Spring 4-13-2020

Identification of Heavy Metal Contaminants in the Upper Clark Fork River Basin Using Laser Induced Spectroscopy and Hyperspectral Spectroscopy

Rachel Hadley
Montana Technological University

Marihelen Held
Montana Technological University

Xiaobing Zhou
Montana Technological University

Identification of Heavy Metal Contaminants in the Upper Clark Fork River Basin Using Laser Induced Spectroscopy and Hyperspectral Spectroscopy

Rachel Hadley, Marihelen Held, and Xiaobing Zhou

Background & Significance

The Upper Clark Fork River Basin is home to many current and abandoned mining sites which contribute to the presence of heavy metals. Heavy metals on surface sediments can harm human and ecological health, so it is important to identify these contaminants for removal.

Laser Induced Breakdown Spectroscopy (LIBS) is an active spectroscopy method because it uses a laser pulse to remove a small amount of mass through laser ablation. As the electrons return to their ground states, the unique spectral signatures and intensity can determine the percentage of the element in the sample.

Hyperspectral Spectroscopy (HS) is a passive method that uses natural light reflected from the sample to determine the range and concentration of the wavelength emitted. The resulting plot compares reflectance versus wavelength. HS can be applied to an airborne survey.

Method

We collected samples from two different sites:

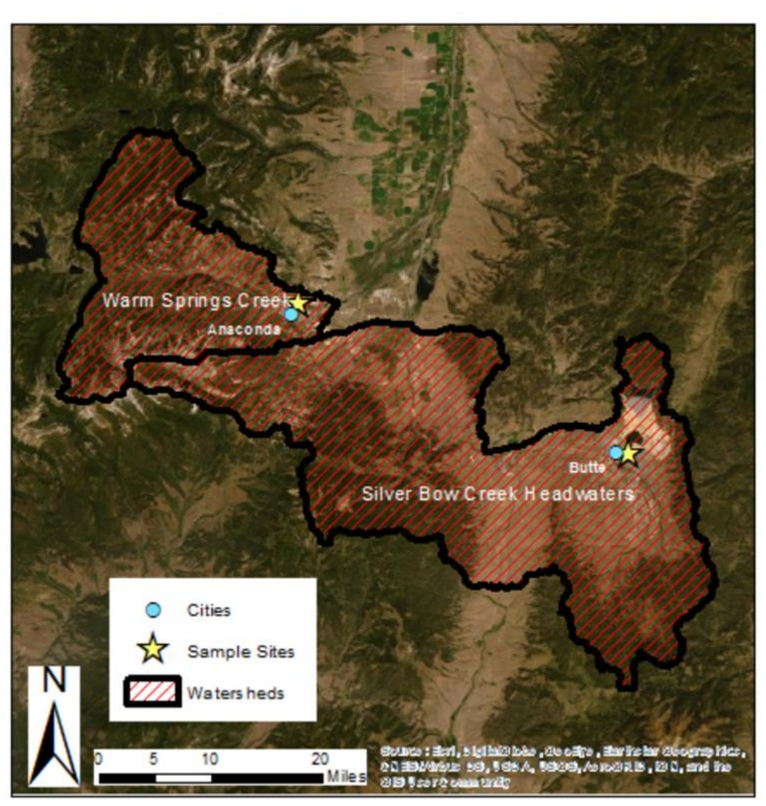
1. Stucky Ridge in Anaconda (100 samples)
   - Lies across a valley from a smelter
   - The top of the ridge has already been remediated
2. Parrot Tailings in Butte (20 samples)
   - Has already been remediated, however some tailings are still left/exposed

We also purchased 35 samples of known and uniform concentration to reference for one of our instruments.

