airsheds, (ii) coal combustion, and (iii) Missouri smelter emissions have been identified as contributors of Pb in wet deposition at Bondville in the mid-1990s. Following methods outlined in Gobeil et al. (1995), a three component Pb isotope ratio mixing model will be used to quantify the contribution from the smelters in Missouri versus the other sources. To use this model the Pb isotopic composition of the three endmembers needs to be constrained. There is a range in the $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios from the southeast Missouri MVT ores (Fig. 7 c,d) that might cause the Pb isotope ratios from smelter emissions to vary on a temporal basis. The average (ave) and standard deviation (sd) of the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios from the MVT ores mined in Missouri (Fig. 7d), $1.884 \pm .012$ and $2.529 \pm .015$ respectively (n=28), were used to capture the variability in the Missouri smelter emission endmember. The ave and sd of the urban aerosols from the United States (Fig. 7f) yields $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ values of $2.052 \pm .026$ and $2.448 \pm .012$ (n=30). These urban airshed values plot along a mixing line that crosses over the vw average Pb isotope ratios from the NE cluster in this study (Fig. 7b). The ave and sd of United States coal samples from Fig. 7d yields $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ values of $2.055 \pm .019$ and $2.470 \pm$

.008 (n=26). The values from these coal samples plot along a mixing line that crosses over the vw average values from the SE, SE-R, and SW-R clusters from this study (Fig. 7b). The vw average for the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotopes from all of the precipitation samples analyzed in this study, 2.007 and 2.473 respectively (Fig. 7b), was used as the isotopic mixture from which the endmember attribution was then calculated.

Solving the three endmember isotope ratio mixing equations for the composite value from all of the precipitation samples results in a Missouri smelter contribution to precipitation at Bondville of $26 \pm 13 \%$, industrial processes in urban airsheds $56 \pm 19 \%$, and coal combustion $18 \pm 7 \%$. The mixing model can likewise be solved on an individual cluster basis. The contribution of Missouri smelters to the Pb in precipitation from the SW meteorological cluster was $47 \pm 11 \%$, the St. Louis urban airshed $37 \pm 22 \%$, and coal combustion $16 \pm 8 \%$.

The emission controls at the Herculaneum smelting complex have been improved since the time when these precipitation samples were collected, and the smelter at Glover was closed in 2003. This is reflected in the large decrease in Pb emissions from Missouri smelters as reported to the TRI (Fig. 4a). Pb emissions from other sources have not decreased as dramatically (Fig. 4c), so the present day Missouri smelter contributions to wet deposition at Bondville are likely less than in the 1990s.

Conclusions

Method development using ICP-SFMS allowed Pb isotope ratios to be directly measured on precipitation samples with no need for pre-concentration or purification steps. Optimal Pb isotope ratio precision was obtained on samples with concentrations between 1.0 and 1.5 ppb, high precision results from samples with concentrations as low as 0.10 ppb were possible.

Major differences in Pb isotope ratios, multi-element concentrations, and elemental ratios were found in archived precipitation samples collected over a period of 16 months in central Illinois in the mid-1990s. These results were coupled with meteorological based cluster analysis as a means to assess source contributions from smelter derived Pb versus other anthropogenic sources.

Multi-element signatures including enhanced Pb and Cd in precipitation from the SW; Zn, Cu, Sb, Cr and Mo from the NE; and S, Se, As, V, and Ni from the SE-R meteorological cluster were coupled with differences in Pb isotope ratios to assist in source definition and attribution. Industrial sources from urban areas, and throrogenic Pb from coal use, could be differentiated from smelter emissions from Missouri by coupling Pb isotope ratios with the multi-element fingerprints. The unique Pb isotopic signature of MVT ore from southeast Missouri was used in a three endmember isotope ratio mixing model to indicate that smelters in Missouri contributed $26 \pm 13 \%$ of the Pb wet deposited in Bondville in the mid-1990s.

