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Trace metals in fugitive dust from unsurfaced roads in the Viburnum Trend resource mining District of Missouri—Implementation of a direct-suspension sampling methodology

Emitt C. Witt III^{a,b,*}, David J. Wronkiewicz^{a,e}, Robert T. Pavlowsky^c, Honglan Shi^{d,e}

^a Missouri University of Science & Technology, Department of Geologic Sciences and Engineering, Rolla, MO 65409, United States

^b United States Geological Survey, National Geospatial Technical Operations Center, Rolla, MO 65409, United States

^c Missouri State University, Ozarks Environmental and Water Resources Institute, Springfield, MO 65897, United States

^d Missouri University of Science & Technology, Department of Chemistry, United States

^e Missouri University of Science & Technology, Environmental Research Center for Emerging Contaminants, Rolla, MO 65409, United States

HIGHLIGHTS

- A new cyclonic dust sampler is applied to the collection of suspended road dust.
- We measure differences in dust chemistry from 18 unsurfaced roads.
- Lead is the most abundant trace metal measured in dust from VT district roads.
- Maximum enrichment factor for Pb in VT district roads is 241.
- Fugitive dust concentrations are compared with the Federal standard.

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ABSTRACT

Fugitive dust from 18 unsurfaced roadways in Missouri were sampled using a novel cyclonic fugitive dust collector that was designed to obtain suspended bulk samples for analysis. The samples were analyzed for trace metals, Fe and Al, particle sizes, and mineralogy to characterize the similarities and differences between roadways. Thirteen roads were located in the Viburnum Trend (VT) mining district, where there has been a history of contaminant metal loading of local soils; while the remaining five roads were located southwest of the VT district in a similar rural setting, but without any mining or industrial process that might contribute to trace metal enrichment. Comparison of these two groups shows that trace metal concentration is higher for dusts collected in the VT district. Lead is the dominant trace metal found in VT district dusts representing on average 79% of the total trace metal concentration, and was found moderately to strongly enriched relative to unsurfaced roads in the non-VT area. Fugitive road dust concentrations calculated for the VT area substantially exceed the 2008 Federal ambient air standard of $0.15 \mu\text{g m}^{-3}$ for Pb. The pattern of trace metal contamination in fugitive dust from VT district roads is similar to trace metal concentrations patterns observed for soils measured more than 40 years ago indicating that Pb contamination in the region is persistent as a long-term soil contaminant.

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1. Introduction

There are hundreds of miles of unsurfaced roads (gravel, sand, and/or native loam) in Missouri's rural road maintenance program. Many of these roads are located in southeast Missouri where a leg-

acy of Pb mining and smelting has left the area with substantial Pb contamination issues (U.S. Environmental Protection Agency, 2010a). Dusts created by traveling these roads may potentially become a biohazard under numerous scenarios including but not restricted to: inhalation and/or ingestion of dust particles by occupants of vehicles, dispersal of dusts into homes located adjacent to roadways, and dispersal of dusts into soils or playgrounds frequented by children. The U.S. Environmental Protection Agency (USEPA) in collaboration with the Missouri Department of Natural Resources conducted a study in 2008 to determine the extent of Pb contamination in soils along roadways in Missouri's Pb-producing region. Portable X-ray fluorescence results show Pb concentrations

* Corresponding author. Address: United States Geological Survey, National Geospatial Technical Operations Center, 1400 Independence Road, Rolla, MO 65409, United States. Tel.: +1 573 308 3679; fax: +1 573 308 3652.

E-mail addresses: ecwitt@usgs.gov, witte@mst.edu (E.C. Witt III), wronk@mst.edu (D.J. Wronkiewicz), BobPavlowsky@MissouriState.edu (R.T. Pavlowsky), honglan@mst.edu (H. Shi).