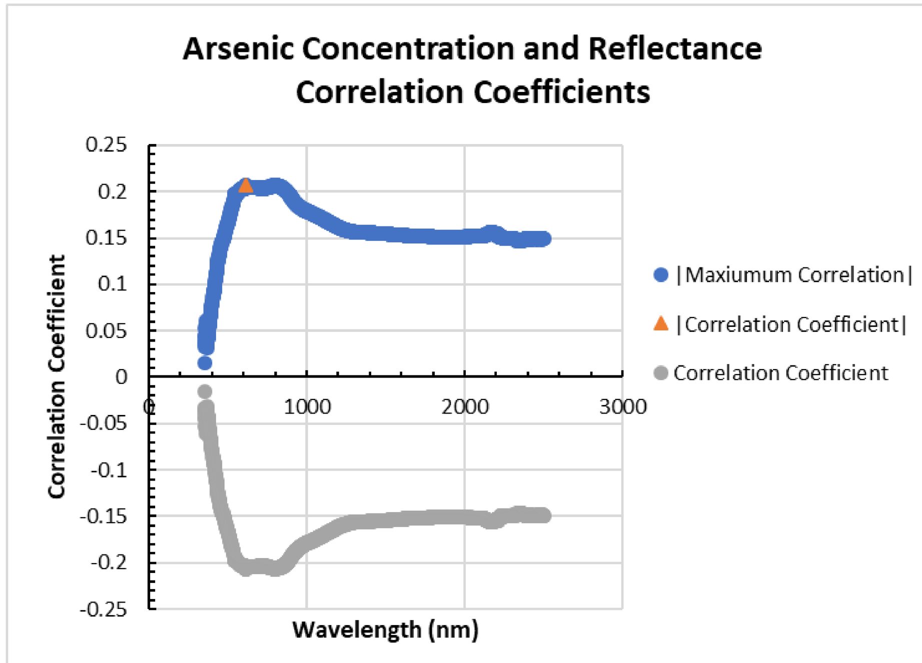
Every sample was sieved and shot with a HALO which is a passive spectroscopy instrument. The samples collected in the field were also shot with the LIBS. Our LIBS machine, however, is meant to be used on pelletized dirt.

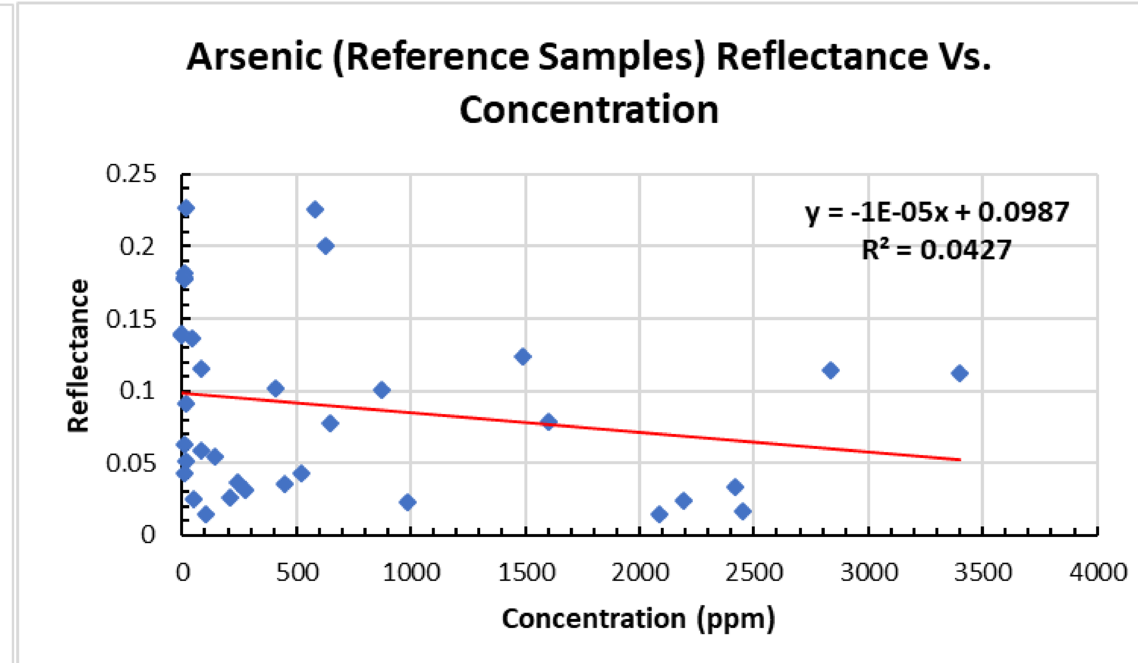
We then correlated the reflectance and concentration data in attempt to determine a characteristic wavelength for the elements of As, Cd, Cu,, Pb, and Zn. We then plotted reflectance vs. concentration of the characteristic wavelength to determine the strength in the relationship between concentration and reflectance of the characteristic wavelength.

