

HUMIC SUBSTANCES SEMINAR IV

**Northeastern University
Boston, MA, USA
March 22-24, 2000**

Humic Substances Seminar IV was dedicated to Frank J. Stevenson, former Professor of Soil Science at the University of Illinois and an Honorary Member of IHSS. The Honorary Chair was Michael Hayes of the University of Limerick and the Honored Guest was Morris Schnitzer who (with Dr. Stevenson) received the Wolf Prize for Agriculture in 1996. Also very welcome was Robert Wershaw (USGS, Denver), who prompted HSs Seminar I and was Honorary Chair of Seminar II in 1998. Greetings from Fritz Frimmel (President, IHSS) and Donald Sparks (President, Soil Science Society of America) were read. The Honorary Chairs of Seminars I (Wolfgang Ziechmann) and III (Cornelius Steelink) were recognized. Also participating were IHSS Past President James Alberts, President-Elect Yona Chen, Past Presidents Michael Hayes and Nicola Senesi, newly elected Board Member Maria De Nobili and the IHSS Coordinators of Canada, Egypt and USA (Ming Huang, Elham Ghabbour and James Rice).



Honorary Chair Michael Hayes with Seminar Chair Geoffrey Davies (right) and Co-Chair Elham Ghabbour (left)

Industrial interest in the Seminars is growing. Seminar IV featured an Exhibit by the following organizations: Arctech, Inc. (Chantilly, VA, D. Walia), Biomin, Inc. (Ferndale, MI,

G. Alther), Fisher Scientific LLC (Suwanee, GA, M. Clifford), Horizon Ag-Products, Inc. (Kennewick, WA, D. King), Humate International, Inc. (Jacksonville, FL, B. Galbraith), US Chapter, IHSS (J. Rice), Live Earth Products (Emery, UT, R. Taylor), Micromass UK Ltd (Manchester, D. Churchman), The Royal Society of Chemistry (Cambridge, UK, R. Andrews), Springborn Laboratories, Inc. (Wareham, MA, J. Hoberg), U-Mate International, Inc. (Scottsdale, AZ, D. Jones) and USDA-NRCS-National Soil Survey (Lincoln, NE, H. Smith). A full day of HSs applications papers was included in the program of 36 presentations with nearly 100 authors from 16 countries.

We followed the sequence HSs Formation, Characterization, Separation, Solute Sorption, Metal Binding, Coal-derived HSs and Applications. Two topics of high current interest were HSs aggregation and redox chemistry, as presented by leaders of these fields. The work ranged from aqueous NOMs to solid HAs. The program and abstracts are available at <www.hagroup.neu.edu>. The proceedings will be published as the book *Humic Substances: Versatile Components of Soil and Water*, E. A. Ghabbour and G. Davies, Eds., by The Royal Society of Chemistry in November 2000. Each paper will be abstracted by Chemical Abstracts. Research presented at Seminar IV by the individuals named is summarized below.

R. Wershaw recommended detailed HSs formation studies rather than seeking structures of transient (even in geological time) HSs. M. Huebner reviewed evidence for free radical humification process components. M. Schnitzer reported that composted duck farm-bedding waste mostly consists of holocelluloses, lignins, phenolic esters and lipids (with sterols prominent). Lipid components may favor HSs aggregation. He emphasized studies of whole samples rather than isolated HSs fractions. Y. Chen reported that according to ¹³C NMR data, HAs from composted cattle manure and municipal solid waste have increased carboxylic acid and aromatic content and decreased aliphatic character and carbohydrate content. P. M. Huang compared the products of catechol air-oxidation catalyzed by aqueous hydroxoaluminum at acid pH with the IHSS standard HA. L. Tremblay (winner of the *Best Graduate Student Presentation Award*) described a rapid diffuse reflectance-IR-Fourier transform (DRIFTS) method to measure the FAs and HAs contents of dried, ground sediment samples.

Humic Substances Seminar V will be held at Northeastern University, Mar. 21-23, 2001. The Honorary Chair is Dr. C. E. Clapp of the University of Minnesota. Registration and abstracts deadline is Dec. 30, 2000, <www.hagroup.neu.edu>. See you there!!!!



