Soil Heavy Metal Contamination in Baia Mare, Romania: An Exploratory Study

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ABSTRACT
Soil pollution with heavy metals is a common environmental concern in many Eastern European towns where ore extraction and refinement historically occurred. Pollution from these activities was often dispersed over larger areas by sending smoke and dust up large dispersant smokestacks. Today, the pollution remains in the soil, posing health threats to residents; many of whom have no idea of the danger underfoot. This pilot study was undertaken to determine the viability of using portable x-ray fluorescence spectrometry for rapid assessment of soil heavy metal concentrations in-situ. Seven soil samples were evaluated at the abandoned smelter site and showed the soils were rife with pollution. Both Cu and Pb were more than 30 times the Romanian action limit for remediation; Zn was five times the action limit. As such, a high resolution survey will be undertaken in the summer of 2015 whereby 100-150 points will be scanned, high resolution maps of pollution rendered, and association with documented health problems (developmental delay, mental retardation, cancer, etc.) will be undertaken.

Keywords: Heavy Metal, X-ray fluorescence spectrometry, in-situ

Soil pollution is among the most pervasive problems denuding soil health in parts of Eastern Europe. For many decades, mining, ore extraction/refinement/smelting, and petrochemical processing produced toxic dust and smoke; substances which were emitted into the atmosphere and settled all across many localized villages. A limited number of research studies have identified the impact of heavy metal upon soils (Damian et al., 2008; Ene et al., 2010), vegetation (Mihăiescu et al., 2011), animals (Lăcătuşu et al., 1996), even people (Neamţiu and Gurzău, 2009). Krüger and Carius (2001) identified 14 villages and small cities in rural Romania rife with environmental pollution. These include: CopşaMică, Baia Mare, Zlatna, Ploieşti-Brazi, Onesi, Buciu, Suceava, Petesti, TârguMures, TurnuMagurele, Talcea, Isalnita, Brasov, and Govora.
Figure 1. Scanning remnant industrial spoil left unsecured at an abandoned smelter facility with portable x-ray fluorescence spectrometry in Baia Mare, Romania.
Approximately 5.3% of Romania’s total population lives in these heavily polluted areas, often at periurban agricultural interfaces. In addressing these persistent threats to soil health, the Romanian Ministry of the Forest, Waters, and Environment (1997) issued government mandated action limits for soil elemental concentrations as follows: Cu (200 mg kg$^{-1}$), Mn (2500 mg kg$^{-1}$), Pb (100 mg kg$^{-1}$), V (200 mg kg$^{-1}$), and Zn (600 mg kg$^{-1}$).

Baia Mare is a city of ~123,000 residents in Maramures County, in northern Romania. The city is near the Gutâi and Ignis Mountains with some elevations reaching 1,400 m. Precipitation of the area is ~1000 mm y$^{-1}$. The Sâsar River bisects the northern part of the city, running from east to west. Near the eastern side of town, the Phoenix copper smelter features a 352 m smokestack constructed in 1995; the stack is the tallest freestanding structure in Romania. The facility has since been decommissioned and left in a state of disrepair, with gypsies commonly scouring piles of rubble by hand in search of remnant ore or scrap they can sell for profit (Fig. 1).

Two limitations plague many previous research studies in Romania concerning heavy metal assessment in soils: (1) limited sampling numbers, and (2) improper analytical techniques. Paulette et al. (2015) summarize several studies prone to these types of limitations (e.g., Damien et al., 2008; Oros et al., 2009; Ianculescu et al. 2009). They note several projects whereby fewer than 50 samples were used for various research studies. Also, such studies commonly employ the use of nitric and/or hydrochloric acids which only afford partial digestion of soil; thus, not a total digestion (USEPA 1996a; 1996b). As such, our study utilized portable x-ray fluorescence (PXRF) spectrometry to scan several soils at the smelter site in-situ. PXRF is now widely recognized as a quality analytical approach for elemental quantification in soils (USEPA, 2007; Soil Survey Staff, 2014). Previous studies have successfully used PXRF for in-situ assessment of heavy metal pollution in soils worldwide (Carr et al., 2008; Clark and Knudsen, 2014). Insidiously, heavy metals cannot be seen or smelled in polluted soils. Thus, threats to human health require high resolution maps of contaminants such that the public can be protected from dangerous metal contamination. Once maps of pollutants are rendered, impacted areas can be cordoned off, removing them from public access. In an effort to determine whether pollution at Baia Mare, Romania is sufficient to warrant a full scale study with widespread scanning and analysis, the present study was undertaken as a pilot study to evaluate the most polluted soils near the smelter facility. As such, the objective of this research was to use PXRF to determine heavy metal contents in soils near the smelting facility in Baia Mare, Romania as preliminary data to justify or discount the need for future in-depth study.

