Kearney Foundation Fellowship
Final Report Summary

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Project Title: Spatial distribution and accumulation of nickel in serpentinite soil horizons

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Background

The ubiquity of nickel in the environment and its common presence in food and water mean that humans are constantly exposed to nickel. Although nickel is not acutely toxic at low levels, it is a carcinogen and has been linked to cellular oxidative stress [1]. Soils that develop on serpentinite, a metamorphic rock type derived from ultramafic igneous rocks (and the state rock of California), are well known for their elevated concentrations of nickel and chromium [2]. The degree of nickel accumulation in serpentinite soil horizons, thus its bioavailability to plants, is controlled by soil characteristics such as pH, amount of organic matter, clay and iron oxide content, and competitive adsorption with other dissolved species [3-7]. These biogeochemical factors are influenced strongly by climate, rainfall, vegetation, and weathering of primary ultramafic minerals. In locations where serpentinite and ultramafic soils have been used for agriculture, nickel transfer to plants has been documented [8], with potential transfer through the food chain to humans.

Our areas of study were focused on two sites: the Red Hills Management Area (RHMA), in Tuolumne County, California, and Bagby, near Coulterville, California. The RHMA and Bagby are unique areas to study because they represent exposed serpentinite terrains in a semi-arid climate with low rainfall, no urban or agricultural development, and limited grazing. Previous studies in the RHMA have examined plant species and nickel accumulation in arthropods [13], but other than regional geologic studies, no work has looked specifically at metal distribution, accumulation, or mobilization in the RHMA. The aim of this study was to look at metal distribution, accumulation and mobilization in the RHMA and Bagby sites.

Method

Soil and rock samples were taken from the RHMA site, and soil, rock, and plant samples were taken from the Bagby site. At the RHMA and Bagby, soil samples were taken from rocky slopes and flat areas with more soil development. At many sampling sites, soils were not sufficiently developed to identify distinct A and B horizons, but where possible, surface (<5 cm) and sub-surface (5-10 cm) samples were collected by hand digging. Soil and rock were sieved, dried, size fractioned into course (>1.7mm), medium (<1.7mm, >250μm), and fine (<250μm) fractions. Approximately 0.5g of the fine sample was microwave digested in a 12mL aqua regia (3:1 6M HCl to 6M HNO_3) solution. After digestion, the samples were diluted with deionized water and analyzed for total elemental concentration by ICP-MS. Plant matter was washed with deionized water, dried, crushed. The plant matter was then microwave digested with 4.5mL of 6M HNO_3 and 1.5mL of 6M HCl. The digested plant matter was diluted and analyzed for total elemental concentration by ICP-MS. Detection limits for ICP-MS for Ni, Cr, Mn, Co, Zn and U are approximately 0.5 µg/L; for Fe, Mg, Al and Ca, approximately 25 µg/L; and for Si, approximately 100 µg/L.

Sediment bulk mineralogy was investigated by synchrotron transmission X-ray diffraction. Powder samples were finely ground to 1-5µm grain size and randomly orientated on aluminum mounts, and sealed with clear tape. Diffraction data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 11-3 with tunable X-ray energy set at 12713.77 eV and a focused spot size of 150µm x 150µm. Laue patterns were collected from an averaged region of 2mm x 2mm, using 200µm steps and 0.1 second integration time. Detector distance and Laue patterns were calibrated with a LaB_6 standard and converted to wavelength using non-linear curve fit and the Bragg equation. Data analysis was performed using the Jade software package (MDI Products). Mineral identification was based on matches to three dominant peaks or to two dominant peaks with multiple minor peaks in the reference database (ICDD database).

Results

The terrain and vegetation of serpentine regions are very distinct from surrounding areas, as the terrain is quite rocky and there is a noticeable absence of large trees and dense vegetation. The RHMA and Bagby sites display the traits of typical serpentine regions. Based on the terrain and vegetation, we expected the RHMA and Bagby sites to have high concentrations of nickel, magnesium and chromium relative to soils developed on the surrounding metamorphic rocks.

Comparison of major and trace elements (< 250 um fraction) shows elevated Ni concentrations, compared to a non-serpentine soil sample take near the Bagby site. Calcium is in general several thousand mg/kg lower in concentration than Ni; other trace elements have variable concentrations. Preliminary X-ray diffraction analyses of several soil samples indicates the dominant presence of the serpentine minerals antigorite ($[Mg_3[Si_2O_5](OH)_4]$) and lizardite ($[Mg_3[Si_2O_5](OH)_4]$). Further chemical and mineralogical analyses of soil samples collected over the summer are in progress. Digestion and trace element analyses of root and shoot samples of three different plant species taken from rocky and soil areas of the Melones serpentine outcrops show variability in the accumulation of Ni, Mg, and Ca. *Streptanthus polygaloides* is a known Ni accumulator, and our data show high Ni concentrations in these samples compared to the other two species. Interestingly, *Lupinus spectabilis,* not recognized as a Ni accumulator, shows variability in its Ni concentrations, which appear to vary depending on which part of the plant was sampled. There appears to be no clear trends in Ni, Mg, and Ca concentrations. Although these soil and plant data are preliminary and limited in scope, they confirm variability in trace element concentrations in soils and plants collected from different sites, and suggest that Ni, Mg, and Ca in particular will be useful elemental indicators.

Summary and Research in Progress
Currently we are performing sequential chemical extractions on selected soil samples with high levels of nickel. The sequential chemical extractions will allow us to determine the relative strength of element binding and potential for bioavailability. Based on the outcomes of the sequential extractions and complete characterizations, a suitable extraction protocol for "bioavailable" metals will be selected for soil samples collected on a weekly basis in conjunction with plant samples during the spring flowering season. Future goals of our project are to characterize and compare changes in plant community, soil properties, bioavailable elements, and element uptake by plants during the spring (February-June) change from wet to dry conditions (a) between RHMA and Bagby sites, and (b) between rocky sites and those with soil development within each site. At regular 10 day intervals, plants and surrounding soil will be collected to investigate the seasonal variations in total elemental content of serpentine soil and flora. Samples will be measured for soil moisture, pH, electrical conductivity, and bioavailable metals. Depending on the outcomes, more extensive analysis will be done on selected samples. Representative rock samples from RHMA and Bagby will be crushed, powdered, and analyzed by XRD to determine mineralogy. Sample will undergo total digestions (using HF + HNO_3) and measurement by ICP-MS to characterize differences in major and trace element composition. Plant samples (roots and shoots) will be air-dried, weighed, crushed with mortar and pestle, and acid-digested (with aqua regia) for analysis of total metals.

Another future goal for our project is to investigate the response of the plant community during a spring flowering season to changes in water availability and addition of black carbon using field experimental plots. Field experiments will focus on testing the potential effects of changes in water availability, and the influence of black carbon (BC) on bioavailability and uptake of nutrients and metals, on the plant community (both in composition and density). Experiments will take place in a seasonal framework in order to address temporal variation in plant responses.

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