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Lead speciation, bioaccessibility and source attribution in Missouri's Big River watershed

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Abstract

The Southeast Missouri Lead District is among the most productive lead deposits exploited in modern times. Intensive mining conducted prior to regulations resulted in a legacy of lead contaminated soil, large piles of mine tailings and elevated childhood blood lead levels. This study seeks to identify the source of the lead contamination in the Big River and inform risk to the public. Isotopic analysis indicated the mine tailing piles at the head of the Big River are the primary source of the lead contamination. The isotopic signature of the lead in these mine tailings matched the lead over 100 km downstream. All of the other potential lead sources investigated had different isotopic signatures. Lead concentrations in soils and sediments decrease with distance downstream of the mine tailings piles. Additionally, the speciation of the lead changes from predominantly mineralized forms, such as galena, to adsorbed lead. This is reflected in the in-vitro bioaccessibility assay (IVBA) analysis which shows higher bioaccessibility further downstream, demonstrating the importance of speciation in risk evaluation.

Keywords

Pb; Stable isotope analysis; IVBA; Source attribution; Big river watershed; X-ray spectroscopy; XANES; Mine tailings

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2020.104757>.

1. Introduction

The Southeast Missouri Lead District is historically among the most productive lead deposits in the world. According to Seeger's history of the region, the district is composed of three major sub-districts, the Old Lead Belt, Mine La Motte-Fredericktown, and the Viburnum Trend as well as several smaller sub-districts. The study area for this investigation is the Old Lead Belt which lies to the east of the Viburnum Trend and the northwest of Mine La Motte-Fredericktown. The Old Lead Belt was first mined in the 1700's, though this was limited to small scale operations going no more than 10 feet deep. Larger scale operations in the region of interest for this study started in 1864 and ran until 1972. In addition to mining operations, a lead smelter also operated in Herculaneum from 1891 until 2013 approximately 30 miles to the northeast of the Old Lead Belt on the Mississippi River (Seeger, 2008).

The lead ore in this region is primarily found as galena (PbS). There is also a substantial amount of cerussite (PbCO₃), a product of lead ore oxidation, which was also mined before large scale operations commenced. The lead deposit is a Mississippi Valley type deposit and, as such, zinc and copper were also produced from the Old Lead Belt. The major lead bearing formation is the Bonnetterre formation where the lead ore is hosted in carbonate minerals, primarily dolomite. In the Old Lead Belt this formation ranges from the surface to 300 feet below ground leading to the presence of both surface and underground mining (Seeger, 2008).

The 100 plus years of industrial scale lead mining operations with minimal regulations for nearly all of that time period has resulted in the dual problem of contaminated residential and industrial areas as well as difficulty in attributing the contamination to a specific source (Seeger, 2008). The lead mine waste was placed in large tailings piles that were often higher in elevation than the surrounding landscape, making the piles susceptible to weathering via dispersion by wind and rain (Murgueytio et al., 1998). Additionally, the tailings were used as inexpensive backfill in residential and industrial building and landscaping that spread the material in unpredictable and uneven ways throughout the area without any consistent recordkeeping (McHenry, 2006; National Academies of Sciences et al., 2017). A 1998 study determined that the mining activities resulted in children in the Big River area having twice the blood lead level of children in a control area and 17% of the children having a blood lead level above 10 µg/dL, the lower limit for lead poisoning at the time (Murgueytio et al., 1998).

The suspected source of the lead pollution are the tailings piles left behind after lead ore processing upstream of the contaminated soils and sediments. There are six major piles in the study area (Table S1), all of which have been addressed by joint or unilateral administrative orders by the United States Environmental Protection Agency (USEPA) in the last two decades (Murgueytio et al., 1998; USEPA, 2011). Another pile, Doe Run, is located south of the sampling area in the St. Francois River watershed rather than the Big River watershed. This pile has not yet been addressed by the USEPA (USEPA, 2011). The tailing piles consist mainly of the parent material, in this case dolomite, with some residual ore material that was not removed in the beneficiation process (Murgueytio et al., 1998).

