



NEWSLETTER

INTERNATIONAL HUMIC SUBSTANCES SOCIETY

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On December 17, Prof. Dr. Dr. h. c. **Wolfgang Flaig** celebrated his 90th birthday. He grew up in Freiburg, Germany, where he attended school and studied chemistry at the University. As research assistant he moved to the Universität Würzburg, where he obtained his PhD. Following his special interest in macromolecular chemistry, he joined the group of Karl Ziegler, later Nobel Prize laureat at the Universität Halle, and finished his habilitation on the reactions of crotonaldehyds in 1944. Back in those days, Wolfgang Flaig also got infected by the fascination of the chemistry of soil organic matter. This infection even survived the chaos of the end of World War II. So, when life returned to normal again, Wolfgang Flaig joined his mentor Ziegler at the Max-Planck Institut for Carbon Research in Mülheim/Ruhr. In 1948, he took his most important step into soil science by becoming Director of an institute for humus investigations in the newly established Research Centre for Agriculture in Braunschweig. Under his leadership, the institute grew and became world renowned for its modern approach to the biochemistry of soil. More than 250 papers on the formation, structure and function of humic and fulvic acids, including their physiological effects on plants, bear the name of Wolfgang Flaig. About 30 PhD students and many international visitors joined the laboratories and experimental fields in Braunschweig. Due to his broad scientific view centred around chemistry, his devotion to teaching and his great management skills, Wolfgang Flaig served as President of the Agricultural Research Centre for several years and in 1961 he was appointed Professor at the Technische Universität Braunschweig. He also served on the boards of the German and International Soil Science Societies and the Peat and Peloids Societies. His engagement in international cooperations led to a number of highly renowned appointments as fellow of several Academies of Science and research organizations. In 1978, he was awarded the honorary doctorate of the Catholic University of Leuven / Belgium. Several Soil Science Societies awarded him the honorary membership, which he also obtained from the IHSS at the Birmingham Conference in 1984.

In addition to all his scientific merits, Wolfgang Flaig's personality needs to be particularly mentioned. He is an honest, open minded scientist, optimistic also in difficult situations and he always enjoys company. Even now, when nature begins to show us that strength is not unlimited, he continues to offer his charm and fine sense of humour to his friends and the people around him.

We congratulate Wolfgang Flaig dearly to his birthday and wish him all the best.

Fritz H. Frimmel



Wolfgang Flaig amongst other humic researchers at the Dahlem Conference 19

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International Humic Substances Society on the World Wide Web

Visit our home page at:

<http://www.ihss.gatech.edu>

NEW UPDATE!!! The website now contains a lot of analytical data on the standard and reference samples of the IHSS Collection

Dr. E. M. Perdue is coordinating the development of the IHSS WEB page. You can follow the progress on the above WEB site which is located on the server of the Georgia Institute of Technology, Atlanta, USA.

Suggestions and comments regarding the content and organization of the WEB pages are actively requested from all IHSS members.

E-mail Dr. E. M. Perdue at michael.perdue@eas.gatech.edu for more information.

20th Anniversary Conference of the International Humic Substances Society - IHSS

Conference Summary

The 20th anniversary conference of the IHSS was held in Boston, Massachusetts, USA, on July 21-26, 2002. The conference theme was: "Humic Substances: Nature's Most Versatile Materials".

The conference was organized by the following committees:

1. **IHSS Board Members:** Yona Chen, President; Fritz Frimmel, Past President; Maria De Nobili, Vice President/President-Elect; Teddy Miano, Secretary; Ed Clapp, Treasurer; Gudrun Abbt-Braun, Board Member; Ladislau Martin-Neto, Board Member; and Paul Bloom, Chairman Reference Collection.
2. **Organizing Committee:** E. Ghabbour (Chair), G. Davies (Chair), D. Amarasiriwardena, B. Burns, Y. Chen, K. Czerwinski, T. Gilbert, J. Julien, S. Martin, J. Nascarella, J. Rice, D. Ryan and B. Xing.
3. **Scientific Committee:** P. Bloom, Y. Chen, G. Davies, M. De Nobili, J. Drozd, F. Frimmel, E. Ghabbour, P. Hatcher, P. Huang, M. Kaemmerer, L. Martin-Neto, J. Rice, N. Senesi, K. Spark, D. Sparks, M. Spiteller and K. Yonebayashi.

Humic substances research dates back about two centuries, but in the last two decades our understanding of the structure and reactivity of these complex materials has increased dramatically. The IHSS, which actually evolved twenty years ago from an effort to create an internationally accessible reference and standard humic substances collection, and a standard procedure for their extraction, has played a pivotal role in enhancing the rate of intensive research aimed at elaborating the structure, function and reactions of these materials. Humic substances which were created by nature to prevent decomposing organic material from forming a chaotic collection of molecules, were in the past considered to be a black box. Researchers have now elaborated their tremendous range of structures and reactivity in soil and water environments. Yet, to date we have only taken the first step on the indefinitely long road towards unveiling the properties of humic matter. It is and will be the society's role to assist researchers in the essential process of information exchange and in stimulating and establishing joint research activities.

The bi-annual IHSS meetings are a major tool in this process and the Boston conference marked the 20th milestone in this conference series. Of the 1050 members of the society and a large number of researchers who are not members, about 220 attended the conference in Boston. Among them were 8 students who were selected out of 15 applicants to be the recipient of the IHSS travel bursaries. Following the welcome and opening ceremony, an opening session took place, dedicated to a discussion on the history of the IHSS from the very beginning through two decades of its existence. P. MacCarthy was congratulated by the conference attendees for his excellent summary. Discussion in this session included: the establishment of a web based Natural Organic Matter Forum, for quick publication and discussion of extended abstracts; the structure of humic substances (HS); and the application of synchrotron-based X-ray spectroscopy and microscopy to studies on humic substances.