Right is a map if the locations where we collected soil samples, which were at the Parrot Tailings in Butte and Stucky Ridge in Anaconda. We tried to hit areas with a wide range of concentrations.



Results

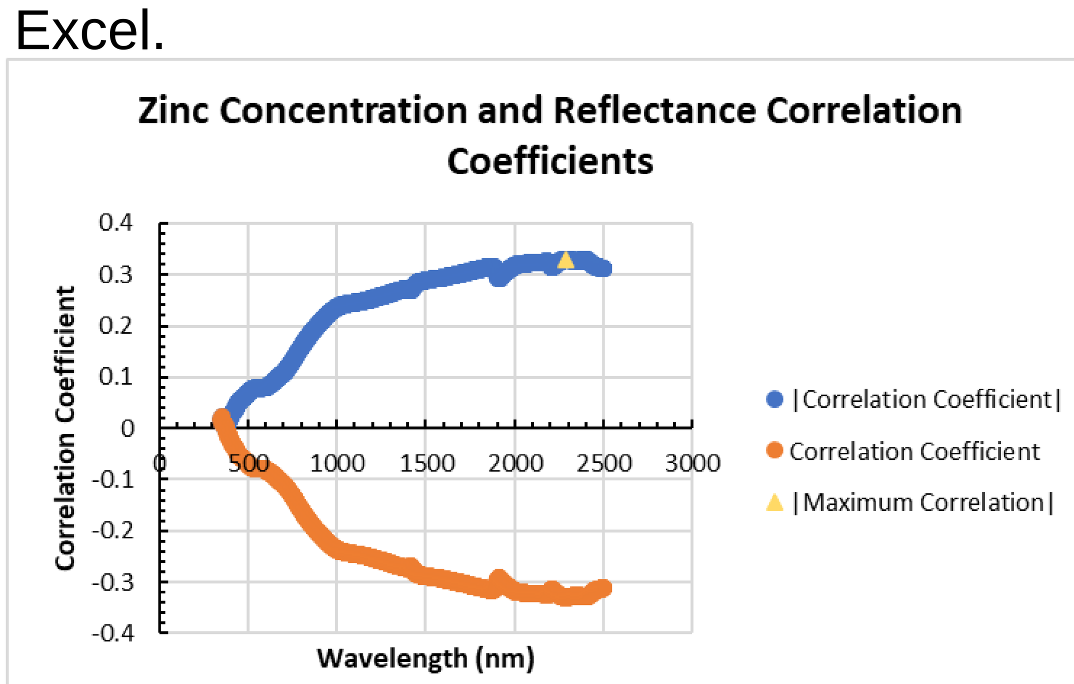


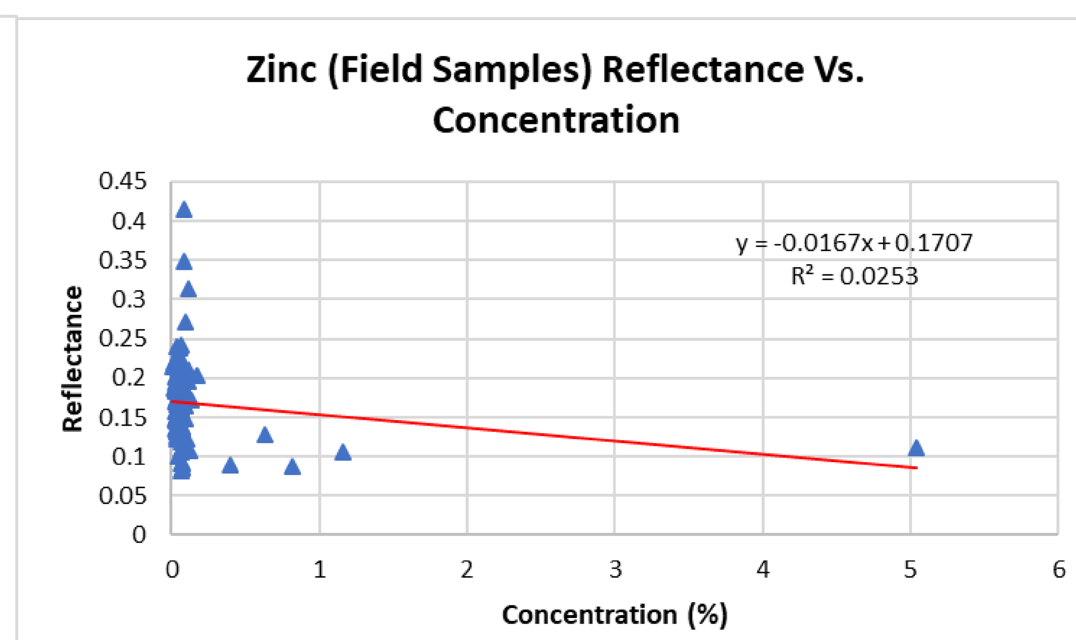


Above (left) is a plot of correlation coefficient vs. wavelength. The correlation coefficients were calculated in MATLAB and plotted in Excel**. Above (right)** is a plot of reflectance vs. concentration for the maximum correlation wavelength and the best fit linear relationship determined in Excel. Both of the above results are for the element arsenic from the reference samples with a known concentration.

Reference Samples Correlation Summary			
Element	Maximum Correlation	Wavelength (nm)	R^2
As	0.1666	800	0.0427
Cd	0.3352	354	0.0873
Cu	0.1466	1584	0.0215
Pb	0.2117	355	0.077
Zn	0.3947	354	0.1558

Above is a table of the correlation results of all five elements for the references samples developed using MATLAB and their corresponding maximum correlation wavelength. The table also shows the coefficient of determination as calculated by Excel.

