

Development of a Method for the Quantification of Organic Nitrogen in Environmental Samples by N-XANES

P. Leinweber, (1), J. Kruse, (1) F.L. Walley (2), A. Gillespie (2)

(1) University of Rostock, Germany

(2) University of Saskatchewan

35

PRINCIPAL CONTACT:

P. Leinweber

Professor,

University of Rostock, Germany

peter.leinweber@uni-rostock.de

Introduction

The organic nitrogen (N) compounds of nonliving organic matter are an important pool in the global N cycle. They are the basis for the microbial formation of NH_4^+ and NO_3^- which are essential major plant nutrients. Moreover, open N cycles in agricultural systems can also be the cause of serious environmental pollution such as groundwater contamination with NO_3^- and gaseous emissions of N_2O which

contribute to climate change. Therefore, the chemical nature of soil N, especially of the 'unknown N' that may account for one-third to one-half of soil N [1], is a challenge for organic soil chemistry.

Science

Our general aim is the development of a multi-methodological approach that combines destructive analytical pyrolysis and mass-spectrometric methods with less destructive N *K*-edge XANES. Based on a detailed overview of reference compounds [2] the objective of the ongoing research is to improve the data evaluation of the mass spectra and N-XANES spectra by combination of the two methods.

We spiked known and well-investigated soil samples with increasing contents of amino/peptide-containing reference compounds (albumin, N-acetyl-D-(+)-glucosamine), to measure the spectral response of N-XANES to the increasing concentrations of specific N-functions. Subsequently, we subjected spiked samples to temperature-resolved pyrolysis-field ionization mass spectrometry (Py-FIMS), removed samples after certain heating steps (300, 400, 500, 700°C) and investigated these partially pyrolyzed samples by N-XANES. The XANES spectra were recorded on the 11ID-1 SGM beamline.

Discussion

The baseline-corrected N-XANES spectra in Figure 1 show that spiking with albumin resulted in proportional increases in intensities of the typical main peak of albumin at 401.5 eV. The magnitude of the two pre-edge features also was enhanced with increasing albumin spiking. In previous publications we attributed these features to radiation damage and/or heterocyclic N in histidine, which accounts for 1 to 3% (w/w) of albumin. The feature at 402.5 eV, which correspond to heterocyclic N in pyrroles, gradually disappeared with

increasing levels of albumin spiking. Indirectly, this confirms our interpretations of the N-XANES spectra of cultivated prairie soils [3].

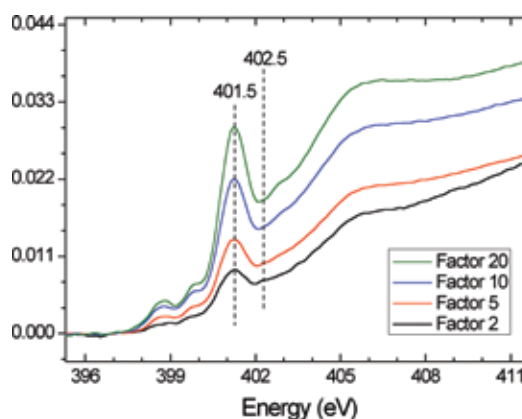


Figure 1. N *K*-edge XANES spectra of a soil sample spiked with albumin to increase the N-concentration by factor 2 to 20.

Spiking the same soil with N-acetyl-D-(+)-glucosamine similarly resulted in increasing intensity of the main amide peak at around 401.4 eV (Figure 2). However, new features appeared when these samples were pyrolyzed stepwise and the pyrolysis residues investigated by N-XANES. The normalized, stacked spectra in Figure 2a and b indicate the pyrolytic formation of two structural families of N-compounds with binding energies around 398.9 and 399.9 eV in the 300 to 700°C temperature range. According to our own N *K*-edge XANES results of a wide range of reference compounds together with published data [2] we surmise that these structures probably comprise pyridinic N in pyridines, imidazoles, pyrazoles, pyrazines and pyrimidines (398.7 to 400 eV) and nitriles (399.9 eV). The latter feature was more pronounced in samples spiked with lower concentrations (Figure 2a) than those receiving higher concentrations, where only a shoulder appeared in this eV-range (Figure 2b). During subsequent heating to 700°C the first peak (398.9 eV) disappeared in the lower spiked sample. This disappearance indicates intermediately formed pyrolysis products which were volatilized during heating from 500 to 700°C. It follows that these pyrolysis products should be detected in the Py-FI mass spectra in the temperature range >500°C. Furthermore, the peak around 401.4 eV, indicative of the spiked N-acetyl-D-(+)-glucosamine [2], gradually became smaller or was slightly shifted with increasing pyrolysis temperatures in both of the samples. This could be due to volatilization which should then be detected by Py-FIMS over the whole temperature range, but with greatest intensity up to 400°C.

