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Abstract

Nitrogen (N), in humic substances, serves as a major N reservoir in soil; what role nitrogen plays in supplying the soil as a nutrient to the environment, how and at what rate the humic nitrogen is mineralized, and what role it plays in biogeochemical cycles, is poorly understood. The primary source of nitrogen in the humic substances is decomposition of organic matter broken down by microbes and fungi, ultimately resulting in changes to the chemical form of N present in soil. This project is designed to establish baseline scientific information on soil N before construction of a solar farm on Long Island Pine Barren (LIPB). The specific objectives of this study are: a) to identify N from the humus layer of the A-horizon, and b) to identify the chemical changes that N undergoes in the soil during degradation of organic material. We used Near-Edge X-Ray Absorption Fine Structure (NEXAFS), a synchrotron based spectroscopy of specific elements, to obtain electronic and structural information on nitrogen speciation. The total amount of N in the soil samples was quantified by comparing the spectra to a known standard of boron nitride. Our results indicate an average of 0.35 percent N content in soil samples taken from various sites representative of different Pine Barrens sub-environments, with a range varying from ~0.1 to 1 percent. The initial hypothesis was that the chemical speciation of N in soils would vary among different site location, due to the fact that vegetation and habitat type varied significantly. However, it was observed that N speciation was nearly identical in all samples. One possible explanation is that the organic form of N in all plant species present is similar, preliminary data supports this hypothesis.

Introduction

Nitrogen (N) is an essential nutrient critical for all biological and chemical processes. The source of N is the atmosphere; atmospheric N is not readily available for use and therefore must be converted to mineral forms (e.g. nitrates, nitrites and ammonia) for uptake by plants [1]. In our research we investigated the Long Island Pine Barrens (LIPB) forest, a distinctive region of sandy, acidic, and nutrient poor soils made up of coarse sands and gravels, to detect and quantify N in these soils. The region is housed with pines, oaks, and cedar type vegetation, with an understory of mainly heath shrubs that are known to grow in acid soil conditions. Early studies on LIPB soils indicated trace amounts of N, most of which were observed from leaf litter located just above the soils organic surface. Since most of plant roots are located in the soil, they can play an important role in adsorption.

The primary source of nitrogen in the humic substances is decomposition of organic matter broken down by microbes and fungi, ultimately resulting in changes to the chemical form N present in soil. Increases in the level of soil N occur through the fixation of dinitrogen (N_2) by some microorganisms. There has been a considerable amount of research done on soil N over many years, these studies focused mostly on proteins, amino acids and inorganic compounds however the transformation of N in soil is complex [1]. As a result of analytical limitations, environmental and economical issues combined, knowledge of N in soil and its' chemical components remains a pressing issue and thus the need to better understand the role of N in soil.

In general, to quantify and identify N using traditional methods, has proven to be complex; many methods have yield inconclusive results as regarding speciation. Near-Edge X-Ray Absorption Fine Structure (NEXAFS), a synchrotron based spectroscopy of specific

elements, to obtain electronic and structural information on a specific element such as N and to yield structural sensitive results [4]. The primary objective of this investigation is to: a) to identify N from the humus layer of the A-horizon without destroying the chemical components, and b) to identify any correlations between N and vegetation habitat type that would provide additional information about the chemical make-up of N in LIPB soils.

Materials and Methods

Site characterization

The loam type soil we used was extracted from Long Island Solar Farm (LISF), where we used the solar farm area as raw sampling data and the LIPB as the controlled samples (Fig 1). Loam is a rich soil consisting of a mixture of sand, clay and decaying organic matter. This region contained different soil types based on classification by the US Department of Agriculture and were identified as such: Riverhead sandy loam (RdA), Deerfield sandy loam (DE), Plymouth loamy sand (PsA), Sudbury fine sandy loam (Su) and Atsion sand (At) type soils. Soil samples were collected from a depth ranging from 3 to 6 inches below the humus layer of the A-Horizon.