ranging from 20 to more than 89000 mg kg⁻¹ in areas adjacent to and distributed throughout the Mark Twain National Forest along ore haul roads. Rucker (2001) also found Pb concentrations ranging from 10550 to more than 30000 mg kg⁻¹ in forest soils located within 2 km of the Buick Pb recycling smelter in Iron County, Missouri. Both Bolter et al. (1975) and Bornstein (1989) found nearly identical results for soils collected in the same locations documenting a history of Pb accumulation and persistent contamination. Studies concerning Pb contamination in the Viburnum Trend (VT) mining district were conducted during the 1970s under a National Science Foundation, Research Applied to National Needs study; however, none of these studies focused on the contamination of suspended road dust. Dorn et al. (1975) investigated Pb-dust deposition on pasture grasses that resulted in Pb poisoning of livestock, however, their results focused on deposition from the smelting operations and not recurring road dust suspensions. Furthermore, review of the literature has found only three papers that remotely focus on the chemistry of fugitive dust re-suspension from unsurfaced roadways in areas associated with resource extraction and metals processing (Kerin and Lin, 2010; Brumbaugh et al., 2011; Mandal et al., 2012). No investigations have been identified where a high-volume sampler was used to collect suspended road dusts generated by a moving vehicle.

The VT mining district is one of three major Pb-producing areas in Missouri's mineral resource producing region. The Tristate District is located in southwest Missouri and was a leading lead and zinc producer in the 1800s. The Old Lead Belt is located about 50 km to the northeast of the present study area and began crude Pb mining as early as 1720. Large-scale mining began about 1900 and production declined greatly by 1962 with the last mine closed in 1972. In 1955 a large stratabound layer of Pb and Zn was found west of the Old Lead Belt district at depth of nearly 300 m. This New Lead Belt area, the VT district, became the next primary Pb-producing area with 10 mines producing nearly 500 million tons of ore. (Seeger, 2008). The VT mining region currently produces 70% of the Nation's Pb needs and has an active secondary Pb smelter (Buick Smelter) that is currently used to recycle lead-acid batteries.

Exposure to high Pb concentrations in air-borne dust is associated with adverse effects on human health (Bellinger et al., 1991). On October 15, 2008, the Federal government promulgated a revised National Ambient Air Quality Standard for Pb. The revision strengthened the 1978 standard tenfold, decreasing the allowable concentration from 1.5 to 0.15 µg m⁻³ Pb (USEPA, 2010b). This strengthening of the standard suggests that many air contamination pathways that were previously within the Federal regulatory standard should now be revisited. Unsurfaced roads in Missouri's Pb-producing region are potentially a substantial contributor of metal contamination to the atmosphere. This has been facilitated by the large accumulation of metal particulates on soil and road surfaces for the more than 200 year legacy of mining and smelting.

The purpose of the paper is to present findings of a fugitive road dust survey where a novel sample collection device was used to ascertain the differences in dust chemistry from unsurfaced roads located both in and outside the VT mining district. Unsurfaced Roadways sampled in the VT district were randomly selected to include a combination of heavily and lightly traveled roadways that surround the extraction, ore hauling, and ore processing and smelting activities. Unsurfaced roadways outside the mining region were selected as a comparison for non-mining related dust chemistry. These comparison road reaches represent rural agricultural activities such as manure hauling, livestock routing, logging, and general residential travel that includes the transportation of children in school buses. The scope includes a description of our sampling methodology, analytical procedures, and results and discussion documenting that metal concentrations in fugitive road

dusts in the VT area exceed background levels from other rural areas and that these high concentrations may pose a health risk in relation to the Federal ambient air standard.

2. Methods and materials

2.1. Dust sample collection

Fugitive road dust samples were collected for this study using a cyclonic fugitive dust (CFD) collection system for collecting all fugitive particle sizes that become air-borne behind a moving vehicle. The CFD sampler is designed to collect a sample that provides the best estimate of human exposure because it draws a sample directly from suspension similar to mechanism for human inhalation and ingestion. A complete description of the CFD construction and preliminary assessment characteristics that include an investigation into particle sizes preferentially collected, quantity of sample collected per kilometer, and chemical variability of replicate sampling can be found in Witt et al. (2013).

The CFD sampler was deployed for this investigation by positioning the unit in the rear of a pickup truck bed so the intake reaches over the edge behind the rear tires on the opposite side of the exhaust pipe about 50 cm above the road surface. A hand-held Geospatial Positioning System unit with a track log setting is used to record the distance, speed, and location of sample collection. At the conclusion of the sampling event, the sample was transferred from the 10 L collection container to a labeled certified acid-washed 118 mL storage container. All field notes were cross-referenced with labeled sample storage containers prior to placing in a clean dry cooler for transport to the laboratory. Between sample collection events, the entire unit was dismantled for washing and acid-rinsing (5% HNO₃) of the cyclone, replacement of the PVC intake, and cleaning of the vacuum intake.