Separation and fractionation of humic substances were discussed in a series of papers. Capillary zone electrophoresis (CE) and electron ionization/mass spectrometry (ESI/MS) of natural organic matter (NOM) were introduced. The discussion included charge and mass distributions in mixtures, the characterization of dissolved organic matter (DOM) and borate complexing by HS. Reference was made to the complexity of structure and poly disperse nature of the materials studied. A symposium session focused on substantial analytical issues of interest to HS researchers. Quantitative analyses and predictive modeling of reactivities as a gateway to practical application of HS were discussed and debated. Modern analytical techniques such as electro-spray ionization and high field FT ion cyclotron resonance MS were described and well presented to an audience that was only partially familiar with these techniques.

Since the number of submitted abstracts exceeded the capacity of a symposium with only one lecture hall, a large number of posters were presented and, for the first time in IHSS symposia, one

day also included parallel sessions. The pros and cons of the decision to conduct discussion in parallel sessions were debated during board meetings preceding this conference and during the general assembly of the society. In general, the membership accepted the fact that we run a large society and fortunately have a large number of presenters with high quality papers. A compromise, like the one implemented in the 20th meeting program, was therefore unavoidable.

One of the parallel sessions focused on adsorption reactions of xenobiotics on HS and metal oxides. An excellent lecture was presented in this session by Ms. Illes, an IHSS Malcolm and a Travel Bursary Awardee. She spoke about effects of HA adsorption on the aggregation of magnetite nanoparticles. Heavy metals interactions with NOM and HS were discussed in the other parallel session. Catalytic effects of Ni-HS complexes in dehalogenation reactions, as well as the interaction of HAs with actinides were discussed. Hydrophobicity of soils induced by HA via wetting and drying cycles of the soil, swelling of organic matter in soils and the association of nonpolar contaminant with humic matter, were presented in an additional parallel session which raised the interest of many of the participants. This session reached its peak with an exciting lecture by A. Simpson, on the fundamentals of HS and their humic-clay complexes. The biological and agricultural activities of HS as well as char formation issues were discussed in the last two sessions of the conference.

We believe that future conferences should include more sessions that will deal with functions (in the environment, in agriculture and in medicine) and reactions. Although structure, which was the focus of the 20th anniversary conference is most important, research should continue, in parallel fashion, on functions and reactivity, postponing expectations to fully understand all structural aspects of HS.

The general assembly of IHSS took place on July 25th, in the late afternoon. Yona Chen presented the President's report on societal issues, which was followed by the Secretary's (Teddy Miano) and Treasurer's (Ed Clapp) financial report. The financial report was approved by the general assembly. Several questions were raised by the audience, in relation to difficulties they faced with registration and accommodation reservations for the Boston conference. It seems that a number of members did not attend the conference because of these problems. The Board was aware of these problems and steps have been taken to avoid such difficulties in future meetings. In fact, the Board adopted a series of guidelines for the organizers of future symposia.

The IHSS membership and Board thank Elham Ghabbour and Geoffrey Davies for their effort and sincerity in organizing the 20th IHSS conference. Following a unanimous decision by the Board, the IHSS flag has with pleasure been transferred to the Brazilian Chapter, headed by Ladislau Martin-Neto. The Brazilian Chapter will host the 21st IHSS conference in São Pedro in July 2004 and we look forward to what promises to be an excellent conference.

Yona Chen, *President*

Maria De Nobili, *Vice-President*

PAST MEETINGS

2nd Symposium of IHSS-Canadian Chapter, Guelph, Ontario, Canada, August 2001 **"Dynamics and Transformations of Organic Matter in the Environment"**

by Dr. P. M. (Ming) Huang

The objective of this Symposium was to address the issues on the dynamics and transformations of organic matter in soil and related environments. This symposium provided a forum for interactions of soil chemists, soil biochemists, soil microbiologists, soil mineralogists, and environmental scientists across Canada. This Symposium was organized by the Canadian Chapter of the International Humic Substances Society and co-sponsored by the Canadian Society of Soil Science and Working Group MO "Interactions of Soil Minerals with Organic Components and Microorganisms" of the International Union of Soil Sciences. This Symposium was organized by R. Paul Voroney, Department of Land Resource Science, University of Guelph, Guelph, Ontario.

MEETINGS

Humic Substances Seminar VII, Boston, MA, USA, March 19-21, **2003**. Humic Substances Seminar VII will be held as usual at Northeastern University. By popular demand, Seminar VII is dedicated to Professor Fritz H. Frimmel of the University of Karlsruhe, Germany, and the Honorary Chair is Professor Russell F. Christman of the University of North Carolina. Please contact Dr. E. Ghabbour, Barnett Institute, 341 Mugar Hall, Northeastern University, Boston MA 02115, USA, Phone: (Int.+) (617) 373-7988, Fax: (Int.+) (617) 373-2855, E-mail: e.ghabbour@neu.edu, Web <www.hagroup.neu.edu>

9th Nordic IHSS Symposium on "Abundance and Functions of Natural Organic Matter Species in Soil and Water", Mid Sweden University, Sundsvall, Sweden, May 19-21, **2003**. For further information please contact Prof. Ulla Lundström, Prof. Soil Chemistry, Dept. of Natural and Environmental Sciences, Mid Sweden University, SE-851 70 Sundsvall, Sweden. Ph. +46 (0)60 148416; Fax: +46 (0)60 148802; E-mail: Ulla.Lundstrom@kep.mh.se or visit the web site: http://www.ntm.mh.se/nordic_ihss

5th Meeting of the Italian Chapter of the IHSS, Lerici, Italy, June 5-6, **2003** - "*The Role of Organic Matter in a Sustainable Agriculture*". Internationally renowned speaker will be invited. For further information please contact: Dr. Fabrizio Adani (adani@mailserver.unimi.it) and Prof. Pierluigi Genevini (PierLuigi.Genevini@unimi.it), Ricola group - DiProVe - Sezione di Fisiologia delle Piante Coltivate e Chimica Agraria, Università Studi di Milano, Via Celoria, 2, 20133 Milano, Italy.