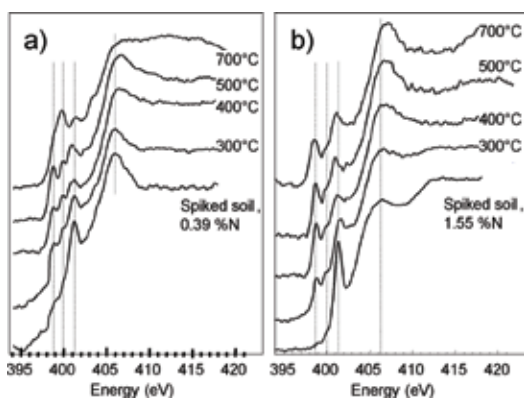


Figure 2. N K-edge XANES spectra of a soil sample spiked with N-acetyl-D-(+)-glucosamine: (a) N content enriched by factor 2 (0.39% N), (b) N content enriched by factor 10 (1.55% N).

For the evaluation of the Py-FI mass spectra, thermograms of N-acetylglucosamine in the spiked soil samples were calculated from the relevant indicator signals [3]. The thermograms for the sum of these marker signals in Figure 3a show distinct peaks of maximum volatilization at 240–250 °C. It can be calculated that about 55–68% of added N-acetyl-D-(+)-glucosamine was thermally volatilized up to 300 °C and 84–86% up to 400 °C. This conforms to the visible reduction of peak area in the N K-edge XANES spectra (Figure 2a, b). Furthermore, Figure 3b shows thermograms for pyridine, methylpyridine, alkylhydroxypyridine, methyl-pyrimidine, C4-pyrazole, indolethanol and propylcholine, which represent basic structures showing N K-edge XANES peaks around 399 eV. Both samples revealed volatilization maxima at 450 °C; however, only the sample with 1.55% N showed a prominent peak at about 250 °C. Figure 3a shows that this is the characteristic temperature of N-acetylglucosamine release from the sample. This indicates that the evaporation and thermal cleavage of high concentrations of N-acetylglucosamine in the sample led to the formation of N-heterocyclic compounds, mainly of methylpyridine. First cautious estimates indicate that about 5% (spiked soil 1.55% N) to 10% (spiked soil 0.39% N) of the added N-acetylglucosamine may have been transformed into heterocyclic and nitrile N. These preliminary data evaluations demonstrate the methodological approach by which possible pyrolytic formations of non-proteinaceous N-compounds will be detected and quantified to validate the interpretation and evaluation of Py-FI mass spectra. Progress in this research will provide multi-methodological evidence for the organic N forms in nonliving organic matter.

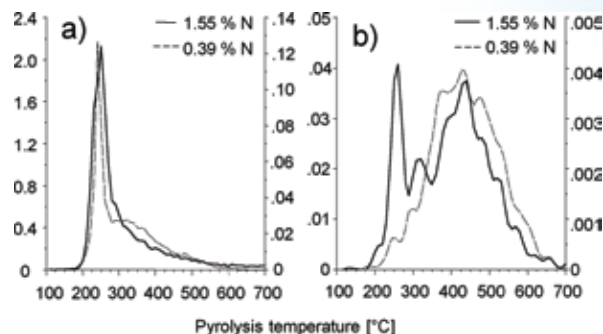


Figure 3. Thermograms for the volatilization of marker signals for N-acetyl-D-(+)-glucosamine [5], and thermograms for the summed ion intensities of marker signals for heterocyclic N-compounds which were indicated by the N-XANES features in Figure 2a,b.

Conclusions

The response of N-XANES spectra to increasing concentrations of various forms of amide N as well as the pyrolytic formation of N-heterocycles confirm that N-XANES can be developed as a complementary tool for the investigation of N-species in soil and its changes due to management or environmental impacts. Together with an improved data evaluation of Py-FI mass spectra, a new multi-methodological approach will be developed for a reliable and sensitive quantification of ‘unknown’ organic N in environmental samples.

References

- Schulten, H.-R., Schnitzer, M. 1998. The chemistry of soil organic nitrogen: A review. *Biology and Fertility of Soils*. 26, 1-15.
- Leinweber, P., Kruse, J., Walley, F.L., Gillespie, A., Blyth, R.I.R., Regier, T. 2007. N K-edge XANES – An overview of reference compounds used to identify ‘unknown’ organic nitrogen in environmental samples. *Journal of Synchrotron Radiation*. 14, 500-511.
- Bahr, U., Schulten, H.-R. 1983. Pyrolysis field ionization mass spectrometry of cell wall components and bacterial cell walls. *Journal of Analytical and Applied Pyrolysis*. 5, 27-37.

Acknowledgements

This research was funded by the German Academic Exchange Service (project D/05/50492), and the Ministry of Education of Mecklenburg-Western Pomerania (HSPIII project 4200/0037 5001, project UR 07 079.). We would like to thank the beamline scientists, Robert Blyth and Tom Regier, for their assistance.