Samples were collected from eighteen unsurfaced roads in rural southern Missouri (Table 1 and Fig. 1). Five of 18 samples were collected to the west of the VT district to represent fugitive dust sources not influenced by proximal mining and smelting activities. One of these five control samples was collected in replicate 9 times to test the variability and representativeness of the CFD collection process (Witt et al., 2013). The remaining 13 samples were collected in the VT district from randomly selected unsurfaced roads surrounding the mining, processing, and smelting activities. All samples were collected over several months from June to November 2011 only during periods of extended dry weather to optimize the quantity of sample collected. Collection distances varied from 5.63 to 24.8 km and in some cases a road was traveled two or more times to obtain the largest possible sample (Table 1). Between 6.0 and 36.6 g of dust were collected from each road reach and no further preparation of the sample (drying, sieving, and sorting) was done before analysis. Results presented here required about 3 g of sample to be distributed as aliquots among the various analytical techniques. The remaining portion of the sample was archived for any potential future study.

2.2. Sample digestion and analysis

Cyclone collected particle samples were analyzed at the Missouri University of Science & Technology (MS&T) Environmental Research Center for Emerging Contaminants (ERC) laboratory for the elements Fe, Al, Pb, Zn, Co, Ni, Cu, Cd, and As. For each sample and standard reference material, approximately 0.5 g of material was weighed accurately and added to 50 mL acid washed disposable digestion vessels and digested using method 200.2 (USEPA, 2003). This extraction method uses hot hydrochloric and nitric

Table 1
Collection specifications and results for unsurfaced road reaches in Missouri.

Reach#	Location (beginning Latitude/Longitude)	Location relative to Smelter	Distance sampled (km)	Dust mass sampled (g)	Air volume processed (m ³)	Sum of trace metals (mg kg ⁻¹)	Pb fraction (%)	XRD mineral phases	EF _{Pb}	FRD (μg m ⁻³)	EF _{AAS}
1	N 37° 52.06', W 091° 46.74'	Non-mining	22	12.3	166	23.7	18.1	Q, D	–	0.45	2.13
2	N 37° 57.26', W 092° 0254'	Non-mining	24.8	13	215	23.7	27	Q, D	–	0.39	2.58
3	N 37° 38.89', W 091° 05.74'	3–12 km E	23.5	33.3	193	148.3	34.2	Q, D	2.00	8.70	58.2
4	N 37° 38.81', W 091° 09.10'	3–11 km NW	15.3	27.7	138	5304	86.5	Q, D, PC	241	919	6131
5	N 36° 62.05', W 092° 26.94'	Non-mining	18.7	22.5	166	49.6	31.6	Q, D	–	2.13	14.2
6	N 36° 39.38', W 092° 14.48'	Non-mining	19.9	11.5	166	49	24.3	Q, D	–	0.83	5.51
7	N 37° 36.30', W 091° 10.07'	5 km S-SW	19.3	6.73	152	154	55.3	Q, D, C?	6.39	3.77	25.1
8	N 37° 34.54', W 091° 10.11'	10 km SW	23	15.9	202	69.2	38.2	Q, D, C?	2.41	2.07	13.8
9	N 37° 35.73', W 091° 08.24'	15 km SW	20.6	19.2	139	66.7	55	Q, D	2.91	5.04	33.6
10	N 37° 33.99', W 091° 03.41'	10–15 km E	22.8	16.9	204	123	37.6	Q, D	3.71	3.83	25.5
11	N 37° 32.20', W 091° 03.87'	6–12 km S-SE	20.4	13.2	188	101.2	57.8	Q, D, PC?	4.23	4.11	27.4
12	N 37° 40.21', W 091° 04.23'	7 km NE	18.5	13.9	160	202.5	46	Q, D, PC?	5.36	8.08	53.9
13	N 37° 40.28', W 091° 04.05'	10 km NE	20.1	17.1	185	437.9	75.6	Q, D	21.4	30.7	204
14	N 37° 44.52', W 091° 07.02'	15 km NW	23.8	36.6	196	68.3	57.5	Q, D	1.82	7.35	49.0
15	N 37° 48.31', W 091° 08.46'	20 km NW	20.8	26.5	180	75.1	51	Q, D, PC?	2.13	5.63	37.5
16	N 37° 48.55', W 091° 06.42'	20 km N	17.8	21.8	200	84.2	49.9	Q, D, PC?	2.16	4.57	30.5
17	N 37° 42.05', W 091° 08.05'	7 km N-NW	10.9	19	107	120.4	50.9	Q, D, PC?	4.58	10.9	72.8
18	N 36° 62.05', W 092° 26.94'	Non-mining	5.63	6	82.8	42.3	27.8	ND	–	0.90	6.02