7th International Conference on the Biogeochemistry of Trace Elements (ICOBTE), Uppsala, Sweden, June 15-19, **2003**. An interdisciplinary conference dedicated to links between biosphere phenomena and physical & chemical reactions in the lithosphere. SLU Conference/7thICOBTE, PO Box 7059, SE-750 07 Uppsala, Sweden, www.conference.slu.se/7thICOBTE

16th International Symposium on Environmental Biogeochemistry (ISEB16), "*Biogeochemical Shaping of the Earth System: Past, Present and Future*". The Symposium is organized by Prof. Tsutomu Hattori in Oirase, Japan from September 1 to 6, 2003. Information is available on website <http://www.iseb16.com>.

2nd National Conference of the Bulgarian chapter of IHSS, Borovets, Bulgaria, 17-19 September, **2003** - "Humus Substances and the Environment". International participation is expected. Information: Dr. Ekaterina G. Filcheva and Dr. Svetla Rousseva, N. Poushkarov Institute for Soil Science, 7, Shosse Bankya, str., 1080 Sofia, P.O.Box 1369, Bulgaria, Tel: + 359 2 24 87 44; Fax: +359 2 24 89 37; E-mail: filcheva@bqnet.bg; svetrou@abv.bg or Ira G. Stefanova, Institute of Nuclear Research and Nuclear Energy (INRNE), 72, Tsarigradsko Shosse Bld., +359 2 9751028; Fax: +359 2 975 3; E-mail: irast@inrne.bas.bg

XII International Meeting of IHSS will be held in Brazil (July 2004)

by *Ladislau Martin-Neto*

The XII International Meeting of IHSS will be held in Brazil, in July (26-30), 2004. This decision was taken by the IHSS General Assembly, during the last IHSS Meeting in Boston. The chairman of the next meeting will be Dr. Ladislau Martin-Neto, a Member of Board of IHSS and Coordinator of the Brazilian Chapter. The meeting theme will be "**Humic Substances and the Soil and Water Environment**" and the following symposia will be included: Soil Humic Substances; Aquatic Humic Substances; Soil Carbon Sequestration; Characterization of Humic Substances: Emphasis on Advanced Methodologies; Soil Amendment and Remediation; Applications of Humic Products: Plant Growth, Organic Agriculture, Medicine, Sensors, etc.; Complexes of Humic Substances with Metal Ions; and Pesticide Reactions.

The meeting will be held in the city of São Pedro (a small tourist city, 35,000 inhabitants), in the State of São Paulo, in the center of Brazil and will be hosted by the Brazilian Corporation of Agricultural Research (Embrapa), the largest agricultural institute of Latin America, in cooperation with the University of São Paulo (USP), the Federal University of São Carlos (UFSCar) and the State University of São Paulo (UNESP). This region has a pleasant climate (700 m altitude) and is known for its tourist attractions: water sources, water falls, historic coffee farms, and several sugarcane factories, which also produce large quantities of ethanol as renewable automobile fuel. A call for papers and more information, including other tourist attractions such as the Amazon Rain Forest, Iguacu Falls, Rio de Janeiro, and others, will soon be available on the conference internet site. The Brazilian membership of IHSS is highly motivated and excited about holding the XII International IHSS Meeting and they will do their best to organize an outstanding conference. So please make a note of the conference dates and we look forward to welcoming you to Brazil in July 2004.

NEW BOOK

NEW BOOK

Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spitteller, M. (Eds.):

Refractory Organic Substances (ROS) in the Environment.

John Wiley and Sons, New York (2002).

ISBN 3-527-30173-9

(546 pages, with 212 figures and 96 tables, hardcover, 140,- \$, 159,- €)

REFRACTORY ORGANIC SUBSTANCES IN THE ENVIRONMENT provides the results of six years priority research which was funded by *Deutsche Forschungsgemeinschaft*. The aim of the research programme was to investigate the structure and function of ROS in different parts of the environment. Chemists, physicists, biologists and soil scientists joined their effort in order to elucidate the role of ROS in aquatic and terrestrial ecosystems.

For the first time, a suite of reference samples from Central Europe was systematically studied with multidisciplinary approach. The samples were obtained from a bog lake, from soil seepage water, from ground water and from waste waters of a brown coal processing plant and a secondary effluent. This covers typical parts of the hydrological cycle and includes even strong anthropogenic influences. The aquatic samples and the isolated reference samples were investigated by advanced chromatographic and spectrometric methods including high performance size exclusion chromatography, nuclear magnetic resonance spectroscopy, steady state and time resolved luminescence spectroscopy and mass-spectrometry combined with analytical pyrolysis. Basic characterization focussed on elemental and isotopic composition and on identifiable building blocks like amino-acids, carbohydrates and carboxylic acids. Of further interest was the application of X-ray microscopy and of biochemical methods. The book clearly reveals the serological characterization, biochemical formation and utilization of ROS and their effects on microorganisms. In addition, specific interactions of ROS with different substances like enzymes, polycyclic aromatic hydrocarbons, pesticides and other xenobiotics were studied.

Thus not only structural features of ROS are given but also their function in aquatic systems and soils is highlighted. This also includes the influences of civilization which are reflected e.g. in the bound residues, and the ROS resulting from microbiological waste water treatment. It is beyond doubt that ROS are closely related to the carbon intensity which has been identified as one of the driving forces in the dynamic of green house gas emission. As a consequence ROS have a key function in sustainable development. Their diversified functionality in the environment should be of special interest for students and researchers interested in life sciences.

by Gudrun Abbt-Braun

IHSS VOLUMES (and related publications)

UNDERSTANDING HUMIC SUBSTANCES: ADVANCED METHODS, PROPERTIES and APPLICATIONS (286 pp.). Edited by E Ghabbour and G Davies, Royal Society of Chemistry, Cambridge, England, 1999. **ISBN 0-85404-799-9**

HUMIC SUBSTANCES: VERSATILE COMPONENTS OF PLANTS, SOILS AND WATER (341 pp.) Edited by E Ghabbour and G Davies, Royal Society of Chemistry, Cambridge, England, 2000. **ISBN 0-85404-855-3**

HUMIC SUBSTANCES AND CHEMICAL CONTAMINANTS (502 pp.). Edited by CE Clapp, MHB Hayes, N Senesi, PR Bloom, and PM Jardine, Soil Science Society of America, Inc., Madison, 2001.