The interest in the tailing piles is due to the risk they pose to public health, especially children who are most susceptible due to the severe impact lead has on neurological development and the increased exposure to soil lead via hand to mouth ingestion (Lanphear et al., 2005). When lead is ingested it must dissolve in the low pH stomach solution and be adsorbed across the gut before it can have a negative impact on an individual's health (Li et al., 2019). The fraction of the total Pb dose that crosses the gastrointestinal epithelium, becoming available to the target organs is referred to as the bioavailable fraction (USEPA, 2012). The fraction of Pb in a soil that is bioavailable is dependent on many factors including the chemical properties (eg. solubility of Pb mineral phases), physical properties of the Pb (eg. Pb encapsulation in insoluble non-lead minerals etc.) as well as the other compounds in the soil (eg. iron and phosphate) that will interfere with systemic absorption into the body (Bradham et al., 2018, 2019). As an alternative to in vivo animal assays, in vitro methodologies have been developed that measure the extent of Pb solubilization in an extraction medium that resembles gastric fluid. EPA's in-vitro bioaccessibility assay (IVBA) procedure was developed to estimate the percentage of lead that can be solubilized, becoming available for absorption into the body, or the bioaccessible fraction (USEPA, 2012, 2017).

There are two main objectives in this study. The first is to determine the source of the downstream lead contamination using lead isotope ratio analysis. The second is to inform exposure risk from lead contamination in the study area through x-ray spectroscopy to determine lead speciation and IVBA data to measure the physiological solubility of lead in contaminated soils and sediments.

2. Methods

2.1. Sampling

In total, 25 soil and 25 sediment samples were collected from the Big River watershed in St. Francois, Jefferson, and Washington Counties in Missouri (see Table S2 for location and site descriptions). The Big River often floods and deposits sediment material on floodplain soils. A total of 6 field duplicates were taken, 3 soil and 3 sediment chosen at random. The sediment and soil samples were collected between 0 and 6 inches below the ground surface where possible, using stainless steel spoons and trowels. Each soil sample was a composite of 5 different sample collection locations within an approximately 100 square foot area. Each sediment sample was a composite of 5 sample collection locations taken in a linear pattern along the edge of a stream within the area of sediment deposition. The target collection mass for each sample was approximately 250 grams (g). It was not possible to collect down to 6 inches below the ground surface at sample sites P2, P3, P5, P10, P13 and P48. The 5 subsamples at each sample site were homogenized in a plastic bag before being transferred to a glass jar for shipment. The samples were placed in a drying oven and heated to ~60 °Celsius (C) for 4 days to remove the water. Following the drying process, the samples were sieved to pass through a 250 µm (µm) sieve. Light grinding was employed to break up the large pieces of silt and clay that consolidated in the drying process, but not to reduce the size of the particles. The <250 µm fraction was used for the remaining procedures. The amount of material that passed the 250 µm sieve was highly variable

ranging from only 0.4%–65% of the total mass. The 250 μm sieve was chosen in accordance with the IVBA method. Additionally, for many of these samples, sieving the samples was a necessary step to increase the concentration of Pb and therefore the signal to noise ratio of the XANES analysis. Sieving also serves to reduce the amount of silica sand that can cause diffraction peaks in the XANES spectra rendering them unanalyzable. Size dependent fractionation was investigated previously and found to be negligible (Karna et al., 2017), though we were cognizant of the possibility.

2.2. Total metals analysis

The dried and sieved samples were digested according to EPA SW-846 Method 3051a (USEPA, 1997) for microwave assisted acid-digestion. Digestions were performed in duplicate for each sample. Each digestion batch included a digestion blank, a digestion blank spiked with a standard mix of metals, a spiked sample and a sample of National Institute of Standards and Technology (NIST) standard reference material (SRM) Montana Soil 2710a for quality assurance. The digestate solutions were analyzed using an Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES, Thermo Scientific iCAP 6500 Duo) for a suite of metals including lead (Pb), zinc (Zn) and copper (Cu). A full calibration was performed before analyzing blanks, samples and reference materials with secondary source quality control checks performed every 10 samples which had to be within $\pm 10\%$ of the known value, in accordance with EPA SW-846 Method 6010B (USEPA, 1996).