EF_{Pb}, enrichment factor for Pb in sample; EF_{AAS}, exceedance factor for Pb in air; FRD, Fugitive Road Dust concentration; Q, quartz; D, dolomite; C, chalcopyrite, PC, cerussite; ND, no data.

acids to partially digest dry samples for the determination of trace element concentrations with the exclusion of acid resistant silicate bound metals.

The trace elements Pb, Zn, Co, Ni, Cu, Cd, and As were measured with a model Elan DRCe ICP-MS instrument (PerkinElmer SCIEX, Norwalk, CT, USA) equipped with a cyclonic spray chamber, a

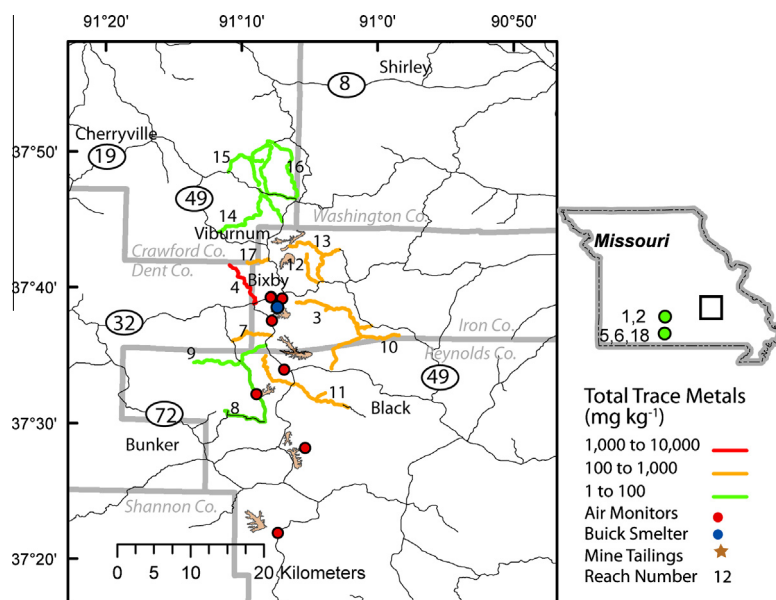


Fig. 1. Map showing location of unsurfaced road reaches sampled in the VT district comparing total trace metal concentration. (County boundaries are from 2009 Census TIGER/Line release; mine tailing ponds and air monitor stations are from the Missouri Department of Natural Resources; and State roads are from 2011 TeleAtlas. Map compiled using ESRI ArcMAP version 10.1 and Adobe Illustrator CS5.1.).

Meinhard nebulizer, and platinum cones. Quantitation was performed using a standard calibration mixture and internal calibration method by continuous online addition of internal standards. The elements Fe and Al were measured using a Perkin Elmer Optima 2000 DV ICP-Optical Emission Spectrometer. Digestion extracts were appropriately diluted for all dust samples and standard reference materials before analysis.

Laboratory quality control included measurement of blanks, standards, and duplicates. All digestion vessels, lids, watch glasses, and extract containers were soaked in 5% HNO₃ for 24 h, rinsed with trace element grade de-ionized water and allowed to air dry before using. All laboratory consumables were used only once and discarded. National Institute of Standards and Testing standard reference materials SRM2711 and SRM2587 were analyzed in triplicate to assure method recovery and measure the variability of the analytical process. Pb had the largest variability of all trace metals measured with relative standard deviations for SRM2711 and SRM2587 of 0.36% and 1.5%, respectively.

