

ENSC 101 Pollutant Movement through Air, Land and Water

Week 8. Extraction of Heavy Metals from Soil

Heavy metals can be found in many different forms in soils and sediments, and not all of these forms are potentially toxic. Metals that are part of the mineral structure of the soil will only become available over geological time scales. One of our problems is to be able to distinguish contaminant metals from natural, background levels. We will do two types of extractions to estimate total and potentially available metals. A third method to determine “easily” available metals will be discussed.

Total metal analysis is rarely performed because it requires tedious and extremely hazardous sample preparation to completely dissolve all soil minerals. Silicate minerals are particularly difficult to digest. Two accepted procedures are heating the sample with a mixture of HF and HNO₃ or fusion (high temperature heating) with lithium metaborate. Both produce fairly toxic solutions containing the dissolved metals.

The most commonly used procedure is EPA method 3050, which involves boiling the sample with concentrated HNO₃. It is difficult to remove or oxidize organic matter in an acid digestion and hydrogen peroxide is commonly added to aid this process. (Another accepted procedure is to add perchloric acid for this purpose but a special chemical hood is required.) Newly developed procedures use a microwave oven instead of a hotplate for heating.

We will use 1.0 molar (*M*) HNO₃ instead of concentrated (about 16 *M*) and we will not use heat. This simplified method has been shown to give results almost equivalent to EPA 3050 if the shaking time is over two hours.

Potentially available metals are measured by a large number of different extractions, many using organic compounds such as EDTA to complex (chelate) and remove the metals from loosely to moderately-bound forms in the soil (exchangeable, recently precipitated, complexed with soil organics, adsorbed on surfaces). The purpose of this extract is, as stated in its name, to provide an estimate of heavy metals that could move into solution over time and be toxic.

For this purpose in Vermont, we use the same extractant that provides our soil fertility test. It is ammonium acetate buffered at pH 4.8 (1.25 *M* acetate). The low pH and the acetic acid both help remove some bound forms of heavy metals. The ammonium (NH₄⁺) removes any exchangeable metal cations.

Readily available metals are those released into a solution that mimics natural conditions. This is the basis of the Toxicity Characteristic Leaching Procedure (EPA Method 1311). Water moving through soils contains dissolved anions and cations that will potentially exchange or remove some quantity of the metals present. If this quantity exceeds the regulatory limits, then the soil must be considered as a hazardous site. We will not do the TCLP because of time constraints. The full method is detailed at this website and if you have never read an EPA method before, it is enlightening: <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1311.pdf>. The method uses ammonium acetate but at a much weaker concentration.

Extraction Procedure

Use the soils you collected in the field. A standard soil will be provided for QC purposes.

1. Put each sample through a 2 mm sieve. Brush the sieve clean between samples. For trace level analysis of metals, the sieve should be plastic or teflon. [**Do not sieve the soil standard, it has already been pulverized.**]
2. Weigh 5 g of each sieved, mixed sample into a weigh boat and add to a 50-mL centrifuge tube. Prepare 3 tubes of each of your soils **but only 1 tube of the QC soil (for nitric acid extraction)**.
3. Add 20 mL of one of the extractants (1 M HNO₃ or 1.25 M NH₄-H₃C₂OOH) to a set of your samples, cap, and shake for 15 minutes. Duplicate the nitric acid extraction.
4. Add nitric acid to the QC soil (not NH₄-acetate). Run a blank with nitric acid (no soil). You should end up with 8 extractions as detailed in the table below.

Sample	Number of extraction tubes with nitric acid	Number of extraction tubes with NH ₄ -acetate
Soil 1 (composite)	2	1
Soil 2 (grab)	2	1
Certified reference soil CRM023-050	1	0
Blank	1	0

5. Centrifuge the tubes at medium speed to obtain a clear filtrate.
6. Carefully decant into a test tube for ICP analysis. If the solution is still cloudy, use a clean syringe and filter to provide a clean sample. Label the tube clearly with your group's name, the sample ID and the extractant used.

The extracts will be run on the ICP and results will be provided for your interpretation.

Instrumental analysis

The concentration of most metals can be determined on one of two instruments: ICP or AA. The ICP/AES is an inductively coupled plasma atomic emission spectrophotometer (or spectrometer). The AA is an atomic absorption spectrophotometer and can be either "flame" or "graphite furnace". Both work on similar principles with the sample heating and detection of electronic transitions through the emission or absorption of light at wavelengths characteristic for each element. There are many other types of instruments that can detect metals, but none are common in environmental analytical labs.