2.3. X-ray absorption near edge structure (XANES) spectroscopy

Approximately 50 mg of the dried and sieved soils and sediments were ground and pressed into 7 mm diameter pellets using a handheld pellet press. The binder polyvinylpyrrolidone (PVP) was added to allow the pellets to maintain their shape. The pellets were enclosed in Kapton tape and taken to Argonne National Laboratory for analysis at Sector 10, beamline 10-ID, of the Advanced Photon Source (Segre et al., 2000). The X-ray absorption near-edge structure (XANES) data were collected in fluorescence across the Pb L_{III} edge (13035 eV) using a Lytle detector filled with pure argon (Ar) gas. The I₀, I_T and I_{Ref} ion chambers were filled with pure nitrogen (N₂) gas. Spectra were collected in a quick scan mode (i.e., where the monochromator is continuously varied) from 12800 electron volts (eV) to 13650 eV with a measure time of 0.075 s. A minimum of twenty scans of each sample were collected. The data were then imported into the XAS analysis software ATHENA (Ravel and Newville, 2005) where the spectra were rebinned, inspected and corrected for glitches or artifacts of the electron beam movement, and merged to create the final spectrum. A linear combination fitting (LCF) procedure was then performed on the XANES region of the spectra using a library of known lead standards and minerals.

2.4. In-vitro bioaccessibility assay (IVBA)

In vitro bioaccessibility assays (EPA Method 1340) were performed in triplicate for each soil and included addition of 1 g test soil to 100 mL (mL) simulated gastric fluid consisting of 0.4 molar (M) glycine at pH 1.5 in a 125-mL high-density polyethylene bottle and rotated end over end in a water bath at 37 °C for 1 h (hr). All in vitro extraction solutions were refrigerated at 4 °C for preservation and subsequent analysis by Inductively Coupled

Plasma– Mass Spectroscopy (ICP-MS) (USEPA, 2012). IVBA was calculated and expressed on a percentage basis:

$$\% \text{ IVBA} = (\text{in vitro extractable mg Pb/kg soil} \div \text{total contaminant mg Pb/kg soil}) \times 100$$

A summary of previous research has shown that EPA Method 1340 is a well validated method for evaluating lead bioavailability in soils, which can improve accuracy in risk assessment of metal contaminated soils and sediments (USEPA, 2012).

2.5. Lead isotopic analysis

Aliquots of the digestion solution were oven dried at 60 °C and sent to a United States Geological Survey (USGS) lab in pre-cleaned Savillex Teflon tubes. Columns for Pb separation were prepared using Samco pipets (Cat #242, 8.5 cm × 2.5 mm, National Packaging Services, Inc., Secaucus, NJ, USA) with the tips cut off and fitted with Bel-Art porous frits (0.70 µm pore size, Bel-Art Products, Pequannock, NJ, USA). The columns were loaded using 0.25 mL of pre-cleaned Eichrom Sr (Eichrom, Lisle, IL, USA) specific resin (Gale, 1996; Pribil et al., 2014). The resin loaded columns were rinsed using five 1 mL aliquots of Milli-Q (Millipore Corporation) water conditioned using three 1 mL aliquots of 2M hydrochloric acid (HCl) (Seastar Chemicals, British Columbia, Canada). All chromatographic separation work was performed in Class 100 laminar flow hoods within a clean room. All samples were prepared to yield an adequate volume (10–20 mL) of solution with a final Pb concentration of approximately 20 parts per billion (ppb) after column separation. Samples received from EPA ORD were reconstituted in 0.5 ml 2M HCl and loaded on the preconditioned Eichrom Sr specific resin. The loaded samples were allowed to absorb to the top of the resin bed before rinsing with two 0.5 ml aliquots of 2M HCl, followed by an additional two 1 ml 2M HCl aliquots to remove the matrix elements. Pb was removed from the column using eight 1 ml aliquots of 6M HCl. The eluted Pb fraction was collected in pre-cleaned Savillex® vials and evaporated to dryness. The dried Pb samples were reconstituted in 10–20 mL 2% nitric acid (HNO₃) and allowed to sit overnight on a heating block prior to Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) analyses.