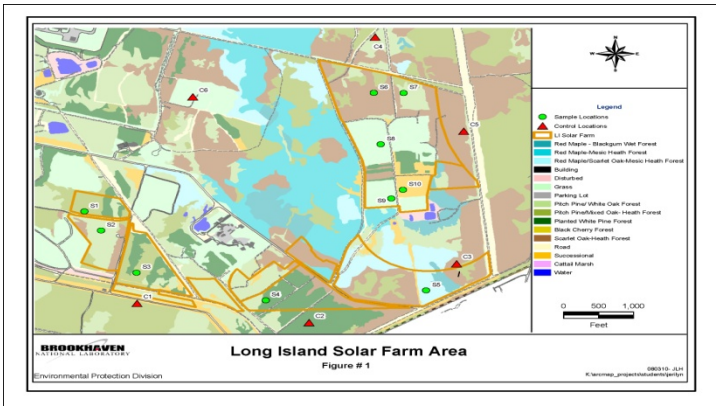

Fig. 1 Location of investigation area; map of Long Island Pine Barrens and Solar Farm located at Brookhaven National Laboratory

Soil sampling and analysis

We used 120 mL amber jars to collect the samples after which soils were air-dried and grounded using a mortar and pestle until they become soft and homogenized. Grounded samples were preserved in soil bags. The K-edge spectra were collected at the U4B beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, using a 600-lines/mm spherical grating monochromator and measuring total electron yield (TEY) with a channeltron electron detector [4]. Samples were pressed on conductive carbon tape and then loaded onto a paddle to minimize disturbance of the soil. We mixed graphite (electro conductive) and boron-nitride as our reference nitrogen spectrum for background subtraction. All measurements were carefully observed at standard room temperature and under high vacuum to reduce sample contamination with air [4].

Calculations of peak area

In our investigation we used statistical analysis to determine the area of each peak, in doing so these calculations provide significant information about the species of nitrogen. We used the Gaussian peak shape formula (Fig 2), where standard deviation squared (σ^2) is used to calculate the width of the peak and A represents the height of the peak. Area = $a\sqrt{2\sigma^2\pi}$

Point	Fit Parameters	Y-axis coefficients
0	edgeJ A	0.00215908
1	pk1 A	0.00578154
2	pk1 sigma	0.376087
3	pk2 A	0.00613002
4	pk2 sigma	4.02137
5	pk3 A	0.00360326
6	pk3 sigma	1.61885
7	pk4 A	0.00468117
8	pk4 sigma	3.94563

Figure 2 Calculation of Nitrogen peak values using an edge jump and the Gaussian shapes.

Results

Figure 3 show the near identical relationship between samples taken from the top leaf litter layer which consisted of pine needles and oak leaves, samples taken just below the humic layer of the A-horizon of the soil and reference spectra of alanine, albumin and chitin (amide group). These results suggested two possible scientific reasoning: a) the initial degradation process of organic matter occurs rapidly, resulting in the 1st stage of nitrogen speciation or b) the organic matter is partially decomposed during the initial stages of decomposition.

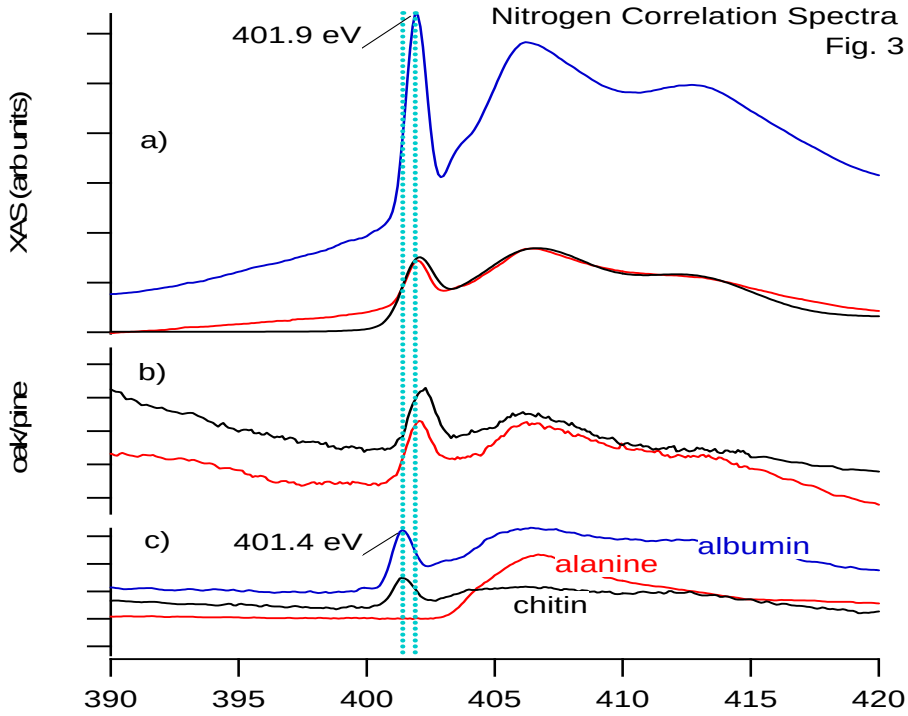

Figure 3 Spectra represents a) collected soil samples from 3-6 inches below organic layer b) samples of pine needles and oak leaves c) reference spectra of albumin, alanine and chitin nitrogen species.

