

Nitrogen Quantification: Long Island Pine Barren Forest Soil, NY.

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Abstract

In many ecosystems, nitrogen, which is essential for plant growth, is a limiting nutrient, and as such determines the overall productivity of an ecosystem. The soil acts as a N reservoir, and as such plays an important role in the nitrogen cycle. Despite its importance, the analysis of N in soils is a challenging analytical problem. Techniques exist that can identify and quantify the amount of soluble nitrogen compounds (e.g. ammonia, nitrate, nitrite), but the majority of the N is contained in the complex, insoluble humic portion of the soil. Several techniques exist that can quantify the amount of N, however, these are all destructive and cannot identify the chemical species of N. There exists a need for new analytic nondestructive techniques that can both quantify and identify the various N species present in soil. Near edge x-ray absorption fine structure (NEXAFS) is a powerful analytical method that can in principle identify both the chemical species and concentration of different elements within soil. Several challenges remain to be solved for NEXAFS to be accepted as a standard soil analysis technique. The first is to establish the sensitivity of the technique. To develop this protocol samples with different concentrations of nitrogen were prepared through the serial dilutions of boron nitride (nitrogen source) in graphite (pure carbon). Samples with concentrations ranging from 11.4% - 0.0286% were prepared and analyzed using soft X-rays at the National Synchrotron Light Source (NSLS) beam line U4B. Data were collected using both total fluorescence yield (TFY) and total electron yield (TEY). The differences between these two detection techniques will be compared and discussed. With this data we were able to quantify nitrogen to 0.1%. Another more challenging aspect to the usefulness of this technique is the interpretation of the NEXAFS spectra from complex soils, which contain a large number of unknown organic compounds. As an initial step towards addressing this issue, N edge spectra will be taken as a function of soil depth from a site in the Long Island Pine Barren forest soil. Soil samples were selected from a sampling site at 20 different depths ranging from 0 - 30 cm. This pattern was used to determine if the soil would display a proportional decrease in the nitrogen concentrations from the organic layer (O horizon 0-15 cm) to the lowest depth of the inorganic layer (A Horizon 15-30 cm). Pellets were constructed from the soil samples. N K-edge spectra were measured in both TFY and TEY mode. Unexpectedly, we observed detectable amount of N in all samples that showed little variation with depth. Due to the unexpected nature of our observations, we plan to repeat the analysis on a new set of soil samples to verify our initial results.

Background

When managing an ecosystem, like the Long island Pine Barrens information on the soil chemistry is required. Pine barrens have a unique make up where the area is characterized by having sandy, acidic and nutrient poor soils composed primarily of sediments deposited by ancient glaciers. One of the properties of this ecosystem is the low content of free nitrogen in its soils, which is undetectable or at most very difficult to detect by traditional analytical techniques. Nitrogen cycling and, the chemical species of N in the soil are poorly understood for the Pine Barrens ecosystem. The organic N found in the soil may provide a N source that can be converted to ammonium and nitrate, which can then be used as a viable source in plants. However, a majority of the N is often contained in the complex, insoluble humic portion of the soil. Even with this being said N in the soil has not been adequately studied or defined. Several methods exist to quantify total nitrogen content of the soil but they are destructive and cannot identify the chemical nitrogen found. Some of these techniques include Solid-state nuclear magnetic resonance, carbon hydrogen nitrogen elemental analysis and the micro-Kjeldahl method. Due to the given limitations of the current methods it has become necessary to develop a new nondestructive method to quantify and qualify nitrogen in the soil. Information given LaMotte test and HACH test suggests that there is a negligible amount of soluble nitrogen in soil and water and pond sediments, but assays are basic methods and only act as indicators. These studies aim at furthering our understanding of the biogeochemical cycle of N in the Long Island Pine Barren ecosystem.