Lab and preparation blanks resulted in detection of less than 7 pg of Pb. Instrument performance and analytical procedure reproducibility were determined by running USGS Basalt Columbia River (USGS BCR-1) and NIST Pb SRM 981 through the sample preparation process multiple times. NIST SRM 981 (n = 32) was analyzed throughout the analysis period, both processed through the sample preparation method and unprocessed, and resulted with an average ²⁰⁸Pb/²⁰⁷Pb of 2.3698 ± 0.0004(2SD) and ²⁰⁶Pb/²⁰⁷Pb of 1.0933 ± 0.0007(2SD). NIST SRM 981 certificate value for ²⁰⁸Pb/²⁰⁷Pb is 2.370 and for ²⁰⁶Pb/²⁰⁷Pb is 1.093. The USGS reference material, BCR-1, was processed with the two individual column batches and resulted in an average ²⁰⁸Pb/²⁰⁷Pb of 2.4763 ± 0.0002(2SD) and ²⁰⁶Pb/²⁰⁷Pb of 1.2030 ± 0.0001(2SD). Multiple samples were processed through the sample preparation method in duplicate and triplicate and resulted within error for both ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb.

3. Results and discussion

3.1. Total metals

The concentration of lead in the samples collected from the Big River watershed ranged from 35 mg/kg to 37500 mg/kg (Table 1). The highest Pb concentrations generally appeared in St. Francois County above the confluence of the Big River and Mill Creek, where the suspected source areas (tailing piles) are located. From the tailing piles there is a general trend of decreasing Pb concentrations as the distance down river increases away from the tailing piles (Fig. 1). The lead concentration in sediments is plotted as a function of distance from the confluence of the Big and Meramec rivers in Fig. 1 showing the trend. The two samples furthest upstream on the Big River (Points 11 and 12) were collected upstream of the Old Lead Belt piles and have the lowest Pb concentrations out of all the sediment samples collected, indicating Big River sediment contamination is anthropogenically influenced from mining activities from the Old Lead Belt tailing piles. The same general trend is seen for copper and zinc (Table S3). In itself, the total metals analysis does not provide evidence of source attribution; however, the expected pattern for soil and sediment contamination is a decrease in contaminant concentration with increasing distance from the suspected source material (National Academies of Sciences et al., 2017).

3.2. Speciation

The results of the soil and sediment samples analyzed using the XANES region are shown on the maps in Figs. 2 and 3. The samples from the source area near the confluence of the Big River and Flat Creek show a higher degree of mineralization than the samples collected further downstream. The major minerals are the main lead ore mineral, galena (PbS), along with cerussite (PbCO₃) and anglesite (PbSO₄), products of galena weathering in an oxic environment (Gee et al., 1997). The downstream samples are mostly composed of Pb adsorbed onto lead free clay and oxide minerals. The standards library used in the LCF analysis contained spectra of Pb adsorbed on several different minerals. Those found to fit the sample spectra most often were Pb adsorbed onto the iron oxides, ferrihydrite and goethite, as well as bentonite clay. It is difficult to quantitatively differentiate between these adsorbed species at the Pb concentration present in the samples using conventional XANES; however, the difference between adsorbed species and mineral phases is easily recognizable. As a result, all adsorbed species were summed and represented as a single category “adsorbed”. While there are minor differences in the behavior of Pb adsorbed to different minerals (McKenzie, 1980), the adsorbed Pb all represents the same weathering transition from ore mineral to Pb ion to adsorbed species.

This transitional behavior of lead is expected as the lead from the galena source material and secondary minerals slowly dissolves in flowing water. Under mildly acidic to basic conditions, the dissolved lead will be removed from the water by adsorbing onto mineral surfaces. Unlike the isotopic data, using speciation data for source attribution will not necessarily show the same minerals at the source and the downstream contaminated site, but rather the final stage lead speciation will be the result of chemical transformations dictated by the environmental conditions between the source and the contaminated site. The transformation from mineral to adsorbed lead appears to occur more quickly in the soil

samples where oxygen is more available than in the sediment samples which have less access to oxygen as they are underwater and rely on the dissolved oxygen in the river.

