

Question:

Do the oxidation states and concentration of Sulfur, Phosphorus and potassium change in the soil of Northern Alberta at various depths when exposed to extreme heat caused by wildfire."

Hypothesis:

General: Due to pyrolysis the speciation of phosphorus and sulfur will change; the vast presence of available nutrients after a fire will cause many new chemical bonds to form. There will be a general trend from organic sulfur/phosphorus to inorganic sulfur/phosphorus, as a result their concentrations will increase. Species bond to inorganic elements will be more numerous in the samples affected by wildfire. Although volatilization of these compounds may actually cause a drop in the overall concentrations.

Sulfur: The oxidation states of sulfur are influenced by being in the presence of anaerobic or aerobic environments. Soil with lots of organic matter and nutrient cycles is mostly aerobic, however specific soils can be anaerobic, due to our observations it appears that the samples we collected contain aerobic soil. It can be inferred that this soil will contain more sulfur in the form of sulphate due to the aerobic conditions and plants preference for sulphate forms for uptake. The question arises what happens to the speciation and concentrations of sulphate after a fire. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures, around 200-300 degrees celsius, wildfires typically reach 1000 degrees, it can be concluded that pyrolysis occurred during the Fort McMurray wildfire. It typically occurs during the charring/burning of wood, which is the main fuel source during a wildfire. It is known that sulfur reacts with oxygen to form gaseous compounds like Dihydrogen sulfide, Sulfur Dioxide, and a few more, these would be released into the air therefore decreasing the concentrations of sulphate in the soil. At the same time the burning of organic matter gives the soil more sulfur. This sulfur will be converted to sulphate and sulfide forms, yet because pyrolysis is an anaerobic process it is hypothesised that more sulfide compounds will form as a result of this process. Therefore it is hypothesised that there will be a greater concentration and abundance of sulfides in the soil after a forest fire; with sulfates and elemental sulfur being more present in the samples not affected by wildfire. However since samples were taken a year after the fire, the concentrations and speciation may be closer to what it was before the fire.

Phosphorus: Phosphorus is most common in phosphate form in soil, it is also taken up by plants in this form. It is to be noted that most phosphate compounds are insoluble, and therefore are found in solid form. It is hypothesised that there will be phosphorus speciation mainly in the form of phosphates in the non-wildfire soil. Post wildfire it is expected that there will be an abundance of phosphorus in the surface, however high temperatures can cause 50 to 60 percent of the total fuel phosphorus to be lost to volatilization. Studies show that a wildfire that produced higher soil temperatures reduced phosphatase activity and increased the mineralization (**Mineralization**; the

process through which an organic substance becomes oxidized by inorganic substances) of organic P (organic compounds containing phosphorus), which increased ortho-phosphate P and decreased organic P. It is hypothesised that post wildfire there will be larger concentrations and speciation in the forms of mineralized organic phosphorus, and ortho-phosphates, whereas a decrease in organic phosphorus. The wildfire will cause a change in the speciation of organic phosphates, to inorganic phosphates, also resulting in a change of concentration.