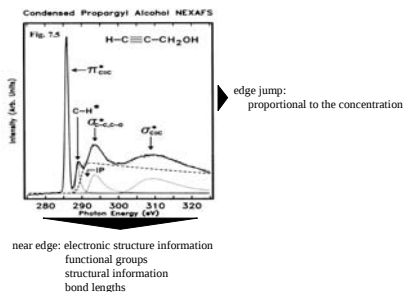
Near Edge X-ray Absorption Fine Structure (NEXAFS)

Near edge x-ray absorption fine structure (NEXAFS) presents promise as a new analytical nondestructive techniques that can both quantify and identify the various N species present in soil

•NEXAFS can

- Detect all forms of nitrogen
- Give a spectral fingerprint, which in principle allows to identify chemical species

Spectroscopic Information: C K edge



Standardization

- To develop this protocol samples with different concentrations of nitrogen were prepared through the serial dilutions of boron nitride (nitrogen source) in graphite (pure carbon)
- 7 different concentrations were created ranging from 11.4% to 0.0286%
- The nitrogen K-edge NEXAFS spectra were then run at National Synchrotron Light Source NSLS Beam line U4B
- Data on the Total fluorescence yield (TFY) and the total electron yield (TEY) was collected and normalization (Figure 1)
- Edge jumps and peak heights were calculated as shown in Figure 2.

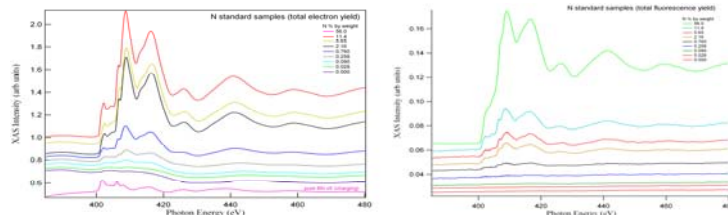


Figure 1. N Standard Samples Total Electron Yield (TEY) and Total Fluorescence Yield (TFY)

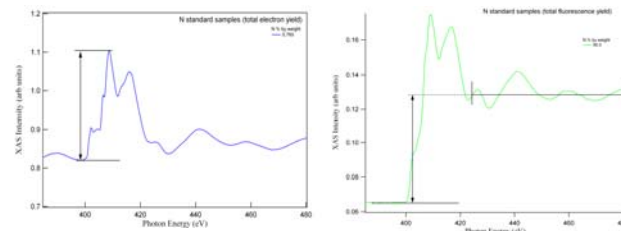


Figure 2. N Peak height (left) and Edge Jump (right) calculation

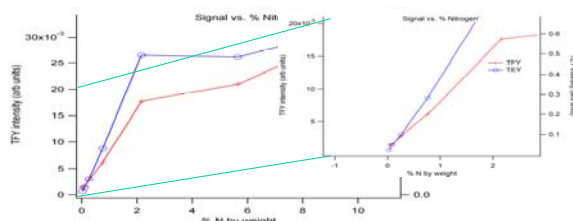


Figure 3. Nitrogen signal vs. Concentration

Soil analysis

- A soil sampling site was identified that was a representative of the LIPB forest
- Any area that had pitch pine-pine oak flora could represent the pine barrens
- When we arrived at the sampling site a pit was dug approximately 30cm deep
- Samples were then collected from the leaf litter, top soil, oak leaf and pine needles. Pellets were constructed and stamped onto copper tape
- Expected to see a decrease nitrogen content as a function of depth
- Change in form of nitrogen as a function of depth

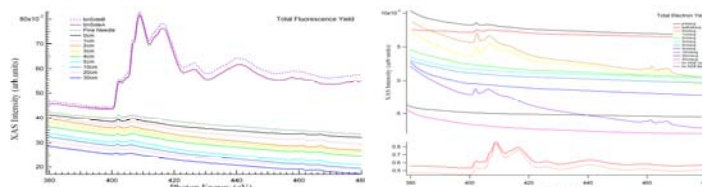


Figure 4. Soil Nitrogen TFY (left) and TEY (right)

Sample	% N
10% BN	11.4
Oak Leaf	>0.1
Pine Needle	0.784421
Soil 0cm	0.472333
Soil 01cm	0.745375
Soil 02cm	0.412763
Soil 03cm	0.348304
Soil 04cm	0.376559
Soil 05cm	0.504377
Soil 10cm	0.272941
Soil 20cm	0.242003
Soil 30cm	0.263529

Table 1.. Soil Nitrogen Concentrations

Conclusions

- ❖TFY is necessary to quantify nitrogen in the soil
- ❖Nitrogen levels in the soil were seen in similar amounts throughout the soil independent of the depth (Table 1)
- ❖No change in nitrogen form as a function of depth
- ❖First centimeter of the O horizon still had the highest nitrogen content shown
- ❖If these initial observations prove to be reproducible, it will shed new light on the distribution of N in the Long Island Pine Barrens ecosystem

References

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