In addition to source attribution, XANES speciation gives insight into the bioavailability of the lead and the risk it poses to the public health. Galena is not exceedingly soluble. It has been estimated that when ingested only approximately 3–4% of the lead from galena is absorbed across the gut (Davis et al., 1994). Due to their higher bioavailability, cerussite and adsorbed lead are a much greater risk to public health (Casteel et al., 2006). The stability of adsorbed lead is very pH dependent and will rapidly desorb from iron oxide minerals in the low pH conditions of the stomach, but not so in the more neutral pH in the intestines (Zhang et al., 1997). It follows that a decrease in lead concentration does not necessarily indicate a proportional decrease in hazard to public health. The lead in the sample locations downstream contain lower concentrations of lead, though in a more highly bioavailable form. An in-vitro bioaccessibility assay (IVBA) study was conducted at EPA facilities in Research Triangle Park to assess the bioavailability of the lead in the collected samples.

3.3. In-vitro bioaccessibility assay

The Pb in-vitro bioaccessibility (IVBA) values for samples collected ranges from 24 to 100% (Table 1). Sediment samples collected near the suspected source material exhibited Pb IVBA values in the range of 24–87%, while soil samples near the suspected source material ranged from 68 to 95%. Downstream from the mine piles the IVBA is above 80% for all soil and sediment samples in the Big River. These ranges are expected based on Pb speciation where a larger portion of the Pb in sediment is present as less soluble Pb mineral phases, most notably galena, near the source. As samples move downstream, Pb phases are characterized as adsorbed species with some cerussite in small amounts. These adsorbed species result in a higher Pb IVBA indicating a higher level of exposure risk to humans and ecoreceptors upon ingestion.

3.4. Isotopic analysis

Lead has four stable isotopes each resulting from a different source. Three lead isotopes, ^{206}Pb , ^{207}Pb and ^{208}Pb are the final daughter products of the radioactive decay of ^{238}U , ^{235}U and ^{232}Th , respectively. The half-lives of ^{238}U , ^{235}U , and ^{232}Th are approximately 7.04×10^8 , 4.47×10^9 and 1.4×10^{10} years respectively (Jaffey et al., 1971; Lide, 2004). There are several more decay steps for the daughter atoms before the stable Pb isotope is produced, each with its own half-life ranging from microseconds to hundreds of thousands of years, however the Pb isotope ratios are stable over the timescale of experiment. The last, ^{204}Pb , is the only non-radiogenic isotope of lead. The Pb isotopic composition of a site can be used to “fingerprint” the lead because Pb isotopes do not undergo mass dependent fractionation in the environment and the different isotopes of lead result from different initial geologic conditions (Bollhöfer and Rosman, 2001). If there is a potential source material with distinct Pb isotope ratios relative to other natural or anthropogenic sources then Pb isotopic analysis can assist in determining if the contamination originated from the suspected source (Pribil et al., 2014).

Fig. 4 shows a binary mixing plot of $^{206}\text{Pb}/^{207}\text{Pb}$ plotted against the inverse of the total Pb concentration. For a single source, the ratio should not change as a function of the lead concentration (Witt III et al., 2016). If the lead present is the result of mixed sources the ratio will change with concentration in proportion to the isotope ratios of the mixed lead sources. The group of 36 samples in the lower left portion of the chart closely clusters around the average isotope ratio of 1.3016 indicating that these samples are the result of a single source of lead and linked closely to the signature of Pb in samples collected near the tailing piles. Additionally, there appear to be two distinct mixing trends shown as well as a single outlier point. Plotting these data in a three isotope plot (Fig. 5) shows that the source signature and two identified mixing trends form two different trend lines. The results are similar independent of the isotope ratios used. Plotting the $^{207}\text{Pb}/^{206}\text{Pb}$ vs. the $^{208}\text{Pb}/^{206}\text{Pb}$ with previously published data of lead from Missouri show that the samples all fall in the range of the Eastern Missouri lead district (Fig. 6) (Witt III et al., 2016).

