REAL METALS FOR THE REAL WORLD: MIXTURE BIOAVAILABILITY & TOXICITY IN SOILS

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Introduction

Metals often occur as mixtures at metal contaminated sites. One can estimate the risk from metal mixtures by combining fixed-ratio dosing regimes and concentration and/or response addition toxicity models. A fixed-ratio dosing regime holds the relative concentrations of metals in a mixture constant and assesses how toxicity and bioavailability changes as total metal content increases.

Soil is typically dosed by applying aqueous metal salts and then leaching to control for salinity. The dose response function is then built upon the measured metal concentration in the soil after leaching. After dosing a soil with 2 ratios of 5 metals, we found that metals were leached at different rates over the dose range, invalidating the fixed ray approach. Over 60% of spiked metal salt was lost from the soil during the leaching process. Other effects, such as loss of fine particles, made our soil properties appear quite different form their original state.

As part of a large multi-institutional project designed to provide risk assessment guidance for metal impacted smelter sites, we developed two alternative methods for adding metal mixtures to soils: applying acid-pretreated commercially available oxides directly on to the soil, and using synthetic minerals created to emulate smelter emissions. The synthetic minerals are made by dissolving the desired ratio of nitrate salts, adding ferric nitrate in a 2:1 ratio, precipitation, and annealing to remove nitrates. We evaluated the three soil spiking methods on 4 soils by assessing metal speciation, bioavailability and toxicity to mites, enchytraeids, collembolan, and soil functions across these 4 different soils. We then compared these artificially created mixtures to those found at contaminated sites.

Results

The ratio rays used are shown in Table 1 and the ratio of metals found in the annealed metal is shown in Table 2. The synthetic minerals were surprisingly close to their intended ratios.

Table 1: Concentration of metals in each fixed-ratio ray used in the experiment.

Mixture	Lead (mg/kg) / Ratio %	Copper (mg/kg) / Ratio %	Nickel (mg/kg) / Ratio %	Zinc (mg/kg) / Ratio %	Cobalt (mg/kg) / Ratio %
CSQG	536 / 17%	483 / 15%	345 / 11%	1532 / 48%	306 / 10%
Flin Flon	202 / 7%	619 / 20%	9 / 0%	2223 / 73%	9 / 0%
Sudbury	2314 / 56%	161 / 4%	297 / 7%	1196 / 29%	153 / 4%
Port Colborne	56 / 3%	381 / 18%	1513 / 71%	163 / 8%	28 / 1%
Peat	612 / 19%	662 / 21%	396 / 12%	1199 / 37%	354 / 11%

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Table 2: Metal ratios found in annealed material**.**

Mixture	Lead (%)	Copper (%)	Nickel (%)	Zinc (%)	Cobalt (%)
CSQG	18%	16%	11%	45%	10%
Flin Flon	6%	23%	0%	71%	0%
Sudbury	62%	3%	7%	23%	4%
Port Colborne	2%	15%	74%	7%	2%
Peat	16%	24%	13%	38%	10%

Figure 1 shows the variation in ratio-ray composition for two different dose methods and soils. The CSQG ray is the ratio of the Canadian Soil Quality Guidelines for Pb, Cu, Ni, Zn and Co. Soil Elora is at pH 6.7, 21% organic carbon, and 20% clay content, and soil 3.22 is at a pH of 3.4, 3% OC, and 45% clay.

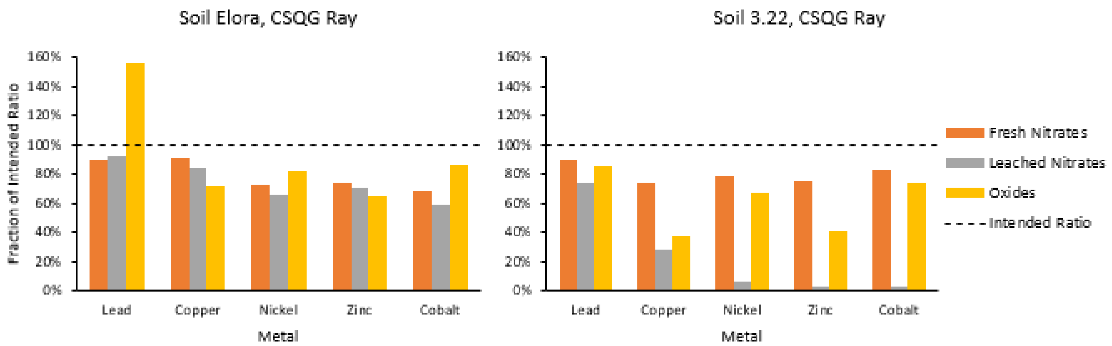

Figure 1: Difference in metal recovery due to soil type, leaching, and dose method.

Figure 2 depicts how *Enchytraeus crypticus* reproduction and survival varies in the Elora soil dosed at 4 Toxic Units (TU) as 5 different ratio rays. Here, 1 TU is defined as the EC50 for *F. candida*. While soil concentrations were similar, those dosed with nitrate salts were much more toxic than oxide dosed soil.

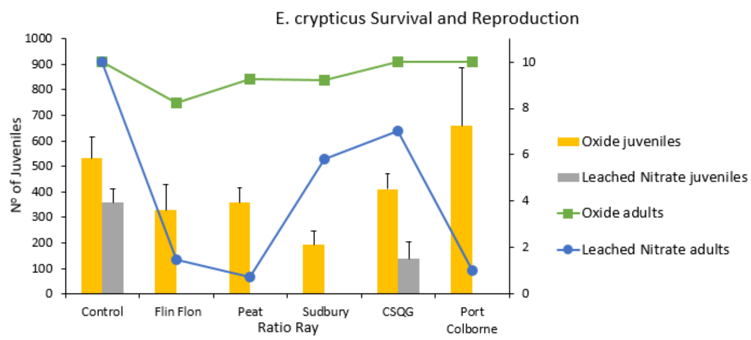

Figure 2. Reproduction and survival of *E. crypticus* exposed to soil spiked with different ratio rays.

Conclusion

We were more successful in creating a fixed-ratio dosing regime using metal oxides than aqueous salts. The synthetic minerals are still being evaluated and seem promising. Toxicity was lower in the metal oxides than the metal salts, and the toxicity is expected to be even lower in the synthetic minerals. The final goal is to compare the speciation and bioavailability of these metals in the soil when spiked with these different approaches to actual soil from contaminated sites. The results from this work will determine the dosing method used to estimate the risk of metal mixtures at Canadian metal impacted sites.

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