ICP-MS calibration standards with concentrations of 0.02, 0.1, 1, 10, and 50 µg L⁻¹ were measured in triplicate resulting in good linearity ($R^2 = 0.9999-1$) for all elements. The 1 and 10 µg L⁻¹ standards were measured for every 10 samples, with accuracy ranging from 1 to 6.3% for all trace elements. ICP-OES accuracy determinations for the 1 and 10 mg L⁻¹ standards were better than 5% for Al and 7% for Fe.

For solid phase analyses, Scanning Electron Microscopy–Energy Dispersive Spectra (SEM–EDS) were acquired using a Hitachi S-4700 and Genesis EDAX system located at the MS&T Advanced Materials Characterization Laboratory. These analyses were conducted in a standardless mode. In addition, all dust samples were analyzed with a PANalytical X'Pert Multi-Purpose X-ray diffractometer (XRD) utilizing a Cu K α source and a PIXcel Detector. Data was collected over the angular range of 2–60° two-theta with a step size of 0.026° and a counting time of 196 s per point. Peak intensities were matched against a current library of mineral spectra to identify potential phases.

2.3. Particle size analysis

Particle sizes were determined for each sample from five randomly selected images collected using the SEM. Samples were prepared by suspending small aliquots of dust in ethanol and pipetting drops onto SEM stubs covered in double-sided carbon adhesive tape. After a short period of drying, samples were sputter coated with gold–palladium (Au–Pd) for a sputter time of 120 s to reduce charging effects.

Imaging conditions during SEM–EDS analysis included a 15 kV accelerating voltage, 10.5 nA emission current, 12.3 mm working distance, and zero degree tilt. All images were acquired at about 1500 times magnification. Particle size was measured manually using the ImageJ software (National Institute of Health, version 1.44p) by measuring the longest axis of all clearly visible particles (maximum Feret diameter) in each of 5 randomly selected sample images. A total of 85 images were used for analysis.

3. Results and discussion

3.1. Sample representation

Fugitive dusts analyzed for this effort were exclusively suspended, mostly non-spherical particle sizes >1 µm. Particle shapes are highly variable ranging from grains of galena that display cubic to rounded weathered surfaces, platy clay particles, highly weathered irregular dolomite, and flaky chert fragments (images in Supplemental Data). Median particle diameters for these samples

ranged from 4.49 to 18.9 µm. By comparison, the mass median diameter of particulates captured from fugitive dust generated by the Buick smelter varied between 7 and 11 µm for Pb; 1.5 and 2.5 µm for Cu; and 2 and 4 µm for Zn and Cd (Wixson et al., 1975). This suggests that the particle sizes collected by our cyclone sampler contain the range of particle sizes derived from smelter emissions in 1975. The collection height of 50 cm above the road surface was optimal for particles remaining in suspension for 15 or more seconds. It has been demonstrated that Pb particles <10 µm can remain suspended in the atmosphere for fugitive movement (Van Der Hoven, 1968).

3.2. Trace metal variation

Road reaches 1, 2, 5, 6, and 18 represent road surfaces that are in rural areas distant from the VT district, but are still underlain by Cambrian–Ordovician carbonate bedrock. Road reaches 1 and 2 are located about 74 km west and reaches 5, 6, and 18 are about 185 km southwest of the VT district and are not located near any manufacturing or other industrial processes that might contribute large quantities of Pb or other trace metals to the environment. Dust from these road reaches have lower trace metal concentration with respect to VT district samples and represent background levels for common unsurfaced roads in rural Missouri's non-mining areas (Fig. 2). Zinc was the dominant trace metal for all non-VT district road reaches and ranged from 4.7 to 32.7 mg kg⁻¹ with the largest concentration measured for reach 6. Lead ranged from 4.3 to 15.7 mg kg⁻¹ and was highest in reach 5. With the exception of Ni and As, these results are below median background concentrations for more than 77000 stream sediment and soil samples randomly collected throughout the United States (U.S. Geological Survey, 2004). XRD and SEM–EDS analysis suggest that non-VT road reaches have the same general mineral composition as roads in the VT district with the primary mineral components being dolomite and quartz (Table 1).