Displaying the Pb isotopic data on a map of the region demonstrates a clear trend (Figs. 7 and 8). Samples located along the Big and Flat Rivers starting in the vicinity of the mine operations in St. Francois County all have the isotopic signature of the tailings. In contrast, the samples identified in the mixing plot are located on Mineral Creek (21, 22) on the Big River upstream of the mining sites (11, 12), on Flat Creek upstream of the mining (13), or in the soil to the west of the Big River at the sites tested as other potential sources and background (20, 23–26, 28, 29). The only exceptions to this trend are points 27 and 29 which were taken from a tailings pond directly east of the Big River where a mixing trend is not unexpected as mine slurry from a number of sources (i.e., barite mining) was placed there (Mugel, 2017).

Several samples that do not match the source signature were taken in other lead ore subdistricts. The samples taken upstream of the suspected piles on the Big River (11, 12) are in the Irondale subdistrict, a similar, but distinct ore body just to the west of the Old Lead Belt. The Irondale pile is likely influenced by tailings from the Irondale subdistrict as well as the Bonneterre formation in the Old Lead Belt due to its close proximity to the Hayden Creek Mine in the Old Lead Belt. Point 23 is located in the Shirley-Palmer subdistrict (Seeger, 2008).

The data appear to pinpoint the source of the Big River lead contamination as the mine operations that were initially suspected in the Old Lead Belt in St. Francois County upstream of the confluence of the Big River and Flat Creek. The Pb isotopic composition of the samples taken above the mine sites is different from the samples at the mine sites and downstream. The other potential sources tested likewise show a different isotopic makeup than the mine sites at the confluence of the Big River and Flat Creek.

4. Summary and conclusion

Soil and sediment samples from 50 locations were collected in the Big River watershed and the isotopic data from all 50 indicate that the source of the contamination is the abandoned mine piles in St. Francois County. The isotopic signature remains consistent from the tailings sites in St. Francois County downstream to the mouth of the Big River. The other

proposed sources in Washington County resulted in a different isotopic composition. Additionally, it is unlikely the contamination came from ore bearing outcrops above the tailings piles as the Pb concentration in the sediment increased from ~50 mg/kg to ~12000 mg/kg upstream and downstream from the piles. The XANES speciation data supports this conclusion as the source sites have a higher proportion of the Pb mineralized as galena and oxidation products cerussite and anglesite. Moving away from the source, the lead is present in a higher concentration of adsorbed lead due to the minerals dissolving and the ionic lead adsorbing onto other mineral surfaces. The distribution of Pb species in soil and sediment is reflected in Pb IVBA results. While Pb IVBA may be lower near the source due to less soluble Pb phases, potential long-term risk could be elevated due to high Pb concentrations of redox sensitive species. Likewise, high Pb IVBA values are noted away from the source indicating up to 100% of the Pb is bioaccessible despite lower Pb concentrations, thus emphasizing the importance of lead speciation on risk to human and ecological health. The total metals analysis, while not conclusive on its own, supports the attribution of the contamination to the mine operations in St. Francois County as the concentrations are highest there and decrease going downstream.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Lead concentration (on log scale) of sediment samples taken from the Big River and Flat Creek as a function of distance from the confluence of the Big and Meramec rivers. The two points low concentration points on the right side of the plot are up-stream of the waste piles. The vertical lines indicated the point at which the indicated tributary meets the Big River.

Fig. 2.
Map of study area showing the lead speciation of the sediment samples. The pink areas are the approximate locations of the waste piles. See Table S4 for data table.

Fig. 3. Map of study area showing the lead speciation of the soil samples. The pink areas are the approximate locations of the waste piles. See Table S4 for data table.

Fig. 4.

Binary mixing plot of $^{206}\text{Pb}/^{207}\text{Pb}$ isotopes versus the inverse of the lead concentration for all soils and sediments. The clustering around the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.3 is indicative of a single Pb source, the mine tailings. There appear to be two additional mixing trends in the plot. Sample matrix is indicated by shape and sample trend is indicated by color.

Fig. 5.

Three isotope plots comparing different combinations of isotopes. All of the combinations show that the samples identified as the source signature in the binary mixing plot (Fig. 4) are closely grouped together while the others consistently form a separate trend. Sample matrix is indicated by shape and sample trend is indicated by color.