Temperature threshold for soil chemical characteristics

Organic matter 100 celsius

Nitrogen 200 celsius

Sulfur 375 celsius

Phosphorus and potassium 774 celsius

Magnesium 1,107 celsius

Calcium 1,484 celsius

Manganese 1,962 celsius

All Possible Standards

Potassium Phosphate monobasic

Potassium Phosphate dibasic

Potassium Sulphate

Ferric Sulphate

Calcium Sulphate

Elemental Sulfur

Copper Sulfide

Potassium Magnesium Sulphate

Ferric Phosphate

Calcium Phosphate

Aluminum Phosphate

Magnesium Phosphate $Mg_3(PO_4)_3$

Iron (II) Sulfide

Zinc Sulfide

We Will be Studying the Oxidation States

Sulphate (+6) using Ferric Sulphate

Sulfide (-2) using Iron(II) Sulfide

Elemental Sulfur (0) using Elemental Sulfur

Phosphate (+5) using Potassium Phosphate monobasic or Ferric Phosphate

Procedure for Comparing Soil Depths

- 1) Run XRF scans on 2 samples, from wildfire source 1 and from no wildfire source 1 at the 2cm depth.
- 2) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 5cm depth.
- 3) Run XRF scans on 2 more samples, from wildfire source 1 and from no wildfire source 1 at the 10cm depth.
- 4) Run XANES Sulfur scan wildfire source 1 at the 2cm depth.
- 5) Run XANES Sulfur scan no wildfire source 1 at the 2cm depth.
- 6) Run Standards scans for Ferric Sulphate, Iron(II) Sulfide, Elemental Sulfur, Potassium Sulphate, Copper Sulfide, Zinc Sulfide and Calcium Sulphate
- 7) Run XANES Sulfur scan wildfire source 1 at the 5cm depth.
- 8) Run XANES Sulfur scan no wildfire source 1 at the 5cm depth.
- 9) Run XANES Sulfur scan wildfire source 1 at the 10cm depth.
- 10) Run XANES Sulfur scan no wildfire source 1 at the 10cm depth.
- 11) Run XANES Phosphorous scan wildfire source 1 at the 2cm depth.
- 12) Run XANES Phosphorous scan no wildfire source 1 at the 2cm depth.
- 13) Run Standards scans for Potassium Phosphate monobasic, Ferric Phosphate
- 14) Run XANES Phosphorous scan wildfire source 1 at the 5cm depth.
- 15) Run XANES Phosphorous scan no wildfire source 1 at the 5cm depth.
- 16) Run XANES Phosphorous scan wildfire source 1 at the 10cm depth.
- 17) Run XANES Phosphorous scan no wildfire source 1 at the 10cm depth.
- 18) *Repeat for Second Wildfire and no wildfire source if there is extra time*

X-ray Fluorescence (XRF)

XRF is a spectroscopy technique that allows us to view the relative concentration of elements in a sample. A beam of photons(light particles) is sent at the sample at a specific energy level. Electrons that exist at an energy level within the atom but not the highest energy level in the atom may absorb these photons and have enough energy to eject the electrons from the atom. When this happens the atom is left in an excited state and an electron from a higher energy level is sent down to occupy the “core hole,” left by the ejected electron. When that happens a photon is emitted from the atom to conserve energy, this is known as the fluorescent photon, the fluorescent photon has an energy that is equal to the difference in the energy levels of the electron that came down to fill the core hole and the electron that was ejected from the atom. There are different types of fluorescent photons that correspond to the difference between these energy levels. There is a letter assigned that is dependent on what energy level the core hole is present at. If the core hole is at the lowest energy level then the fluorescent photon is from the edge, the next level is called the edge, and so on. There is then a subscript that is assigned to the letter and further subscripts after that, but the naming is quite tedious. The energy levels of these fluorescent photons is well known which is why they are often times called characteristic X-Rays. The idea behind XRF is to measure the amount of photons absorbed by a detector at certain energies, so you measure counts of photons vs energy of photons. This will create a graph that has many

different peaks that correspond to different fluorescent photons and different elements. There will also be a peak at the energy level of the photons that you sent in, this is known as the scatter peak. The scatter peak is the count of photons that were not absorbed by the sample. Here is an example of an XRF graph. (The scatter peak is labeled: Compton)

The higher the peak (more counts) of an element means the more of that element you have in a sample. A common technique used to compare XRF graphs of different samples to evaluate relative concentration is normalizing to the scatter peak. Essentially you divide the counts by the scatter peak counts of both graphs and then graph again so that the scatter peak of both graphs is 1.

X-Ray Absorption Near Edge Structure Spectroscopy (XANES)

XANES is a spectroscopy technique that allows us to see the relative concentration of different oxidation states of a single element. An oxidation state is the charge of an atom due to the number of electrons that are either gained or lost in a bond. Electrons usually exist at well defined energy levels, however when an atom has an oxidation state the electrons exist at a slightly shifted energy level. The idea of XANES is to find the shift and figure out the oxidation state(s) of an element in the sample. To do this, photons are slowly sent in over a range of energy. When the energy of the incoming photons reaches the required energy to eject an electron from a specific energy level from the atom there will be a large increase in the amount of photons absorbed. A XANES graph plots the counts of the photons that are absorbed against the energy level of the photons. Peaks with more counts correspond to oxidation states of higher concentration in the sample. Here are some examples of XANES graphs.

Linear Combination Fitting (LCF)

LCF is a data analysis technique that is used to find the relative concentrations of chemical species within a sample. In order to accomplish this there are many XANES scans that are needed, a XANES scan of the sample, and XANES scans of standards (standards are known chemical species). LCF is an attempt to add up all of the XANES scans of the standards in such a way that they recreate the XANES scan of the sample. This is done on a computer program (Athena is commonly used) the scans of the standards are given a weighting such that the sum of the weights of the standards are equal to 1. Comparing the weighting that the computer program gives to each standard gives you an idea of the relative concentrations of each species. Larger weighting means a higher concentration. Here is an example of LCF.