Road reaches sampled in the VT mining district include 3, 4, and 7–17 and are broken into three major categories of trace metal enrichment (Fig. 1). The 1–100 mg kg⁻¹ category includes unsurfaced road reaches 8, 9, 14–16 and represent the lowest trace metal concentration in the mining district region. The 100–1000 mg kg⁻¹ category represents more substantial trace metal enrichment and includes reaches 3, 10, 11, 12, 13, and 17. Reach 4 was the outlier unsurfaced road that fell into the >1000 mg kg⁻¹ category. In general, road reaches that were closest to the active secondary smelter had higher concentrations of Pb, Zn, Cu, and Cd while those more distant had lower concentrations. XRD results suggest that road

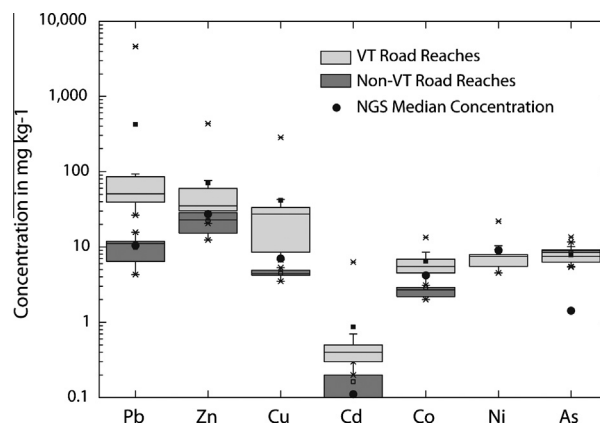


Fig. 2. Combined boxplots comparing range of trace metal results for unsurfaced road reaches located in and outside the VT district with median concentrations from the USGS National Geochemical Survey (NGS) (U.S. Geological Survey, 2004).

reaches 4, 11, 12, and 15–17 contained cerussite (PbCO_3) as a possible mineral phase in addition to the dolomite and quartz phases that dominate all samples. Cerussite has been found among weathered surface deposits of Pb ore in the region and can also be a byproduct of the smelting process (Arseneau, 1976; Seeger, 2008).

Road reach 4 represented the outlier total trace metal concentration and ranked highest with regard to Pb, Zn, Cu and Cd concentration. Soil samples collected along this road reach in earlier studies record Pb concentrations ranging from 23 to 155 mg kg^{-1} , with concentrations on top of leaf litter ranging from 290 to 28000 mg kg^{-1} (Wixson et al., 1975). The same study also determined a general north–south elongated distribution of elevated trace metal concentration with respect to the smelter due to prevailing wind patterns for the area. During the period when the smelter was the primary processing plant for Pb ore in the VT district (1968–1986) it was responsible for producing about 100000 short tons of Pb annually with about 100–200 tons of particulate matter being lost to the surrounding forested area (Wharton, 1969). From 1972 to 1974 the suspended particulate Pb around the smelter ranged from 0.73 to 6.27 $\mu\text{g m}^{-3}$, and settleable particulate Pb from 20 sampling stations ranged from 37 to 2081 mg m^{-2} (Wixson et al., 1975). The average Pb concentration for two air monitoring stations operated from 1993 to 2008 range from 0.35 to 2.55 $\mu\text{g m}^{-3}$ with a maximum 24-h concentration of 16.0 $\mu\text{g m}^{-3}$ (MoDNR, 2012). This suggests that a depositional trace metal component is still available and is probably impacting the area near reach 4.

Other possible sources of trace metal enrichment that can potentially affect fugitive road dust in the VT district are smelter slag applications to roads, spillage from ore hauling trucks, and road resurfacing using mine tailings. Dorn et al. (1975) notes the use of smelter slag as road resurfacing and de-icing material in the VT district and Hemphill et al. (1974) investigated spillage and mine tailings as a possible contributor to roadside trace metal enrichment. Our study identified chalcocopyrite (CuFeS_2) by XRD in dust from road reaches 7 and 8 suggesting ore spillage may be a possibility. Cubic galena (PbS) was observed by SEM-EDS in gravity separated samples for reach 4. Fig. 3 shows one such particle with

possible anglesite (PbSO_4) and cerussite (PbCO_3) as secondary minerals forming within the weathered pits of the particle.