From left: Matthius Huebner, Session Chair Michael Hayes, Robert Wershaw and Morris Schnitzer.



From left: Jingdong Mao, Colin Graham, Kevin Thorn, Barend van Lagen, Baoshan Xing, Michael Hayes and Session Chair Robert Wershaw.



From left: Dula Amarasiriwardena, Session Chair James Alberts, Ming Huang, Best Graduate Student Award Winner Luc Tremblay, Yona Chen and Baoshan Xing.



From left: Seminar Co-Chair Elham Ghabbour, Masakazu Aoyama, Alessandro Piccolo, Session Chair Barry Karger, Maria De Nobili and Seminar Chair Geoffrey Davies.

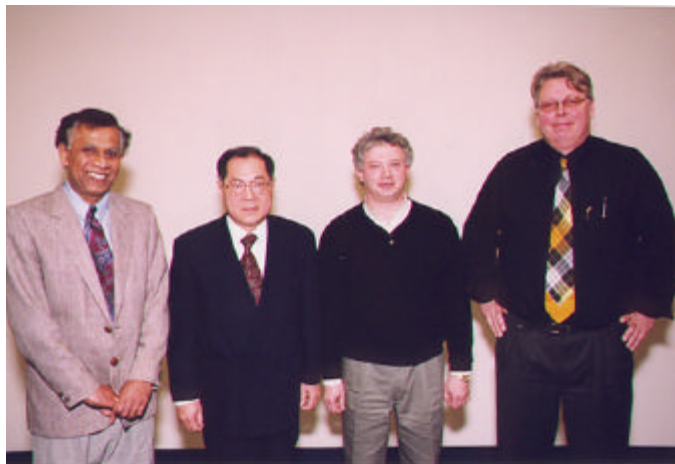
DRIFTS and cross polarization/total sideband suppressed ^{13}C NMR spectra were used by G. Ding to compare HSs products from different cover systems. K. Thorn used ^{15}N spectroscopy to follow coupling to soil components of amine products from soil transformed TNT. Quantitative ^{13}C NMR spectroscopy benefits from variable contact time measurements to help correct the HSs spectra, as reported by B. van Lagen. Two-dimensional $^1\text{H}/^{13}\text{C}$ (HETCOR) sub-spectra described by J. Mao are easier to interpret than conventional data. M. Hayes reported that HPLC with modified eluents that disfavor molecular associations decreases the polydispersity of HSs fractions. He confirmed that 2-D HETCOR is giving new HSs connectivity and structural clues. A. Piccolo reported that peroxidase treatment of supramolecularly associated HSs causes polymerization and earlier elution of the products from HPSEC columns. M. De Nobili said that more work with electrophoretic methods based on charge density and diffusion will resolve questions of high or low HSs molecularity.

M. Aoyama, who is identifying fluorescent “impurities” in HSs samples and their possible origins addressed a fundamental question in HSs photochemical work. J. Rice uses X-ray and laser light scattering to show that HSs aggregation results in little change of predominantly fractal, pseudo-spherical particle morphology. G. Haberhauer uses statistical cluster analysis to improve the information content of HSs mass spectral data.

J. Van Stempvoort found fast and slow Aldrich HA adsorption on a coarse, carbonate rich model aquifer solid, followed by Langmuir behavior at equilibrium. The products retard Cu(II) and PAH mobility in a pilot scale aquifer. This theme was continued by J. Poerschmann, who demonstrated how HSs sorption is activated by treating aquifer materials with iron(III) and aluminum salts. J. Kochany reported that HSs catalyze phenol and formaldehyde removal from water and can support biological activity of raw activated sludge if no other food source is available, as indicated by respiro-



From left: Jurgen Poerschmann, Georg Haberhauer, Session Chair Colin Graham, Dale Van Stempvoort and James Rice.



From left: Dula Amarasiriwardena, Session Chair Ming Huang, Gregory Korshin and Gunnar Buckau.