In the areas where we noted a mere change in N concentration by ±0.3, were the areas that contained a relative amount of Pine and Oak type vegetation. Figure 4, provides an overview of our findings as regards vegetation.

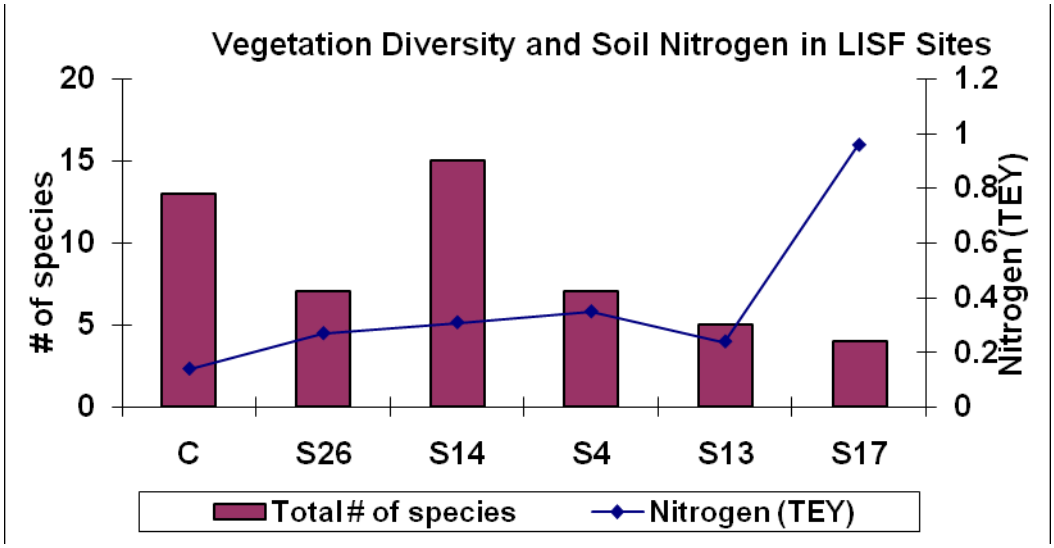

Figure 4, Biomass of vegetation and Nitrogen concentrations taken from LIPB sampling areas

The biomass was proportionate to the nitrogen concentration, where there was an increase in the amount of vegetation of a dominant species in a specific sampling site, there was constant concentration of N. However in the area with the highest quantitative value of nitrogen (greater than the standard deviation for the entire sampling site), there were no Pine needles suggesting that have a higher concentration of N due to different factors not yet researched.

In Figure 5 Note that all sample areas are included in this spectral view. The π*transitions represents the excitation of an electron from the N 1s core level to a π* antibonding orbital however the σ* occurs for all N species.