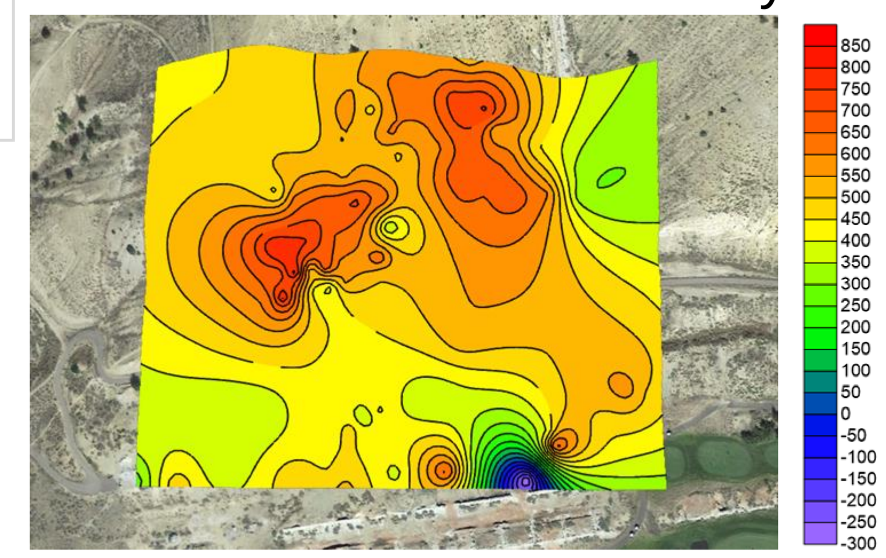




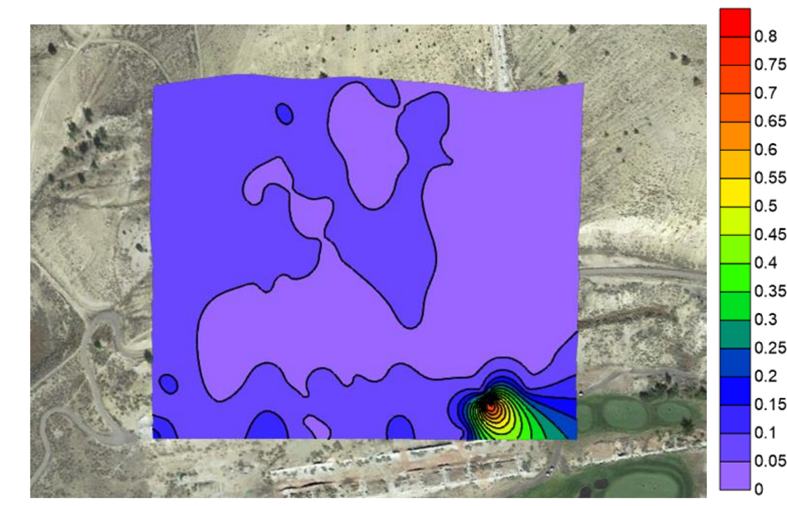
Above (left) is a plot of correlation coefficient vs. wavelength. The correlation coefficients were calculated in MATLAB and plotted in Excel. **Above (right)** is a plot of reflectance vs. concentration for the maximum correlation wavelength and the best fit linear relationship determined in Excel. Both of the above results are for the element zinc from the reference samples with a known concentration.

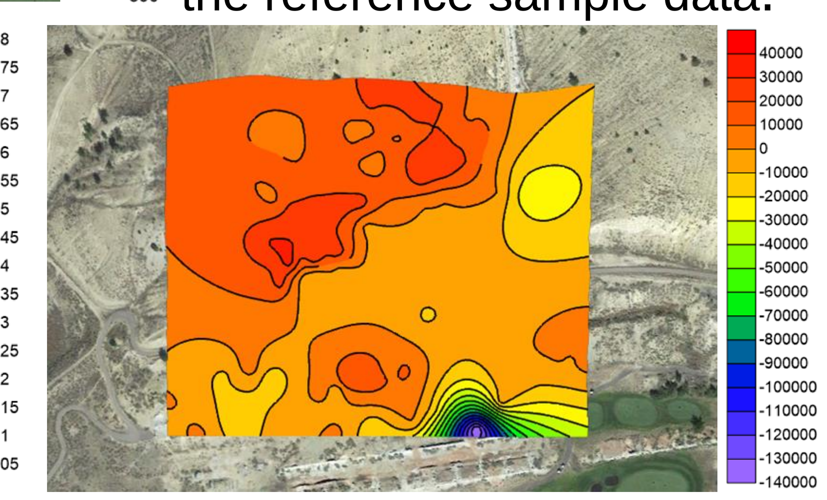
Collected Samples Correlation Summary			
Element	Maximum Correlation	Wavelength (nm)	R^2
Cu	0.4122	531	0.0005
Pb	0.5243	2499	0.0032
Zn	0.3297	2286	0.0253

Above is a table of the correlation results of the LIBS calibrated elements for the field samples developed using MATLAB and their corresponding maximum correlation wavelength. The table also shows the coefficient of determination as calculated by Excel.



Left is a map of concentration for the element of arsenic along Stucky Ridge. These concentrations were calculated based on the reflectance and a relationship determined by the reference sample data.





Above (left) is the concentration of zinc measured by LIBS in % and **(right)** calculated by the reflectance and information from the reference sample data in ppm.

Conclusions

The correlations produced a result of general trends, but no correlation was very strong (close to a value of 1). The R^2 values would ideally approach 1 as well, but they do not which also showed the weakness of the linear relationship. Although we attempted to calculate concentrations based on reflectance, the reliability of these calculations is low because reflectance of a certain wavelength does not seem to rely solely on concentration of a certain element based on these results.

Collecting more samples, as well as pelletizing the samples is recommended for the future, however trying to determine concentration from reflectance may not be feasible.

Acknowledgments

Special thanks to Newmont Mining, W.E.T. employees John Trudnoski, Jay Slocum, and Marcus Holland, and Anaconda Superfund Coordinator Carl Nyman for their help with our project.

Rachel Hadley

I am a senior in geophysical engineering and am from Dayton, NV. After graduation, I will begin work this summer with Water & Environmental Technologies (W.E.T.).

Marihelen Held

I am a senior in geophysical engineering from Great Falls, MT. I will be attending Colorado School of Mines in the fall as part of the Reservoir Characterization Project.