From left: Jan Kochany, Lars Carlsen, Elham Ghabbour, Nicola Senesi and Session Chair Daman Walia.



From left: Copper Langford, Diane McKnight and Session Chair Thomas Gilbert.

metric measurements. L. Carlsen described multivariate analysis of factors favoring sorption of esfenvalerate (a hydrophobic, highly toxic insecticide) by DOMs of different origin. N. Senesi described how endocrine disrupters bisphenol A (BPA) and ethynil estradiol (ED) are sorbed by six different HAs. The data follow the Freundlich relation. Reversible sorption of ED is much more extensive than for BPA. Aniline interacts most strongly with a soil fulvic acid at pH 5.0, as indicated by fluorescence quenching data reported by C. Coolidge. The results suggest an electrostatic interaction in the most favorable quenching conformation.

D. Amarasiriwardena has coupled flow field-flow fractionation to inductively coupled plasma-mass spectrometry to create Flow-FFF-ICP-MS, which gives monomodal fractograms (apparent $M_w \approx 5$ kDa for five different HAs) with different polydispersities containing trace metals. Increased splitting of the first-derivative X-ray absorption near-edge spectra (XANES) of Cu-HSs complexes at high pH

reported by G. Korshin indicates tetragonal distortion presumably due to competing OH⁻ coordination. G. Buckau stated that because of counterion inclusion, only a fraction of proton exchanging HSs functional groups can be loaded with metal ions and that the complexation strength and counterion inclusion correlate. D. McKnight described the effects of Fe-HS complexes on photochemical reductive dissolution of iron oxides and as electron shuttles to iron(III) oxides, which fractionate more aromatic HSs components according to NMR data. Quinoid triplets are key products of HSs photochemistry, as indicated by comparison with a benzoquinone/hydroquinone/phenol (3:3:1) model in work described by C. Langford.

The elemental analyzer-isotope ratio mass spectrometry principle described by J. Morrison is a very powerful tool in plant physiology, environmental science and soil chemistry. The most telling measurement for mechanistic purposes is H/D ratios. G. Buckau reported for 11 co-authors the results of an

EU-funded study of HSs effects on radionuclide migration. Radionuclides are essentially irreversibly bound by NOMs in natural systems, which is a big factor in system models. G. Alther gave a fascinating account of how swellable clays like bentonite can be modified with quaternary amines to exchange anions and remove Cl_2 and HSs from water. J. Alberts described how acidification causes Norwegian lake NOM to lose oxygenated aromatic fragments and make metal loaded NOM more toxic towards the bacterium *Vibrio fischeri*. G. Korshin presented the complicated kinetics of Cl_2 reactions with the hydrophobic fraction of Suwannee River NOM, and with resorcinol and 3,5-dihydroxybenzoic acid as models.

HA technology in the Czech Republic was well represented by HA materials extracted from capucine, a waste material in coal production and oxyhumolite, an oxidized brown coal, as



From left: Gunnar Buckkau, Gregory Korshin, Session Chair Nicola Senesi and James Alberts.

Right Photo: Humic Acid Group hosts. From left: Aleksandr Cherkassliy, Dina Sorour, Yam-Yuen Lam, Rashel Kesilman, Matthew Mulligan, Elham Ghabbour, Ahmed El-Shafey, Marcy Vozzella and Geoffrey Davies.

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reported by D. Gajdošová and L. Pokorná. These materials have more than one feature in common with soil-derived HAs. A. Fataftah described Humasorb™, a cation exchanger that also sorbs organics, destroys chlorinated soil/water products, is insoluble in water and can be modified to exchange anions. K. Day, a pre-eminent consultant, reported that HA products are increasingly being applied in agriculture, especially to prevent tie-up of phosphorus by calcium and by iron and aluminum minerals.



From left: George Alther, G. Ding, Amjad Fataftah, Kenneth Day, L. Pokorná, Session Chair Darryl King & D. Gajdošová.



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Editor: E. A. Ghabbour

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Seminar IV participants outside the Egan Research Center, Northeastern University.