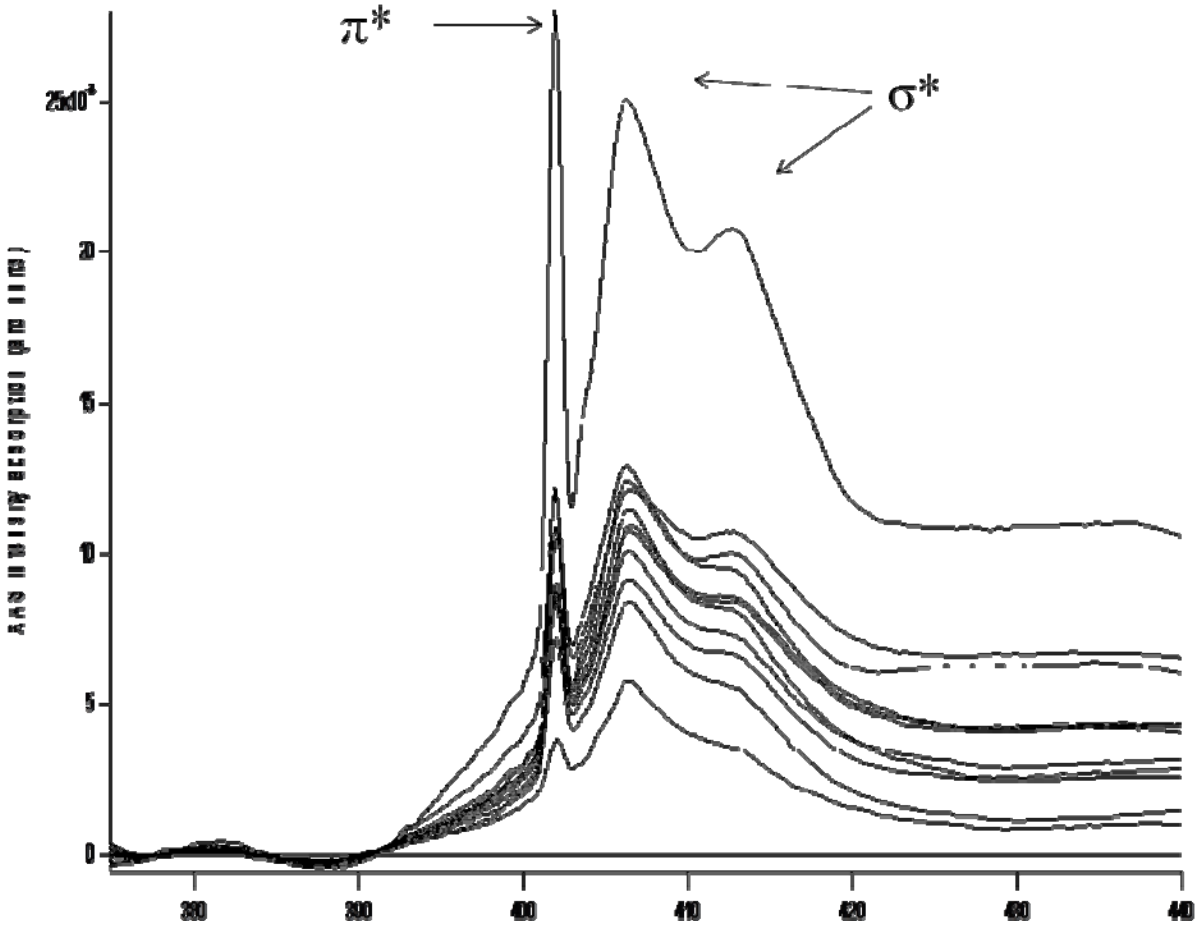

Figure 5 Spectra of all sampling sites, the N concentrations are quantitatively the same amount in each sample location.

The peaks ratio was critical in understanding and identifying the N species displayed in the samples. We divided peak 2 mean values by that of peak 1 to determine its proportionality, shown in Figure 6.

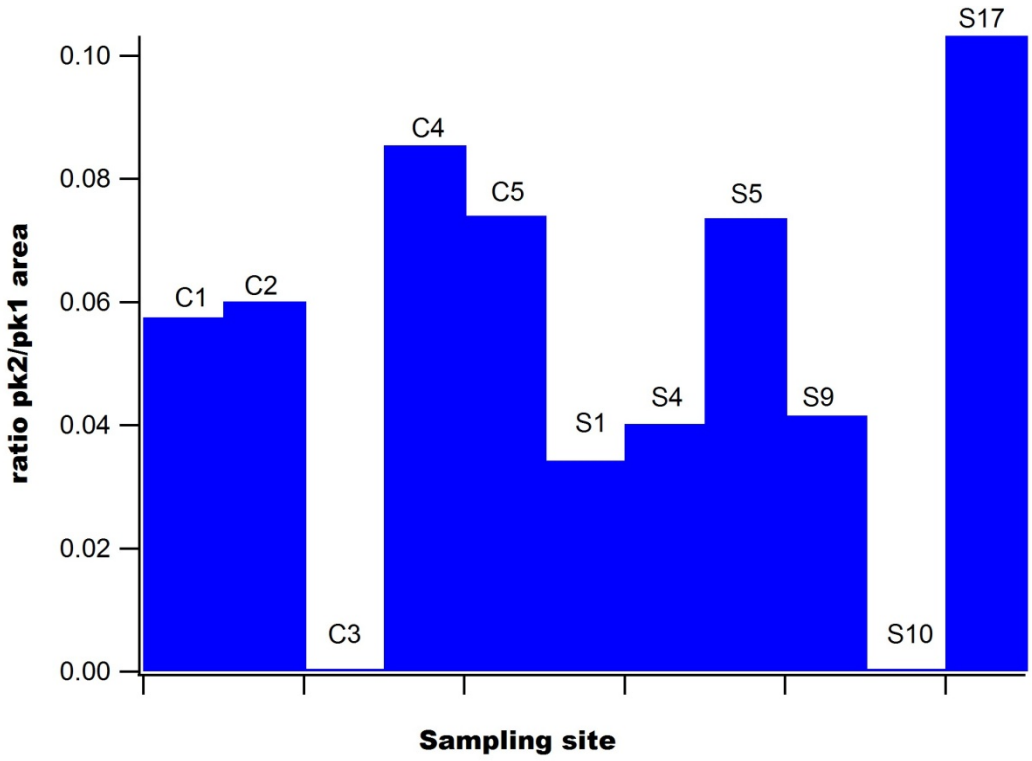

Figure 6 showing the ratio of peak 2 compared to peak 1

In Figure 7, we used the Gaussian shape fit to calibrate the peaks. Each peak illustrate a different energy value (eV) as the electron from the 1s orbital is excited, helpful in identifying different N species.