HUMIC SUBSTANCES: STRUCTURES, MODELS AND FUNCTIONS (387 pp.) Edited by E Ghabbour and G Davies, Royal Society of Chemistry, Cambridge, England, 2001. **ISBN 0-85404-811-1**

UNDERSTANDING AND MANAGING ORGANIC MATTER IN SOILS, SEDIMENTS AND WATERS (600 pp.). Edited by R.S. Swift and K.M. Spark, IHSS, 2001.

REFRACTORY ORGANIC SUBSTANCES (ROS) IN THE ENVIRONMENT (546 pp.). Edited by Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spitteller, M., John Wiley and Sons, New York, 2002. **ISBN 3-527-30173-9**

Book based on HUMIC SUBSTANCES SEMINAR VI and IHSS 11 in July 2002 is in press with Taylor & Francis, New York for publication in March.

BOARD OF DIRECTORS BUSINESS MEETING - UPDATES



At the last Board of Directors Meeting held during the 20th Anniversary Conference at Northeastern University, Boston, USA, the President, Yona Chen, welcomed all Board Members attending the Meeting and officially introduced the new Board Members: in the office of Vice-President, **Maria De Nobili**, Italy; in the office of Board Member, **Gudrun Abbt-Braun**, Germany and **Ladislau Martin-Neto**, Brazil. The President congratulated the Past President, *Fritz Frimmel*, and thanked him on behalf of the Board for his excellent work, activities and initiative taken

in promoting the society issues over the past two years, as President of IHSS. Further, the President thanked *James J. Alberts*, our former Past President for his excellent service to the Society and the Board. Jim Alberts was honored during the General Assembly and was presented with a gift on behalf of the Board of Directors.

Main items and resolutions of IHSS Board of Directors were as follows:

IHSS Guidelines for the organization of IHSS International Meetings

The final revised version of the IHSS Guidelines for potential organizers of International Meetings was distributed to the Board of Directors. It was also given to the organizers of the next meeting. The IHSS Guidelines for international meetings encompass most of the Society's thoughts about IHSS Meetings and are meant to be given by the President of IHSS to any person submitting an application to organize a conference and to the Chairman of an Organizing Committee as a basic ruling tool of negotiation.

IHSS Guidelines for the Election Procedure

The Guidelines for the election procedure will be revised by Fritz Frimmel, based on his recent experience, and given to the Chairman of the Nomination Committee and to the President.

National Chapters and IHSS Organization worldwide

The Board voted unanimously in favor of the merging of the Baltic and Nordic chapters of IHSS and agrees to their proposed Bylaws. An official vote of support was sent to Georg Becher, Coordinator of the newly founded Nordic-Baltic Chapter.

The Colombian, Indonesian and Swiss chapters have been incorporated into the Rest of the World (RoW) chapter.

A meeting of the Spanish Chapter is currently being organized by Josemaria Garcia-Mina (jgmina@inabonos.com). The initiative is strongly supported by the Board, with the hope that the Spanish Chapter, one of the larger chapters in IHSS, may renew its activity and contribute to the general activities of the Society at a level appropriate to the large amount and high standard of

natural organic matter research being conducted in Spain. We hope all Spanish IHSS members will contribute to the success of the meeting and spread the news among other scientists that might be interested in it.

During Prof. Frimmel's and Prof. Chen's visit to Moscow in September 2002, they attended a meeting of a large number of members of IHSS from Russia and several republics of the former USSR. The participants of this meeting decided to form a chapter for all the countries that were represented. A detailed list of countries will be sent to the board by Irina Perminova and Olga Iakimenko, who were elected to lead the united chapter.

Al Olness has become chairman of the US chapter. The President and Board thank Jim Rice for coordinating the US chapter for the last six years.

IHSS Newsletter

The Board unanimously appointed the two Board Members, Gudrun Abbt-Braun and Ladislau Martin-Neto, as assistant Editors of the Newsletter. Their role will be to promote, stimulate, and collect materials to be published in the **three** issues of the Newsletter per annum.

IHSS Sample Collection

The Collection Committee will submit to the Board a written proposal to expand the Collection with additional samples representing other important natural and climatic areas of the world. It will first gather information and proposals related to sampling sites in various parts of the world (tropical soils and waters, etc.). Proposals should include provisional detailed expenses and possible voluntary help from members.

The Chairman of the collection committee, Paul Bloom, invited Mike Perdue to present the project, cost estimates and time schedule for the sampling campaign of the Suwannee River waters and for the isolation of a new HA Standard sample, aiming to replenish our stock. M. Perdue has volunteered to lead the team of the proposed campaign and he presented the project in detail. The project is planned for year 2003. Georgia Institute of Technology (and possibly the US Geological Survey) will co-sponsor the project, along with IHSS. A written agreement has been signed and operations will start in Spring 2003.

IHSS Website

Mike Perdue, the IHSS webmaster, presented to the Board the recent changes incorporated in the Society's website. The number of contacts (visitors) with the site has markedly increased in the last year and amounted to about 22,000.

