GEOCHEMICAL MAPPING OF Cd, Pb AND Zn IN THE TRI-STATE MINING DISTRICT OF MISSOURI
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ABSTRACT
Four locations in southwest Missouri purportedly contaminated with mining wastes, Joplin, Aurora, Springfield and the James River, were investigated for lead and zinc content using spatial and statistical analyses. The content of Pb and Zn concentrations in sediment samples was compared spatially against a regional background concentration map to determine both the contamination level and dispersion of these metals.

National Geochemical Database was extracted, and thus, 1,019 data points were plotted within the study area for meaningful statistical purposes. Concentrations of Pb and Zn in Joplin and Aurora were significantly higher, while the concentrations of Pb and Zn at the two sites near Springfield were lower than that obtained with water samples.

Sediment geochemical data contained total metal content data, since they were collected to primarily fill a spatial gap. The conventional analytical procedure is a digestion of the air-dried sieved solid with aqua regia, (HCl-HNO3) followed by element analysis using an inductively coupled plasma mass spectrometer (ICP-MS).

METHODS
Stream sediment data were retrieved from USGS Geochemical Database (USGS 2018) with which sediment geochemical maps were constructed. Publicly available metal content data for each of four historic mining sites were also retrieved from separate studies. The Pb and Zn concentrations at each of the historic mining sites were compared against background concentrations using geochemical mapping interpolation (IDW method), box plot diagrams, Pearson correlation and rationing.

RESULTS
The contamination is more severe in sediments of and near urban areas of Joplin and Aurora and these deposits have not yet been dispersed but remain relatively well contained. Certain thresholds have been established for residential soils and restoration action, but not yet for sediments. Some formal and informal guidelines are listed in Table 2 below.

Table 1 Selected parameters used to differentiate Pb, Zn content and their associations at each of the four historic mining sites. In this context, % anom is the percent outliers (samples above the upper hinge value in the box plot analysis of background data 49.5 mg kg⁻¹ Pb and 136.5 mg kg⁻¹ Zn).

<table>
<thead>
<tr>
<th>Location</th>
<th>Pb (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
<th>% anom</th>
<th>Pb/Zn (mg mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Joplin</td>
<td>237.0 ± 0.0</td>
<td>100. ± 0.0</td>
<td>100</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Aurora</td>
<td>232.0 ± 0.0</td>
<td>8.9 ± 0.0</td>
<td>100</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>Springfield</td>
<td>327.0 ± 0.0</td>
<td>6.4 ± 0.0</td>
<td>100</td>
<td>0.0 ± 0.0</td>
</tr>
</tbody>
</table>

Pb and Zn were present in a large range of values in the regional background data (values up to 3,460 mg kg⁻¹ Pb and 14,027 mg kg⁻¹ Zn) with a median of 22.0 and 53.0 mg kg⁻¹ respectively.

CONCLUSIONS
Even though mining ceased over 40 years ago and remediation has been applied to the area, some sediments in the area contain potentially toxic concentrations of Pb and Zn, especially around the cities of Joplin and Aurora. The background geochemical maps of the area were instrumental for identifying the sources and extent of these metals in sediments in this area.

SEDIMENTS AS ENVIRONMENTAL INDICATORS
Geochemical analyses of sediment have been used by numerous investigators in studying contaminant impact on streams. Sediments integrate contaminant concentration over time, rendering a long-term picture of the effects of e.g. mining, agriculture and urbanization than that obtained with water samples. Our sediment geochemical data contained total metal content data, since they were collected to primarily fill a spatial gap. The conventional analytical procedure is a digestion of the air-dried sieved solid with aqua regia, (HCl-HNO₃) followed by element analysis using an inductively coupled plasma mass spectrometer (ICP-MS).

THE TRI-STATE MINING DISTRICT
The Tri-State Mining District includes parts of Kansas, Missouri, and Oklahoma and encompasses an area of a little more than 3,000 km² (Brockie et al. 1968), with lesser satellite deposits that extend to the east. The TSMD was first mined for lead in the mid-1800s but soon became a major producer of zinc. Pb and Zn were first mined in the 1800s from the surface to a depth of about 50 m, with mining activities in the Missouri part of TSMD ending around 1950 (Brockie et al. 1968; Besser et al. 2009). All of these metals are known to be toxic to birds and to aquatic life. Although less abundant than Zn in the TSMD ore, Pb is very important for environmental reasons because of its higher toxicity and for having polluted sediments and aquifers in the TSMD (USEPA 2012). Pb is a metal of concern too because of its toxicity (Batagelj et al. 2003) and its close association with zinc in the TSMD (Brockie et al. 1968).

MSU theses have investigated the metal content in key areas (mining towns). These include Trimble (2001), Fredrick (2001), Rodgers (2005), Kothenbeutel (2006), Trimble (2008), and Pfeiffer (2013), and Theses include Trimble (2001), Fredrick (2001), Rodgers (2005), Kothenbeutel (2006), Trimble (2008), and Pfeiffer (2013).

REFERENCES
Kothenbeutel J. 2006. Geoscientific investigation of sedimentary contamination in Chat Creek watershed, southwest Missouri, M.S. Thesis, Missouri State University, Springfield, MO.

MINERALIZATION
Although less abundant than Zn in the TSMD ore, Pb is very important for environmental reasons because of its toxicity and for having polluted sediments and aquifers in the TSMD. Cd is a metal of concern too because of its toxicity (Batagelj et al. 2003) and for having polluted sediments and aquifers in the TSMD (USEPA 2012).

WATERSHEDS
The contamination is more severe in sediments of and near urban areas of Joplin and Aurora and these deposits have not yet been dispersed but remain relatively well contained. Certain thresholds have been established for residential soils and restoration action, but not yet for sediments. Some formal and informal guidelines are listed in Table 2 below.

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