3.3. Pb in fugitive road dust

Pb represents an average of 79% of the total trace metal composition in fugitive dusts from VT district unsurfaced roadways. To determine the geochemically normalized enrichment of Pb relative to background, we calculated an enrichment factor for each VT district roadway using an average of the five non-VT district road reach Pb concentrations as background according to the following equation:

$$EF_{\text{pb}} = \text{Pb}_{\text{sample}} / \text{NB} \quad (1)$$

where $\text{Pb}_{\text{sample}}$ is the ratio of the Pb to Fe + Al concentrations of the fugitive dust sample and NB is the normalized average Pb concentration for non-mining impacted reaches 1, 2, 5, 6, and 18. Fe and Al were used as the conservative normalizing elements because they are relatively unchanged in a horizontal transect of local soils and are not enhanced by the activity of mining, processing, and smelting in the VT district and by agricultural and rural pedestrian conveyance in the non-mining areas. Ghrefat and Yusuf (2006) used Fe as a conservative geochemical normalizing element and note that several authors have successfully used Fe, Al, and Si to normalize the heavy metal concentrations for enrichment determinations. In this study, EF_{pb} values between 0.5 and 2.0 represent concentrations not substantially different from background, those between 2.0 and 10 suggest moderately enriched Pb, and EF_{pb} values exceeding 10 are considered strongly enriched. Sample reaches 7–12 and 15–17 in the VT district have EF_{pb} values indicating moderately enriched Pb concentrations relative to background. Reaches 13 and 4 were the most contaminated samples with enrichment values of 21 and of 241, respectively (Table 1).

To convert sample concentrations to air concentration for comparison with the Federal ambient air quality standard, a Fugitive Road Dust concentration (FRD) for each sample was calculated according to the following equation:

$$\text{FRD Concentration} = M_{\text{sample}} \times C_{\text{sample}} / V \quad (2)$$

where M_{sample} is the mass of sample collected in g, C_{sample} is the concentration of Pb in $\mu\text{g g}^{-1}$, and V is the volume of air processed in m^3 . Exceedance factors in the atmosphere relative to the Federal ambient air standard (EF_{AAS}) for each reach were calculated from the FRD concentration by dividing these concentrations by 0.15 $\mu\text{g m}^{-3}$ (Table 1). All sampled unsurfaced roads exceeded the Federal standard with an EF_{AAS} of more than 2. This primarily results from the higher concentration of Pb-laden particulate material suspended from unsurfaced roads relative to industrial emissions for which the Federal standard was developed. Non-VT unsurfaced road FRD concentrations ranged from 0.3 to 2.13 $\mu\text{g m}^{-3}$ and VT road reaches ranged from 2.07 to 919 $\mu\text{g m}^{-3}$. With the exception of reaches 4 and 13 having high concentrations of Pb, most VT unsurfaced roads produced FRD concentrations in the range from 1 to 10 $\mu\text{g m}^{-3}$.

Comparison of sample concentration with mass per reach, collection distance, and air volume processed suggests Pb concentration in the sample is a good indicator of Pb concentration in the air (Fig. 4). However, variability in sampling conditions can influence the resulting concentrations observed for a road reach. Comparisons between the air volume collected and distances traveled as well as the dust per air volume and dust mass per distance have indicated that variations in average speed and in dust generation from road surfaces can influence the calculated air-Pb concentration. Nevertheless, this methodology provides a reasonable characterization of fugitive road dust chemistry.