Because of the collection of event precipitation samples closer to smelter emission sources, the contribution of Pb from Missouri MVT ore deposits has been better defined in this regional study than those from broader scale aerosol studies. The results from this study verify that mixing Pb from Missouri MVT deposits with Pb from other ore deposits is a likely reason for the differences in Pb isotope space between aerosols from urban areas in Canada and the United

States in the 1990s. Pb isotope ratios from precipitation samples from this study also indicate Pb from thorogenic sources is released to the atmosphere during coal combustion in the United States. This thorogenic coal use signature should become more apparent as Pb emissions from primary metal production decreases in the United States.

Studies that integrate collection of stack emissions, aerosol, and precipitation samples would allow for a more process based source attribution than this archived precipitation dataset. Such studies would be a good way to couple changes in meteorological transport conditions with in cloud processing and below cloud scavenging, to assess aerosol to precipitation transfer functions.

Although emissions from point sources with distinct Pb isotopic signatures may not be common, merging strategic collection of field samples with analysis using ever improving analytical instrumentation will enable further development of coupled source attribution techniques that include use of Pb isotopes on a more routine basis.

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Figure Captions

Fig. 1. $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratios from major ore deposit mining regions from North America and coal sources in the United States. Sources of data used to construct this plot were cited in Graney et al. 1995.

Fig. 2. Precipitation events grouped into meteorology based clusters for Bondville, Illinois (from July 1, 1994 – October 31, 1995). Figure has been adapted from the Supplemental Information in Landis et al. (2002). The locations of the smelters in Herculaneum (H), Buick (B), and Glover (G) Missouri are labeled in panel f).

Fig. 3. a) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ results for Bondville precipitation using an ICP-QMS (quadrupole instrument). Error bars are 1 sigma RSE. b) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ results for the same Bondville precipitation samples as in a) using an ICP-SFMS (sector field instrument). Error bars are 2 sigma RSE.

Fig. 4. Stack air emissions reported in the EPA Toxic Release Inventory (TRI) for a) the composite of the emissions from the Herculaneum, Buick, and Glover smelters in southeast Missouri, b) all sources in Missouri, and c) all of the United States. Note emissions for the electric utility sector were not required to be reported to the EPA TRI until 1998.

Fig. 5. Volume weighted average mass of elements in precipitation in nanograms on a per event basis at Bondville, Illinois for a) elements reported in the EPA TRI database for emissions from smelters in southeast Missouri, and b) other elements common in anthropogenic air emission sources. Relative mass factors for c) Zn, Cu, Pb, As, Sb, and Cd and d) S, V, Se, Ni, Cr and Mo in rainfall events at Bondville grouped by meteorological cluster.

Fig. 6. a) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, and b) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ for Bondville precipitation samples collected between July 1, 1994 and October 31, 1995. Error bars are 2 sigma RSE. c) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, and d) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ for Pb isotope ratios from Bondville precipitation samples grouped by meteorological cluster. e) As/Cd versus $^{207}\text{Pb}/^{206}\text{Pb}$ and f) V/Mo versus $^{208}\text{Pb}/^{207}\text{Pb}$ from Bondville precipitation samples grouped by meteorological cluster.

Fig. 7. Volume weighted average Pb isotope ratios for all Bondville precipitation samples (open circle) and for each meteorological cluster for a) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ and b) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$. Ellipses indicates 1 sigma standard deviation data field for the SW cluster (black solid line), NE and W clusters (filled ellipse), and the SE, SE-R, and SW-R clusters (dot-dash line). c) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, and d) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios for U.S. coal deposits (Chow and Earl, 1972; Diaz-Somoano et al., 2009), Missouri MVT deposits (Goldhaber et al., 1995) and Bondville precipitation (this study). e) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, and f) $^{208}\text{Pb}/^{206}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios from aerosols collected from cities in Mexico, Eurasia (eastern Europe and Asia), Canada and the United States (from Bollhofer and Rosman, 2001, 2002).