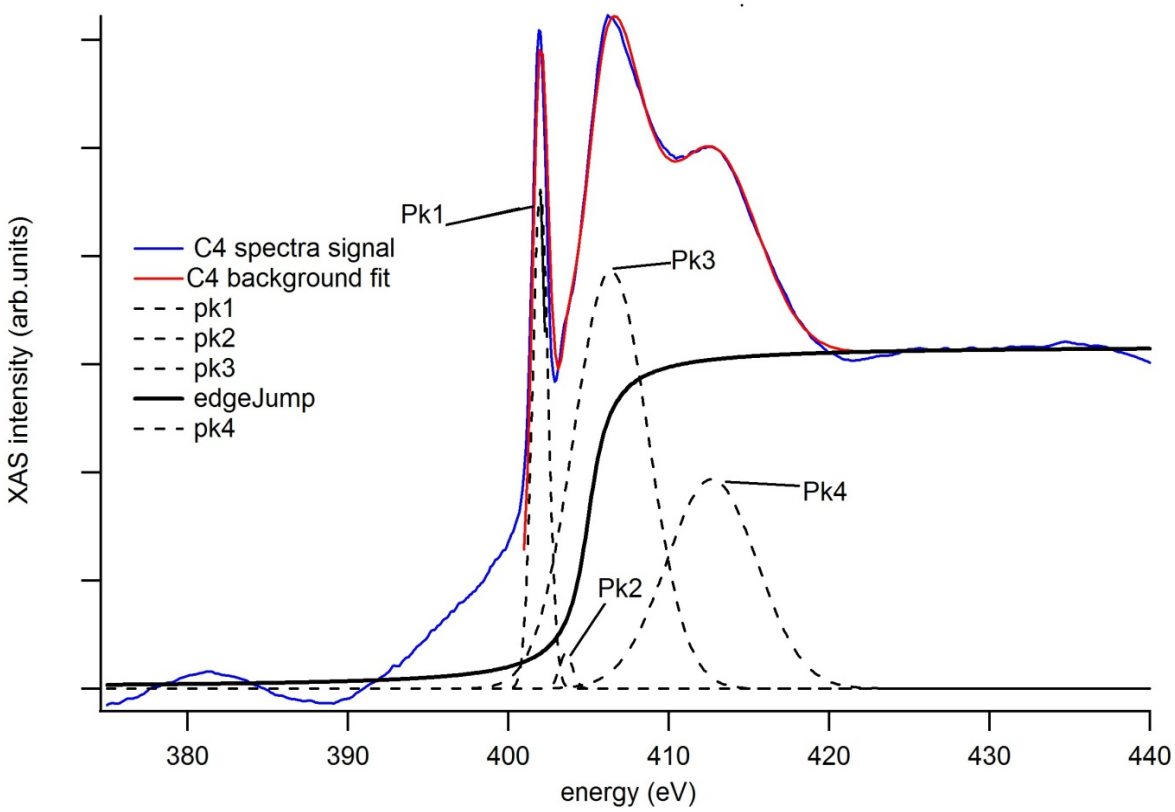

Figure 7 Peak fitting and edge jump of (2) sample spectra.

Discussion and Conclusion

The present study shows that samples taken from the leaf litter layer and samples extracted from the A-Horizon of the soil were nearly identical. Our samples showed an unidentified species of nitrogen at 401.9 eV. Previous research states that electron excitation at 401.4 eV would yield an oxidized pyridine belonging to Pyridine 2,5 dicarboxylic acid and Pyridoxal 5'-phospahte [4]. In our initial hypothesis we expected to see variations in nitrogen concentration and speciation due to vegetation type in the area which was proven incorrect based on current findings. We found that our samples were not of proteinaceous material.

In addition further research is needed to investigate the interrelationships between the diversity in plant vegetation (see Figure), aging of the leaf litter, microbial diversity in soil and other abiotic factors such as temperature, rain fall, soil pH and soil type.

Acknowledgements

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