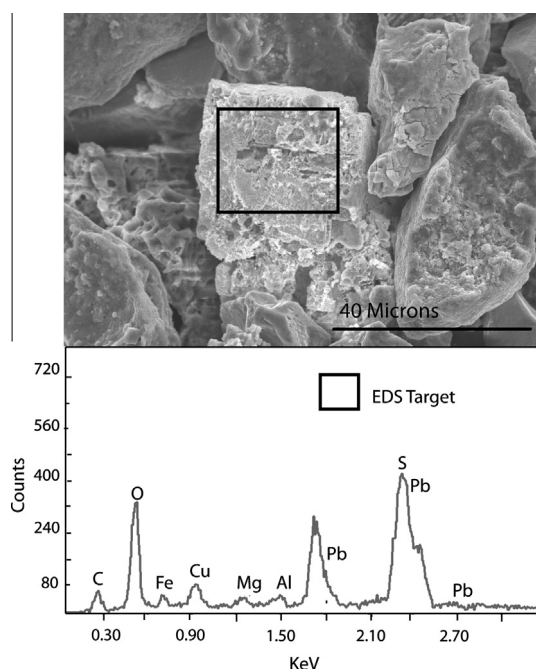


Fig. 3. Scanning electron microscope image and energy dispersive spectrum of a weathered galena particle gravity separated from sample reach 4.

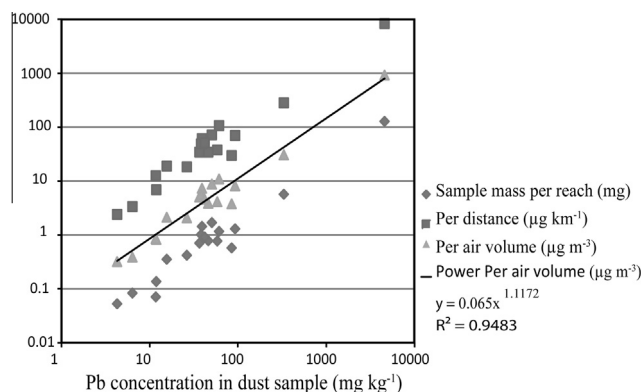


Fig. 4. Comparison of sample mass, distance sampled, and air volume processed in relation to Pb concentration observed in dust samples.

The EF_{AAS} of Pb in air relative to the Federal standard is divided into three severity rankings. EF_{AAS} between 1 and 15 is characteristic of Pb for unsurfaced roads reaches in our selected non-VT area where concentrations in the dust sample are within background levels, but suspension effectively increases contaminant particle concentration. EF_{AAS} ranging from 16 to 100 is characteristic of most unsurfaced roads in the VT area; however, as seen in the case of reaches 4 and 13, there are extreme cases where historic use and location relative to the smelter have created conditions for severe enrichment of Pb in suspended dust. Even minimum exposure to fugitive dust from reach 4 could have substantial health implications. An adult at rest inhaling about 12 L min^{-1} of this dust-laden air could potentially receive an inhaled Pb dose of about 0.02 mg km^{-1} while traveling behind a vehicle on reach 4. Depending on the bioaccessibility of this exposure, this level could potentially increase blood-Pb concentrations of those traveling and/or living along such roads in the VT area or in similar environments globally.

4. Conclusion

The 234 km of unsurfaced road sampled within the VT district showed variable trace metal concentrations ranging from 66.7 to 5304 mg kg^{-1} . The distributions of Pb, Zn, Cu, and Cd are preferentially enriched along a north–south pattern from the Buick Smelter, with the larger concentrations observed for roads closer to the smelter. This is similar to findings of past investigators studying adjacent forest soils, suggesting that trace metal and in particular Pb contamination is persistent in the environment. Moderate to strong enrichment of Pb is observed for all road dusts in the VT district relative to those outside the region. The results of this work suggest there is a potential health concern that deserves further investigation, and that the application of this sampling method to other potentially contaminated regions where unsurfaced roads predominate is warranted.

Our preliminary investigation of contamination has identified galena, chalcopyrite, cerussite, and possibly anglesite. Future study is warranted for specific contaminated sites to determine potential mobility and bioaccessibility of contained metals. Isotopic analysis combined with mineral analysis also may be useful for delineating potential metal sources. An investigation into the blood-Pb levels of residents living along or routinely traveling these roads could link the results of Pb-dust concentrations to human health criteria. Given the profound health concern for Pb in the environment, this additional research will enhance the body of information presently available on environmental Pb contamination allowing regulators to prioritize regions for cleanup, identify applicable and cost-effective

remediation technologies, and determine relative proportions of contaminants derived from local sources.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.04.012>.

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