US EPA ARCHIVE DOCUMENT

Michael B. Hay

Princeton University, Princeton, New Jersey

2004 EPA STAR Graduate Fellowship Conference *Next Generation Scientists—Next Opportunities*

Probing Carboxyl "Structural Environments" in Natural Organics Using Infrared Spectroscopy

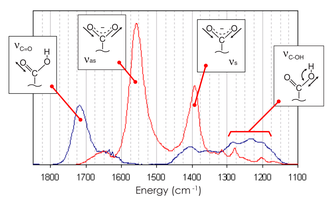
Introduction

Natural organic matter (NOM) is a key chemical component of terrestrial and marine systems. It is known to play an important role in metal speciation and transport, nutrient retention, and mineral weathering. [1, 2] Much of its chemical activity results from a high concentration of carboxyl groups, which often dominate the acidity and metal binding capacity of NOM.

The chemical behavior (acidity, binding affinity) of a carboxyl group is dependent on its "structural environment" (the types and positions of neighboring functional groups on the molecule). However, this information is unavailable for NOM constituents since their chemical structures are largely unknown, making it difficult for researchers to predict the behavior of NOM in the environment.

It has been shown that the infrared spectra of simple organic acids change predictably depending on the structural environment of the carboxyl group (see below) [3,4,5]. We propose that this information can be used to predict what types of structures exist in NOM, allowing us to determine "local" structures in NOM molecules without the need for a complete structural description.

Tricarballylic acid, pH 2.2 (blue) and pH 7 (red)

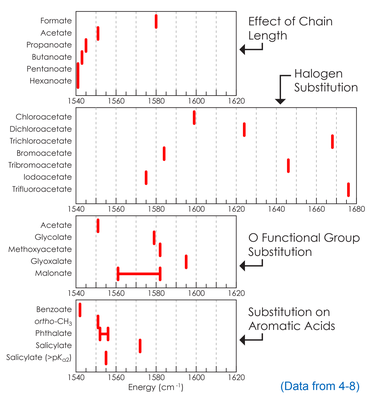


Carboxylate anion absorption frequencies affected by:

- Electron donating / withdrawing functional groups
- Inter / intramolecular H-bonding

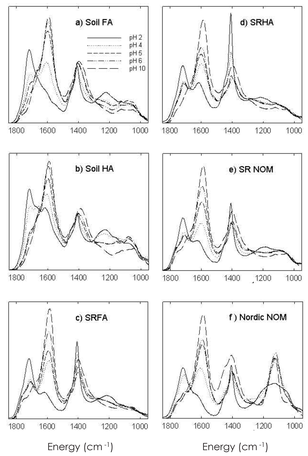
Effects are most apparent in the asymmetric carboxylate mode (ν_{as})

Trends in the Carboxylate Mode



(Data from 4-8)

Approach



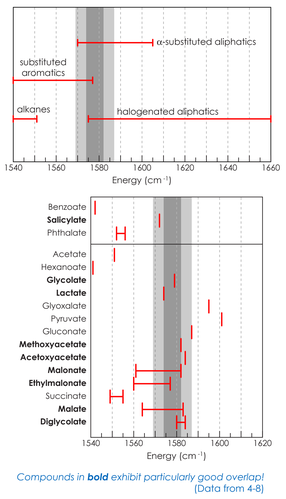
Infrared spectra were collected on humic and fulvic acids from the International Humic Substances Society (left), and a pristine leaf leachate sample obtained from the Pine Barrens, NJ (not shown). Carboxylate features were identified from a comparison of spectra at varying pH. Accurate peak positions and widths were obtained through deconvolution.

It can be seen that carboxyl groups dominate the infrared spectra, due to their high concentration and polarity. Surprisingly, the ν_{as} energy occurs at nearly the same place in all samples, regardless of origin / climate and solubility fraction.

Results

Carboxylate ν_{as} values for the NOM ranged between **1574-1582 cm^{-1}**, (dark gray bar; light gray "error" bars describe heterogeneity, inferred through peak width comparisons). Based on comparison with model compounds, dominant structural types in NOM appear to be ***aliphatic , with substitution on the neighboring C***. Other structural types (aromatic acids and unsubstituted aliphatics) are also present in small concentrations, based on spectral changes off of the main ν_{as} peak.

Based on elemental abundance, these substitutions are mostly in the form of oxygen functional groups, including hydroxyls, ether linkages, and neighboring carboxyl groups.



*Compounds in **bold** exhibit particularly good overlap!*
(Data from 4-8)

Impacts

These results will potentially have a large impact on the way studies of NOM chemistry are approached theoretically and experimentally. Traditionally, it was believed that aromatic carboxylic acid structures dominate in NOM, and many people still use simple aromatic acids (salicylate, phthalate) as NOM analogues when studying metal and mineral surface interactions.

Neighboring groups can affect metal binding in 2 ways:

- Electron withdrawal / donation through bonds, affecting carboxylate chemistry
- Direct participation in binding the metal (or "chelation")

Due to the high metal affinity of NOM, chelate type reactions were known to play a role, but the structures involved were unknown.

Comparison of Metal Binding Constants:

Log K, where $K = \dfrac{[ML]}{[M]\,[L]}$

M = metal, L = ligand

(data from 9-13)

Aromatic: 1.7 - 3.2
Aliphatic: 1.7 - 1.9
Substituted aliphatic: 2.4 - 2.5
Di-acids: Up to 5

NOM: 2 - 7

Many different structures are involved in metal binding, but O-substituted aliphatic carboxylates likely contribute to intermediate NOM binding constants.

This work is being done under the guidance of Prof. Satish Myneni, Department of Geosciences, Princeton University

For more information on what we do, please visit our website: http://geoweb.princeton.edu/research/geochemistry

1. Sposito G. (1989) The Chemistry of Soils. Oxford University Press.
2. Stevenson F. J. (1994) Humus Chemistry: Genesis, Composition, Reactions. John Wiley & Sons, Inc.
3. Goulden J. D. S. and Scott J. E. (1968) Nature, 220, 698-699.
4. Cabaniss S. E. and McVey I. F. (1995) Spectrochim. Acta A, 51, 2385-2395.
5. Cabaniss S. E., Leenheer J. A., and McVey I. F. (1998) Spectrochimica Acta A, 54, 449-458.
6. Tejedor-Tejedor M. I., Yost E. C., and Anderson M. A. (1992) Langmuir, 8, 525-533.
7. Yost E. C., Tejedor-Tejedor M. I., and Anderson M. A. (1990) Environmental Science and Technology, 24, 822-828.
8. Dunn G. E. and McDonald R. S. (1969) Canadian Journal of Chemistry, 47, 4577-4588.
9. Martell A. E. and Smith R. M. (1974-1989) Critical Stability Constants. Plenum Press.
10. Alberts J. J. and Giesy J. P. (1983) in Aquatic and Terrestrial Humic Materials (ed. Christman and Gjessing) Ann Arbor Science.
11. Cabaniss S. E. and Shuman M. S. (1988) Geochimica et Cosmochimica Acta, 52, 185-193.
12. Bresnahan W. T., Grant C. L., and Weber J. H. (1978) Analytical Chemistry, 50, 1675-1679.
13. Logan E. M., Pulford I. D., Cook G. T., and MacKenzie A. B. (1997) European Journal

This fellow is sponsored by EPA's STAR or Greater Research Opportunities (GRO) Program.