Introduction to Urban Watershed Geochemistry
Part 5: Measurement of Bulk and Trace Metals in Soils
Lab Exercise #5

1 Introduction

Few weeks ago we visited Filbin Creek in North Charleston to assess water and soil quality at this creek. As part of that trip we collected two soil cores and began analyzing those soil cores for various chemical and physical parameters. The overall goal of the assessment was to determine if the soils in the floodplain are receptors of contamination from flooding of the creek or from road runoff during storm events.

Last week we assessed anions concentrations in the soil cores as a function of the depth. The main objectives of today's lab are to (ii) determine concentrations of several trace metal contaminants present in the soils, (ii) determine if the concentrations vary with depth in the soil cores, and (iii) assess if the concentrations are representative of soils near urban streams.

This lab has two main steps. The first step involves extracting trace metals from the soils samples and the second step is the analysis of the trace metals using an inductively coupled plasma mass spectrometer (ICP-MS).

The ICP-MS is a combination of an induction coupled plasma (ICP) and a mass spectrometer (MS). In the ICP a plasma (an electrically conductive gas that contains high concentration of ions and free electrons) is generated. The temperature in the core of the plasma is approximately 10,000 K - enough to not just to atomize elements, but to ionize them (all elements are ionized into cations) at this high temperature. The ionized gases are then focused by a series of "lenses" into the next phase of the system, the MS. In the MS, which is maintained at very high vacuum, the voltages are manipulated to separate elements based on mass-to-charge (m/z) ratios. As each element is separated, the number of ions are counted by the electron multiplier (EM) detector. Because mass is the final determinant, multiple stable isotopes of several metals can be measured. Because of the MS and advanced circuitry on board, concentrations of dozens of ions can be measured simultaneously in very short time (on the order of few minutes per sample). This instruments is very sensitive and can measure elemental concentrations in mg/L (group I and II elements) to μg/L (d-block elements) to ng/L (f-block elements). As Beer's Law states, the number of counts by the detector is directly proportional to the concentration of the ions.

The ICP-MS can only measure elements in aqueous samples. In order to measure elemental composition in solid samples (rocks, soils, sediments, etc.), these samples have to be "liquified" by digesting the samples in strong acids on a hotplate. This digestion procedure could take several hours for samples depending on their composition. An alternative to this traditional approach is to digest the samples in a closed vessel at high temperature (up to 250 ℃) and high pressure (up to 800 psi) created by the presence of microwave energy. Microwave radiation are electromagnetic waves that have low frequencies and large wavelengths. At these low frequencies, these waves impart energy to the solid-solution causing localized superheating and speeding up dissolution reactions while not disrupting any chemical bonds. Typically the digesting reactions in this method occur in approximately 10 minutes for up to 12 samples at a time. Once the digestion process is complete, the acid digests are diluted $100 - 1000\times$ to prepare them for ICP-MS analyses.

Since the ICP-MS only generates the counts of the number of ions of any given element, a calibration curve that correlates the concentrations of those ions with the counts of the ions has to be generated. This calibration response is linear and since the instrument is very sensitive, extra attention has to be paid in the preparation of the standards.

Today's lab requires handling very concentrated acids – be very mindful of your safety.

2 Required Materials

The following materials and equipment required for each group for today's lab exercise:

1. Analytical balance
2. Spatulas
3. Soil samples from cores
4. Microwave containers
5. 50 mL centrifuge tubes
6. 15 mL centrifuge tubes
7. Deionized (DI) H_2O in squeeze bottle
8. Kim wipes
9. Gloves, safety goggles
10. Sharpie, Lab notebook
11. Five 50 mL or 100 mL plastic volumetric flasks with caps
12. Concentrated HNO_3
13. ICP-MS standards
14. Agilent 7500cx ICP-MS
15. CEM MARS 5 microwave digester

3 Tasks to be Performed:

A. Student group assignments Break into 4 groups of students. Each group will be tasked with analyses of 6″ of one core sample.

B. Microwaving Soil Samples

1. Use the same soils you used in the previous lab – 3 samples per group.
2. Accurately weigh 0.50 g of representative soil into the microwave vessel.
3. Add 10 mL of concentrated HNO_3 to the soil sample and let sit for 10-15 minutes until no further reactions can be seen. *Be very cautious when handling the concentrated acids. Work in the fume hood – do not bring the acids out of the fume hood.*
4. Prepare the vessel for microwave according to the built in method for the soil samples.
5. After microwaving is complete, remove the samples and carefully remove the sample vessels that contains your samples.
6. Transfer the microwaved digest into a 15 mL plastic centrifuge tube. Label this container with your group's name and sample information.
7. Dilute your samples 100× and 1000× using serial dilutions in 15 mL centrifuge tubes.
8. Label diluted sample containers clearly.

C. Preparation of ICP-MS Standard Solutions

1. You will prepare these standards collectively for the entire class. I recommend Andrea, Ashley and anyone else interested in trace metal analyses to take charge of this portion of the lab.
2. Carefully prepare all standards by mass (not volume) using one of the higher precision balances. Be sure to record all masses.
3. From the provided 10 mg/L multi-element stock standard, dilute the standard stock solution with DI water to prepare 50 mL standard solutions at concentrations of 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} mg/L. *Use 50 mL plastic centrifuge tubes for making the ICP-MS solutions.*

D. Acidification of Samples and Standards

1. Transfer 10 mL of standard solutions into 15 mL centrifuge tubes.
2. Acidify *all* samples (only 1000× samples) and standards to 2% acid strength using con-

centrated HNO_3. (e.g., Add 0.2 mL of acid to 10 mL of solution.)

E. ICP-MS Analyses

1. Load samples in ICP-MS queue and identify samples based on partner's names.
2. Run samples. *It will take a few hours to complete all the analyses, the data will be made available on OAKS by tomorrow.*
3. Convert all trace metal concentrations from mg/L to mg/kg based on the soil mass.

F. Data sharing Share with me all the data you collected and I'll compile the trace metal data and upload the entire information to OAKS tomorrow.

4 What to Include in Your Lab Report:

In additional to the primary objectives, be sure to address these points in your discussion:

1. Summarize all data.
2. Discuss the soil trace metal concentrations in context with previous data and potentially what they mean about the watershed.
3. Are these concentrations comparable to those found in urban soils?
4. Are there any EPA standards for trace metals in soils? If so, how do these concentration compare with those standards?

The lab report format is identical to earlier lab reports and should include the following components:

1. Title of the exercise, your name, name of partner, and date of lab exercise.
2. Abstract (≈150 words)
3. Methods (≈300 words)
4. Results (≈400 words)
5. Discussion (≈400 words)
6. Conclusions (≈100 words)
7. References