New Motto for the Society

The President, Paul Bloom and other members of the board feel that the motto which appeared on the IHSS letterhead and website does not sufficiently describe the activities of our membership and limits the scientific goals and the image of the Society. We think it is important for the scientific community to comprehensively understand the role of humic substances in the environment. The behavior and structure of natural organic matter including humic substances is fundamental to our knowledge of the actions and functions of soil and water ecosystems. This issue was discussed in detail. All board members supported the idea of introducing a term with a broader meaning into the IHSS motto. The final decision was to introduce the term "natural organic matter" and change the present motto "To Advance the Knowledge, Research and Application of Humic Substances" into: "To Advance the Knowledge and Research of Natural Organic Matter in Soil and Water".

IHSS TRAVEL BURSARIES AWARDEES (IHSS 11)



Eight Travel Bursaries providing partial support to young researchers and students for attendance at the 11th Meeting of the IHSS in Boston, USA, have been assigned by an "ad hoc" Committee of the IHSS in year 2002. The Chairman of the Committee, Dr. Yona Chen, received a total of **15** applications within the deadline of January, 2002. In addition, and for the second time in Society's history, the best paper presented among them was also conferred the **Malcolm Award Certificate** by the President of IHSS, Dr. Yona Chen.

IHSS Bursary Awardees 2002

Malcolm Award Certificate

Erzsebet Illes

Department of Colloid Chemistry, University of Szeged, *Hungary*

Effect of humic acid adsorption on the aggregation of magnetite nanoparticles

Jeferson Diekow

Departamento dos Solos, Universidade Federal do Rio Grande do Sul, Porto Alegre, *Brazil*

Soil organic matter storage and stability promoted by cropping systems under no-tillage in southern Brazil

Ademir dos Santos

Laboratorio de quimica Ambiental-USP, São Carlos, SP, *Brazil*

Complexation of metal ions by humic substances and α -amino acids: a comparative study

Julieta Ferreira

Embrapa Instrumentação Agropecuária, São Carlos, SP, *Brazil*

Hydrophobic sites in humic acid as detected by ESR of spin-label stearic acid, ^{13}C NMR of labelled oleic acid and pyrene fluorescence

Luc Tremblay

Institut des Sciences de la Mer de Rimouski, Université du Québec a Rimouski, Quebec, *Canada*

Effects of lipids on the nonlinear sorption of phenantrene to sedimentary humic substances

Li Li

State Key Laboratory of Organic Geochemistry, Chinese Academy of Sciences, Guangzhou, *China*

Characterization of humic acids progressively base extracted from Pahoek peat

Thomas Brinkmann

Engler –Bunte-Institut, Universität Karlsruhe, Karlsruhe, *Germany*

Formation of low molecular weight organic acids from dissolved organic matter by irradiation with simulated UV light

Sandra Spielvogel

Lehrstuhl für Bodenkunde, München, *Germany*

Relationship between soil organic matter, iron content and soil color – an ^{13}C CPMAS NMR spectroscopic study

IHSS STANDARD AND REFERENCE COLLECTION

By Paul Bloom

Sales in 2002

Sales were up slightly from 2001. We processed 217 individual orders from scientists in 20 countries. Most of the sales continue to be to labs in the US, with the remainder distributed among 19 other countries. Humic materials from aquatic sources accounted for 2/3 of the sales. Sales of Suwannee River HA, FA, and NOM alone accounted for more than 1/2 the sales. Suwannee River NOM sales were down but this decrease was more than compensated by an increase in sales of Suwannee River Reference FA. A lower price for 1 gram quantities increased the interest in this FA. The current supply of Suwannee River Reference HA is low. Our inventory is only sufficient for 15 months of sales at the current rate. We will obtain a new batch of the Suwannee River HA this year.

The total sales of humic materials from terrestrial sources were the same as in 2001. However, sales of Pahokee (Florida) Peat Reference HA increased greatly. A lower price for 2 gram quantities increased interest in this HA. However, HA and FA from other sources decreased. Our reserve of bulk source Pahokee peat is low. We are currently in the process of obtaining more peat from the original source.

Efforts to Replenish Pahokee Peat Suwannee River HA

After 20 years, we have sold almost all the bulk source of Pahokee (Florida) Peat and almost all the standard HA obtained from the Suwannee River. We have initiated efforts to obtain a second batch of each of these materials. The University of Florida Everglades Research and Education Center, Belle Glade, Florida, has agreed to ship peat from the site where the original sample was obtained. We signed a contract with Georgia Institute of Technology and Dr. E. Michael Perdue to obtain a new sample of Suwannee River Reference HA. Fortunately, the US Geological Survey in Denver Colorado has allowed us to borrow some of the equipment used to obtain the original sample 20 years ago. We thank Dr. Larry Barber of the USGS for his help.

Price increases

The price of bulk Pahokee peat will be increased. Formerly we sold 500 gram quantities for \$50. In the future we will sell 250 gram quantities for \$50. The prices for shipping and handling will also be increased. Mailing costs have increased and the necessity for documentation has greatly increased, especially for foreign sales.

Dr. Konrad Haider is Awarded Honorary IHSS Membership at the 20th Anniversary Conference, Northeastern University, Boston, USA

As already mentioned in the past issue of the IHSS Newsletter, Dr. Konrad Haider was awarded the Honorary Membership of the IHSS. Konrad Haider published more than 300 scientific papers, most of which are closely related to humic substances formation. He is best known for his work on analytical identification of phenolic building blocks and other constituents of humics. In addition, his work focussed on the decomposition and transformation of humic precursors and the utilisation of the products by plants. Konrad Haider has not only given important scientific impulses on humics research, he also has been one of the strong supporters of IHSS and its activities from the beginning. The IHSS proudly announces the honorary membership of this successful scholar.



Fritz H. Frimmel

The Honorary Membership and Certificate was awarded by the President, Dr. Yona Chen (*right*), the Past President, Dr. Fritz Frimmel (*left*), and the Treasurer, Dr. C. Ed Clapp (*center*), during the Social Banquet of the 20th Anniversary Conference of the International Humic Substances Society, held at Northeastern University, Boston, USA, July 2002.