The ICP has a small cone of argon that is induced into a plasma by radio frequency radiation. The plasma contains atoms that are stripped of their outer shell of electrons and is extremely hot.

The unknown sample is sprayed through this plasma and the elements in the solution absorb energy and emit light. These emissions are at specific wavelengths because of quantum differences between electron energy levels in each element. The spectrometer portion of the instrument detects the emission. A number of different elements can be measured almost simultaneously because a number of different detectors can be used. This is one of the major advantages of ICP over AA. Another advantage is that it tends to have a wider linear calibration range and it tends to have less interferences than AA.

Atomic absorption spectroscopy is an older method but still used because, with a graphite furnace, one can obtain lower detection limits. Two different modes of operation are sample aspiration through a flame or volatilization in a small graphite tube. In both methods, a light beam, at the wavelength characteristic for the element being measured, is passed through the sample as it is "atomized" and the absorption of light is measured. When a graphite furnace is used, concentrations in the sub-ppb range can easily be measured. Atomic absorption methods tend to have more interferences primarily because the sample does not become as hot as in the ICP. To absorb at the proper wavelength, the element needs to be completely separated into individual atoms, they cannot be in a molecular form. There is a range of "modifiers" that can be added to reduce interferences.

Quality control is essential in both types of analysis to assure that the calibration is correct and that there are no interferences. Many types of interferences occur and some can give false positive readings. Standard practices for quality control include:

1. Use a known calibration standard from a different source than the primary calibration to ensure that the instrument is properly calibrated.
2. Repeat this QC standard throughout the analytical run to ensure that there is no drift in the calibration.
3. Extract a known standard sample to ensure that the entire procedure is valid.
4. Spike samples with a known concentration of the metal and measure recovery.
5. Run duplicates to ensure repeatability.
6. Run blanks through the entire procedure to measure background or possible contamination.
7. Run interference standards to ensure that some elements are not interfering with the detection of other elements.

Not all metals can be determined by normal ICP or AA measurements. Although Hg and As can be detected by ICP, the detection limits are not low enough and alternate procedures are needed. For Hg, this involves a separate apparatus to convert the Hg in a sample to the vapor phase, which is then detected by atomic absorption. For As, the technique of hydride generation is often used. More information is available on these methods if desired.

The EPA extraction procedures can be found in Test Methods for Evaluating Solid Waste SW-846. The government document code is EP1.17:846. It is available online at: <http://www.epa.gov/epaoswer/hazwaste/test/main.htm>

References on the instrumental methods are numerous and include:

The above EPA document

Standard Methods for the Examination of Waters and Wastewaters, American Public Health Association

Methods of Soil Analysis, American Society of Agronomy

Methods for the Determination of Metals in Environmental Samples, US EPA

Please let us know if you would like a demonstration of the ICP. It runs nearly all day every day and we can easily arrange a visit. If you would like to help run the samples on the ICP, also please let us know.

Details of Lab Report (Below is all that is needed, i.e. you need to write no more than what is requested (except for your name). To put it another way, please don't provide any more in your lab report than what is requested below.)

1. Provide a brief description of the difference between the two extractants we used and why we used them.
2. Calculate the final results for your analyses in mg per kg of soil. Subtract the blank before multiplying by the solution:soil ratio of 5:1. [We used 25 mL of extractant and 5 g of soil. Assuming that the 25 mL weighs 25 g, the reported concentration in mg/L can also be mg/kg of liquid. 5 kg of liquid were used for every kg of soil and the soil concentration is thus 5 x higher than the solution concentration.]
3. Prepare a QC/QA report by calculating and commenting on the following items (**provide numbers**, e.g. the QC's were 4.8% of their actual value):
 - a. Were all results within the range of the standards used to calibrate the ICP?
 - b. Were the calibration QC's within 5% of their actual value?
 - c. Were your duplicates within 5% of each other?
 - d. Were your blanks consistently low and were they lower than your soil results?
 - e. Were the results for the standard soils within 5% of their actual value?
4. Comment on the results. Were any samples relatively high in any of the metals? Were the nitric acid extracts consistently higher than the ammonium acetate extracts (they should be)? If there were high readings, did the location of the soil make sense, i.e. was it from an area of suspected contamination?