Fig. 6.

Three isotope plot of the Big River samples with data from Witt et al., (2016) (Witt III et al., 2016) study of isotopic data from Southeast Missouri with additional data taken from (Bollhöfer and Rosman, 2001; Goldhaber et al., 1995; Krizanich, 2007). Clearwater Lake is located south of the study area in the Old Lead Belt. The Viburnum Trend is located west of the study area in a different lead ore formation. Sample matrix is indicated by shape and sample trend is indicated by color.

Fig. 7.

Map of the study area showing the locations of the sediment samples color coded according to the isotopic trends identified in the binary mixing plot (Fig. 4). The pink areas in the south east are the approximate location of the waste piles. All of the samples taken from the Big River and Flat Creek below the waste piles share an isotopic signature that is distinct from the samples taken outside of that area.

Fig. 8.

Map of the study area showing the locations of the soil samples color coded according to the isotopic trends identified in the binary mixing plot (Fig. 4). The pink areas in the south east are the approximate location of the waste piles. All of the samples taken from the Big River and Flat Creek below the waste piles share an isotopic signature that is distinct from the samples taken outside of that area with the exception of points 27 and 49 which were taken from the waste impoundment resulting from Barite mining.

Table 1

Results of the total metals analysis and in-vitro bioaccessibility assay (IVBA) for Pb for all samples and field duplicates. See Table S2 for sample location descriptions and Table S5 for absolute IVBA extractable concentrations. S.D. = Standard Deviation for IVBA. FD = Field Duplicates.

Sample ID	Soil [Pb] (mg/kg)	IVBA (%)	S.D. (%)	Sample ID	Soil [Pb] (mg/kg)	IVBA (%)	S.D. (%)
P1	3009	100 [*]	2	P26	131	45	1
P2	7742	68	2	P27	369	40	1
P3 [§]	1892	83	4	P28 [§]	51	70	0
P4	1954	100 [*]	1	P29	122	38	1
P5	9790	76	2	P29 FD	112	40	1
P6	351	95	1	P30 [§]	995	92	5
P7	1105	81	0	P30 FD [§]	912	100	1
P8 [§]	1845	100	NA ^{**}	P31	990	100 [*]	0
P9 [§]	7192	87	5	P32 [§]	444	92	1
P10 [§]	12380	48	1	P33	1077	93	5
P10 FD [§]	11990	34	1	P34 [§]	1155	92	3
P11 [§]	57	34	0	P35	1042	92	1
P12 [§]	45	69	2	P36 [§]	275	89	3
P13	64	66	1	P37	1078	93	0
P13 FD	65	66	2	P38 [§]	428	89	1
P14 [§]	2356	93	10	P39	601	85	1
P15 [§]	471	91	8	P40 [§]	355	85	6
P16 [§]	751	96	2	P41	322	95	6
P17	1245	99	2	P41 FD	293	94	1
P18 [§]	1297	97	1	P42 [§]	334	94	1
P19 [§]	917	95	1	P43	388	93	2
P20	1479	52	4	P44 [§]	413	92	0
P21 [§]	169	84	1	P45	621	87	2
P21 FD [§]	168	82	3	P46	386	91	1
P22 [§]	35	80	3	P47 [§]	299	84	0
P23	460	41	0	P48 [§]	37560	24	0
P24	144	42	2	P49	1252	33	1
P25	1162	67	0	P50 [§]	4496	84	1

[§] - Indicates Sediment sample. Unmarked indicates Soil.

* Three sample had measured bioaccessible Pb concentrations that exceeded total Pb concentrations. This can result from analytical variability, especially when bioaccessible Pb concentrations are at or near 100% of the total soil Pb concentration. Bioaccessible Pb recoveries up to 120% of total Pb are considered acceptable, as these results fall within the stated EPA Method 1340 quality acceptance range, defined for duplicate samples as having a relative percent difference < 20%. The absolute % IVBA values for these three samples were 112%, 115% and 103% for samples P1, P4, and P31 respectively.

** Sample mass for sample P8 was insufficient to analyze a duplicate sample. Therefore, S.D. could not be calculated.