PhD Thesis

Interactions of Organic Substances with Mineral Phases – Investigation with Size Exclusion Chromatography and FTIR Spectroscopy

Christian Specht, Universität Karlsruhe, February 2002. Supervisor: **Prof. Dr. F. H. Frimmel**

Engler-Bunte-Institut, Division of Waterchemistry, Engler-Bunte-Ring 1, D-76131 Karlsruhe, Germany

Groundwater is the most important resource for the drinking water industry in Germany. The transport and reaction of chemicals in the soil are influenced considerably by natural organic matter (NOM). Although much work has been done on the behavior of contaminants in groundwater, only a few systematic investigations were conducted on how NOM influences the transport, reactions and distribution of contaminants in soils.

The aim of this work was to investigate the interactions between organic substances and clay minerals. The focus was on the natural organic matter, which strongly influences the transport of organic and inorganic contaminants in groundwater. The fractions of NOM which are responsible for the retention and/or enhanced transport of contaminants were determined. In addition, some conclusions about their structure were drawn based on data acquired with size exclusion chromatography and FTIR, UV, and fluorescence spectroscopy.

For the adsorption experiments with NOM and clay minerals, it was necessary to set up a DOC detector for size exclusion chromatography. With this detector, it is possible to measure the DOC concentration continuously. The detection limit is 0.065 mg/L and the limit of quantification is 0.2 mg/L. In size exclusion chromatography, specific interactions between the analyte and the gel influence the elution behavior of the analyte. Therefore, to interpret the results of the size exclusion chromatography experiments correctly, it was necessary to determine the influence of functional groups of organic substances on the elution behavior. Aliphatic alcohols, mono and di-carboxylic acids, aromatic acids, and amino acids were used for these experiments. The length of the aliphatic chain has a pronounced influence. The longer the chain, the later the substance elutes. Methanol which is often used to determine the permeation volume, elutes considerably later than water. Therefore, size determination based on a permeation volume determined with methanol are not correct. The aromatic ring of benzoic acid has the same effect. Differences in ionic strength between the sample and the eluent only affects the elution behavior of carboxylic acids. The elution volume of amino acids is predominantly influenced by the isoelectric point.

Adsorption of NOM to clay minerals leads to fractionation. The fractions with a higher molecular mass are adsorbed preferentially. This is true for both kaolinite and montmorillonite. The pH value of the suspension influences the amount of NOM which adsorbs to the mineral surface, but it has no effect on the fractionation. This behavior is similar to the adsorption of NOM to aluminum and iron hydroxide. The zeta potential of the clay particles is lowered by the adsorbed NOM, but no change of polarity could be detected in the pH range below the point of zero charge. The NOM fractions which adsorb preferentially have a higher SUVA than the substances which do not adsorb. On the other hand, the fluorescence intensity with respect to carbon content of the non adsorbed fraction is higher than of the adsorbed fraction. Therefore, the high molecular mass fraction might consist to a great degree of structures with a high content of double bonds and larger aromatic structures which do not fluoresce. The low molecular fraction consists of smaller aromatic structures. Adsorption of NOM to clay minerals has a strong influence on the mobility of the mineral particles in columns packed with quartz sand. In the presence of sodium, the mobility is enhanced, whereas calcium decreases the mobility. Calcium probably acts as a bridge between the quartz particles and the coated clay mineral particles. Due to the adsorption of NOM, aggregates of clay mineral particles break up into smaller aggregates, or even individual particles.

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Characterization of metal-NOM binding and impact on adsorption and transport

Daniel Schmitt, Universität Karlsruhe, January 2002. Supervisor: **Prof. Dr. F. H. Frimmel**

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In this work, the interaction of natural organic matter (NOM) from a bog lake (Lake Hohloh, Black Forest, Germany) with metal ions (Al, Fe, Zn, Pb) was investigated by means of coupling of chromatographic separation techniques (size-exclusion chromatography – SEC, asymmetric flow field-flow fractionation – AF⁴) with highly sensitive elemental detection facilities (ICP-MS, ICP-AES). Further characterization was done by determining the dissociation kinetics of metal-NOM complexes and the adsorption equilibrium of metal-NOM complexes with quartz and different clay minerals. Kinetic data from batch experiments with a cation exchange resin were used to predict the *direct* NOM-facilitated metal breakthrough through quartz sand columns.

Coupling experiments (SEC-ICP-MS(AES), AF⁴-ICP-MS(AES)) confirmed the formation of complexes of trivalent metal ions (Al, Fe) with NOM. In addition to that, Al and Fe hydroxides were detected. Also, Pb-NOM complexes could be found, but only at very low concentration, whereas for Zn no complex formation with NOM was found.

In contrast to that, the presence of NOM generally decreased the adsorption of both, divalent and trivalent metal ions onto mineral phases in batch experiments. Consequently, different information can be obtained from closed (equilibrium systems) and open (kinetically controlled systems). This was confirmed in kinetic studies with a cation exchange resin. Faster metal-NOM complex dissociation was found for the divalent ions compared to the trivalent ions. From these results, it can be concluded that originally formed metal-NOM complexes dissociate during separation in the chromatographic systems and that only kinetically stable complexes can be detected. Metal ions, which were not bound to NOM were irreversibly retained in the SEC column (weak cation exchange resin) or they were separated through the membrane of the AF⁴.

The same process takes place, when metal-NOM complexes are transported through an aquifer. Free metal cations and metal cations whose dissociation time constant is lower than the time constant of the water transport in the aquifer are adsorbed onto the mostly negatively charged mineral surface and are not transported with the water flow. In a mineral-NOM equilibrated system, metal-NOM complexes are not adsorbed. For Al and Fe NOM-facilitated metal transport was found. Also, a very low fraction of the injected Pb was directly transported. No direct breakthrough of Zn-NOM complexes was found.