**Materials and Methods**

Scanning of soils at the Phoenix copper smelter facility were conducted on-site in July, 2014. Seventeen sites were scanned using a DP-6000 Delta Premium PXRF (Olympus, Waltham, MA, USA), generally in accordance with Method 6200 (USEPA, 2007). The instrument features a Rh x-ray tube which operates at 10-40 keV; quantification is made
Table 1. Elemental concentrations of contaminated soils at a smelter site in Baia Mare, Romania determined by portable x-ray fluorescence spectrometry.

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu</th>
<th>Mn</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>293</td>
<td>142</td>
<td>351</td>
<td>55</td>
<td>217</td>
</tr>
<tr>
<td>3</td>
<td>15423</td>
<td>568</td>
<td>5202</td>
<td>188</td>
<td>3811</td>
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<tr>
<td>4</td>
<td>1902</td>
<td>345</td>
<td>1467</td>
<td>69</td>
<td>512</td>
</tr>
<tr>
<td>5</td>
<td>796</td>
<td>511</td>
<td>702</td>
<td>373</td>
<td>932</td>
</tr>
<tr>
<td>6</td>
<td>4680</td>
<td>216</td>
<td>7607</td>
<td>76</td>
<td>1734</td>
</tr>
<tr>
<td>7</td>
<td>4360</td>
<td>1308</td>
<td>1683</td>
<td>55</td>
<td>4885</td>
</tr>
<tr>
<td>8</td>
<td>15741</td>
<td>1138</td>
<td>5062</td>
<td>96</td>
<td>11164</td>
</tr>
<tr>
<td>Avg.</td>
<td>6171</td>
<td>604</td>
<td>3153</td>
<td>130</td>
<td>3322</td>
</tr>
<tr>
<td>Range</td>
<td>796-15741</td>
<td>142-1308</td>
<td>351-7607</td>
<td>55-373</td>
<td>217-11164</td>
</tr>
<tr>
<td>RO Action Limit</td>
<td>200</td>
<td>2500</td>
<td>100</td>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>Paulette et al. (2015)</td>
<td>537</td>
<td>531</td>
<td>4957</td>
<td>49</td>
<td>6456</td>
</tr>
<tr>
<td>Weindorf et al. (2013)</td>
<td>1588</td>
<td>--</td>
<td>1676</td>
<td>--</td>
<td>1209</td>
</tr>
</tbody>
</table>

Results and Discussion

The results of the elemental data collected via PXRF are given in Table 1. Results conclusively show that Cu levels exceeded Romanian action limits for every site scanned. Average Cu concentrations were 6171 mg kg⁻¹, some 30 times the action limit. All Mn levels were <2500 mg kg⁻¹; thus in compliance with mandated action limits. Similarly, V exceeded action limits at only one site, with six sites below the action limit. However, Zn and Pb were problematic showing average concentrations of 3322 and 3153 mg kg⁻¹; some five and 31 times the action limit, respectively.

Relative to PXRF analyses of soils from Copsa Mica (Paulette et al., 2015), Baia Mare features more Cu, Mn, and V, with less Pb and Zn. However, it is noteworthy that the means presented by Paulette et al. (2015) include a variety of impacted soils, not just those in industrial spoil pile areas. Similarly, Baia Mare sites showed more Cu, Pb, and Zn than soils in Zlatna (Weindorf et al., 2013); a study which also considered multiple soil/land use types.

Given the results here obtained, there is strong reason to believe that other soils in the larger metropolitan area of Baia Mare, as well as soils in the surrounding valley and
hills, are similarly impacted by Aeolian metal deposition. As such, this pilot study has provided compelling evidence that impacts can be quickly and accurately detected via PXRF. In light of these findings, a comprehensive research study is planned for the summer of 2015 whereby ~100-150 georeferenced sites will be scanned across the Baia Mare area. Also, soils will be scanned both at the surface and with depth to identify if any metal translocation within the soil profile is occurring. With the collected data, high resolution spatial variability maps will be rendered using kriging interpolation such that areas posing a health threat to residents can be precisely identified. Finally, a statistical analysis will be run between the location/extent of heavy metals within soils via PXRF will lead to enhanced remediation efforts to clean impacted areas, or at the very least, to isolate impacted soils such that human health can be protected.

Conclusions

Soil pollution with heavy metals is a common problem in many eastern European villages impacted by ore mining and smelting operations. This pilot study used portable x-ray fluorescence spectrometry to rapidly evaluate the elemental concentrations of industrial spoil soils left at an abandoned smelter facility in Baia Mare, Romania as a means of determining whether a larger scale, high resolution survey should be undertaken. Results conclusively showed that on average, Pb and Cu concentrations exceeded Romanian action limits for soil remediation by 30-fold. Zn also exceeded action limits by fivefold. Summarily, there is a high likelihood that metal pollution covers the entire town and surrounding hills. We therefore recommend the use of PXRF for a more detailed assessment of heavy metal levels such that human health and environmental quality can be protected.

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