A mathematical model based on the assumption that solely the metal-NOM complex dissociation kinetics control the direct metal transport through a quartz sand column was developed. Prediction of direct metal-NOM breakthrough based on kinetic data from the cation exchange experiments and experimental data from column experiments were in good qualitative agreement. Much higher breakthrough for the trivalent ions compared to the divalent ions could be predicted. Also pH dependence of metal-NOM transport was well predicted by the model. Discrepancies between calculated and experimental data were due to processes like aggregation and metal hydroxide formation which were not considered in the model.

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Trace metal binding by organic matter from municipal solid waste compost and consequences for trace metal mobility in compost-amended soils under semiarid conditions (Gaza Strip).

Arno Kaschl, Universität Hohenheim. Supervisors: **Prof. Volker Romheld & Prof. Yona Chen**

Berichte aus der Umweltwissenschaft, Shaker Verlag, Aachen, Germany

In connection with the application of MSW compost to an experimental field plot in Gaza, the importance of organic complexation for trace metal mobility in the soil was investigated within the framework of this thesis. In a first step, humic substances (HS), which act as important metal complexers in soils, were

extracted from MSW compost. From the characterization of structural and functional elements for compost HS, we found that they have certain characteristics such as lower aromaticity and smaller molecular size setting them apart from soil HS. Hence the qualitative makeup of soil humus will be affected after compost application to soils with little organic matter (OM), as is the case in our study area. Important parameters for trace metal binding were the higher N content of compost HS (as opposed to soil HS), which contributes to complexation, and the apparent smaller number of O-containing groups, which in its turn reduces the number of potential binding sites on the macromolecules. Despite these differences in functional group contents, both the complexing capacity (CC) and the strength of association of compost HS for Cd, Cu, and Zn were in the same range as those of soil HS. Hence a significant increase of the cation exchange complex of the soil can be expected by amending the Gaza soils with MSW compost.

A second step was to examine the metal-complexing capacity (CC: for Cu and Cd) of different fractions of the strictly water-soluble organic matter (DOM) from MSW compost. The two fractions that contained humic material had the highest CCs: HoA, the fraction resembling the most soluble fraction of fulvic acid (FA), as a ligand for Cd; and HoN, a fraction with similarities to humic acid (HA), in the case of Cu. The differences in Cu complexing capacity between the different DOM fractions was directly related to the content of acid-titrable groups on the molecules, which was not the case for the binding of Cd. HiB and HoA molecules had the strongest binding groups for Cu, which altogether formed stronger complexes with all organic ligands (compared to Cd). The strongest binding groups for Cd were found in the fraction HiB, which consists of proteinaceous material with N-containing groups, to which Cd binds preferably. HiB is a minor fraction by weight (13% of DOM), but may, besides HoA and HoN (with a high CC), be important for keeping metal ions in solution, due to these groups of high binding energy. However, higher CC were generally obtained for the more complex, larger and less soluble HA and FA with a molecular weight above 1000 Da, while the strength of their binding groups were essentially in the same range as that of the DOM fractions. Thus a large portion of organically-complexed metals from compost can be expected to remain in the top layer of the soil, due to adsorption of HS-type ligands on mineral surfaces and insolubility of the larger humic molecules with their strong affinity to trace metals.

A study of the aqueous compost extract using size-exclusion chromatography showed that all relevant trace metals in solution were predominantly present as organic complexes, with evidence for inorganic complexation encountered only in the case of Zn. A difference of preference for organic ligands between Fe, Al, and Cr on one hand and Cu, Zn, Ni, and Cd on the other was observed: The former elements, usually forming complexes of higher stability with OM, associated more with the larger and more aromatic organic molecules, while the latter adsorbed to molecules with the highest density of functional groups such as COOH and amide groups.

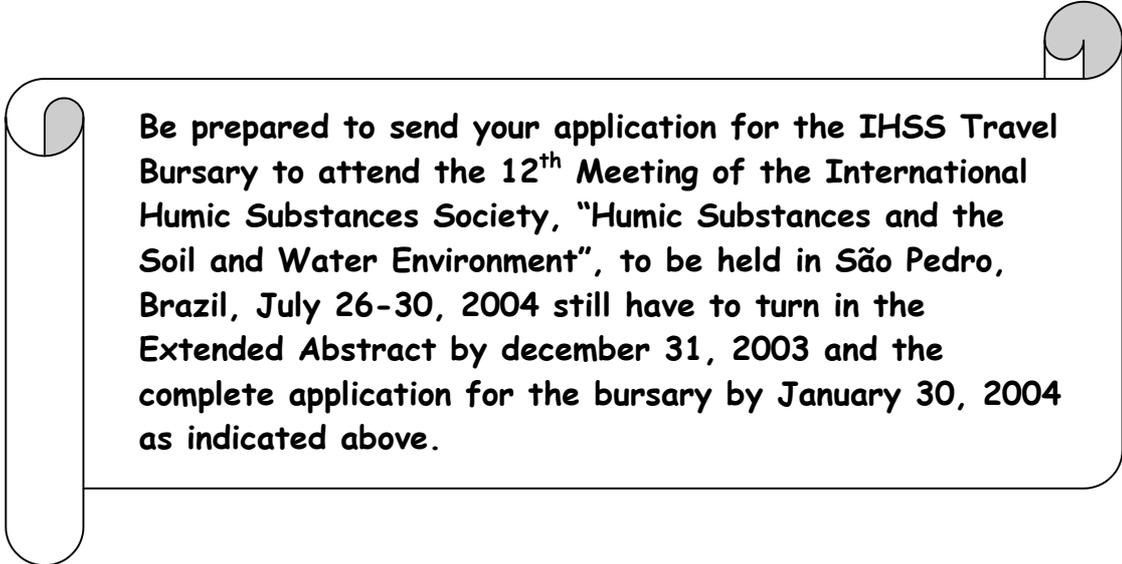
In soil columns under laboratory conditions a worst-case scenario of weekly storm events led to increased leaching of TOM, NO_3^- , P, major cations and the trace metals Cu, Ni, Zn and Cr. This effect was more substantial in the case of the sandy Gaza soil. Cu and Ni were generally the most mobile elements. As was the case in the aqueous compost extract, trace metals in the leachates from soil columns were predominantly present as organically-complexed species. In sandy soil, the TOM washed out from the columns retained distinct features of the compost DOM underlining the importance of compost OM for organic complexation in the solution phase. Thus it is safe to conclude in this case that the mobile fraction of trace metals entered the soil environment as organic complexes from the compost matter, remained in the soil solution phase as organic complexes and were displaced vertically by the water stream. Cu (and Ni) as a strong complexer of OM may thus become partly mobile. Due to the limited mobility of compost DOM, this phenomenon was strongly reduced in the loamy soil.

Notwithstanding these observations, most of the water-soluble, organically complexed trace metals from compost actually accumulated in the topsoil. Likely processes are exchange reactions replacing the trace metal ion on the mobile organic ligands and subsequent association with components of the solid phase or precipitation, or coadsorption/coprecipitation with the organic ligand. The latter case is likely for larger, humified molecules in the compost DOM, which retains high metal complexing capacity (see above).

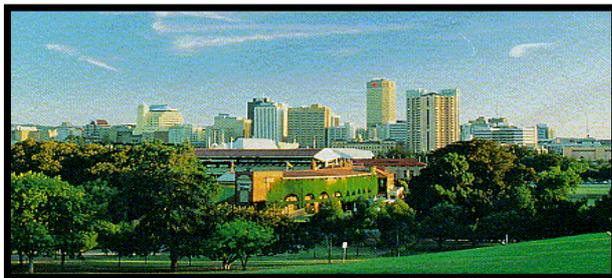
Leaching rates under the extreme conditions in the soil column studies were high, but well within allowable limits for drinking water except for Ni concentrations in sandy soils. Rates on the field during the rainy season receiving average rainfall were considerably smaller. Among the measured trace metals only Cu showed increased leaching compared to the control plots. In a dry year no measurable leaching of any trace metal could be observed. From these results no imminent groundwater threat is apparent. However, long-term effects stemming from metal accumulation in the soil and mobilization of metals, e.g. through microbial breakdown, have the potential of increasing the vertical trace metal displacement. On the field the importance of preferential-flow pathways was noticed for metal leaching, even on very coarse soils and should be taken in account when quantifying leaching rates in the field.

IHSS TRAVEL BURSARY GUIDELINES

1. Travel bursaries will be given only to students. Investigators who have completed their Ph.D. degrees are not eligible for bursary awards.
2. A committee consisting of the IHSS President and at least two other IHSS members appointed by the IHSS President will evaluate applications for travel bursary awards.
3. The deadline for receipt of the applications is **six (6) months** prior to the IHSS International Meeting with evaluations and notifications of awards given to the applicants **four (4) months** prior to the IHSS International Meeting.
4. Applications must contain a letter of application, recent curriculum vitae including a record of classes taken and grades received, a letter of evaluation from the applicant's major professor and a manuscript of the paper to be presented. Three (3) copies of the application are to be sent to the President of IHSS (Prof. Yona Chen) so that they are received before the submission deadline.
5. Awards will be based primarily on the quality and originality of the scientific content of the manuscript and the applicant's record of scientific achievement. It should be clear that the student has had a major part in designing and conducting the research and wishes to pursue a career in a field in which humic substances science is important.
6. The number and amount of the awards will be determined by the President in consultation with the Treasurer and members of the travel bursary selection committee.
7. Travel bursary award recipients will be honored at the conference banquet with their cash award, a certificate acknowledging their status as an award winner and a one (1) year membership in IHSS.
8. **Malcolm Award** - in the judgment of the travel bursary selection committee, the top applicant for a travel bursary award will be designated the Malcolm Award winner. This individual will be recognized with a certificate and cash award of 250 US\$ in addition to the normal travel bursary.



Be prepared to send your application for the IHSS Travel Bursary to attend the 12th Meeting of the International Humic Substances Society, "Humic Substances and the Soil and Water Environment", to be held in São Pedro, Brazil, July 26-30, 2004 still have to turn in the Extended Abstract by december 31, 2003 and the complete application for the bursary by January 30, 2004 as indicated above.



Understanding and managing organic matter in soils, sediments and waters

Editors: R.S. Swift and K.M. Spark

Proceedings of the 9th International Conference of the International Humic Substances Society, University of Adelaide, Adelaide, Australia, 21st-25th September 1998.

The proceedings has been organized into five sections under the themes:

- ***Characterization of organic matter,***
- ***Dynamics of organic matter in composts, peats and soils,***
- ***Geochemistry and organic matter,***
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The proceedings are excellent value as they incorporate 75 papers highlighting the presentations given at the conference, have a hardcover and are approximately 600 pages in length.

Some of the papers included in the proceedings are:

- ♣ Progress towards understanding aspects of composition and structure of humic substances. *M.H.B. Hayes and R.S. Swift*
- ♣ Long- and short-term changes in soil organic matter quality and aggregate stability as affected by agricultural management. *R.J. Haynes*
- ♣ Fate of refractory organic matter in water treatment -degradation and reaction. *F. H. Frimmel, G. Abbt-Braun, S. Hesse, and G. Kleiser*
- ♣ Characterisation of native and non-native organic matter in soils by means of ¹³C CPMAS NMR spectroscopy. *I. Kögel-Knabner and H. Knicker*
- ♣ Capillary electrophoretic behaviour of humic substances of different origin. *M. De Nobili, G. Bragato and A. Mori*
- ♣ Transformation of organic matter to humic substances in composted municipal solid waste. *G. Abbt-Braun F.H. Frimmel, Y. Chen, B. Chefetz and Y. Hadar*
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