

NEWSLETTER

INTERNATIONAL HUMIC SUBSTANCE SOCIETY

Number 8

AUGUST, 1992

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SIXTH INTERNATIONAL MEETING INT'L HUMIC SUBSTANCE SOCIETY Monopoli (Bari), Italy September 20 to 25, 1992

We are very pleased to invite you to attend the Sixth International Meeting of the International Humic Substances Society (IHSS), "Humic Substances in the Global Environment and Implications in Human Health", which will be held in Monopoli (Bari), Italy from September 20 to 25, 1992.

The 6th IHSS Meeting will celebrate the Decennial of the founding of the Society. The most recent advancements in the chemistry and biochemistry of humic substances and their interaction with organisms in soil, aquatic, and sedimentary systems will be presented and discussed in 5 main topics:

1. Advances in the Chem. and Biochem. of Humic Substances: Isolation, Characterization, Function.
2. Humic Substances in Soil and Crop Production
3. Humic Substances in Aquatic and Sed. Systems
4. Interaction of Humic Substances With Organic and Inorganic Xenobiotics and With Organisms
5. Application Aspects of Humic Substances: Industrial and Medical Issues

We are confident that the Meeting will be an excellent and exciting opportunity for world scientists to get together and discuss matters of mutual interest that can provide a stimulus for the progress and development of humic substances research for the next decade.

The venue for the Meeting on the sunny and pleasant Adriatic coast of Italy, surrounded by historical and natural sites, is ideal to facilitate scientist, social and cultural activities in a friendly mediteranean atmosphere. We are looking forward to welcoming you in Monopoli this September.

Sincerely yours,

Professor Nicola Senesi
Chairman of the Organizing Committee

INTERNATIONAL HUMIC SUBSTANCE SOCIETY

ELECTION OF OFFICERS

Dear IHSS Member:

According to the current Bylaws of the International Humic Substances Society, the Vice President and Secretary are elected for two-year terms, and the Treasurer and Board Members are elected for four-year terms. It is now time to begin the process of electing new officers to fill several positions that will become available in January of 1993.

By this letter, the Nominating Committee solicits nominations from the membership for any or all of the following positions.

Vice President
Secretary
Treasurer
One Board Member

It should be noted that the Board of Directors have suggested that the Bylaws be changed to elect the secretary for a four year term as per IHSS minutes attached.

The Nominating Committee will accept nominations in writing through the Bari Meeting (September 20-25, 1992), at which time we will review all nominations, contact selected nominees to determine their willingness to serve, and prepare the final list of nominees for the election. Ballots will be mailed to IHSS members shortly after the Bari Meeting. Please forward your nominations to one of the members of the Nomination Committee:

Dr. E. Michael Perdue
School of Earth and Atm. Sciences
Georgia Institute of Technology
Atlanta, Georgia 30332

Dr. Jean-Marc Bollag
Pennsylvania State University
119 Tyson Building
University Park, PA 16802

Dr. Petr Dolejs
Czechoslovakia Academy of Science
Hydrobiological Institute
Na sadkach 7
370 05 Ceske Budejovice
Czechoslovakia

We look forward to your input and hope to see all of you in Bari.

Sincerely,

E. Michael Perdue

HISTORY OF THE INTERNATIONAL HUMIC SUBSTANCE SOCIETY

The International Humic Substances Society (IHSS) was founded in 1981, in Denver, Colorado, in order to bring together scientists from the soil, water, and coal disciplines with interests in the composition, structures, and interactions of humic substances. During the 11 years since its foundation, the Society's achievements have been remarkable. Five international meetings have been held (Estes Park, Colorado, USA, 1983; Birmingham, England, 1984; Oslo, Norway, 1986; Matalascanas, Spain, 1988; Nagoya, Japan, 1990) and the sixth is scheduled for Bari (Italy) in 1992.

Prior to the founding of IHSS, soil, coal, and water scientists seldom shared their research experiences in their separate studies of humic substances. It was clear at the first International meeting (Estes Park) that many of the scientists from the different disciplines were ill-informed about the work which had been carried out by other groups in areas away from their specialties (in soil, or coal, or water). The different groups left Estes Park with a mutual respect for each other, and it was clear at the meeting in Birmingham in 1984 that much had been learned from Estes Park.

The first two meetings were designed primarily to produce books which would present the states of the art with respect to genesis, isolation and purification, compositions, structures, and interactions of humic substances in soils, sediments (including coals), and waters. The first book in the series "*Humic Substances in Soil, Sediment, and Water*," edited by G.R. Aiken, D. McKnight, R.L. Wershaw, and P. MacCarthy, was published by J. Wiley (N.Y.) in 1985. The second, "*Humic Substances II: In Search of Structure*", edited by M.H.B. Hayes, P. MacCarthy, R.L. Malcolm, and R.S. Swift, was published by J. Wiley (Chichester) in 1989, and the third in the series, which will incorporate some of the material covered in the Birmingham conference as well as some dealt with in Oslo, is entitled "*Humic Substances III: Interactions with Metals, Minerals, and Organic Chemicals*" is edited by P. MacCarthy, M.H. B. Hayes, R.L. Malcolm and R.S. Swift and will be published by J. Wiley early in 1993. Volunteered papers presented in Birmingham were published as a separate volume, edited by M.H. B. Hayes and R.S. Swift, and is available from the Society. Volunteered papers presented at Estes Park were published in a special issue of *Organic Geochemistry*, and those from Oslo and Matalascanas are now available as special issues of "Science of the Total Environment". The proceedings for the Japan meeting are in press in the "Science of the Total Environment" and the Bari meeting will be published in this journal.

IHSS has been cosponsor of a number of conferences and of sessions within conferences. As a result, a number of additional publications are available which have a strong Society involvement. For example, a joint symposium of Commissions II, III and IV of the International Soil Science Society (ISSS) and IHSS dealt with the "*Dynamics of Organic Matter in Soils*" at the XIIIth Congress of ISSS in Hamburg, Germany in 1986, and the Proceedings are published in the Transactions of that Congress. (Vol. VI, pp. 599-5656, 1987). A joint symposium with the American Chemical Society in 1987 has led to the publication, "*Aquatic Humic Substances. Influences on Fate and Treatment of Pollutants*", I.H. Suffet and P. MacCarthy (eds.), American Chemical Society, Washington, DC, 1989, and another with the American Society of Agronomy in Madison WI in 1985 has led to the publication, "*Humic Substances in Soil and Crop Sciences*", P. MacCarthy, C.E. Clapp, R.L. Malcolm and P.R. Bloom (eds.), 1990.

The objectives of the Society are to advance knowledge, research, and applications of Humic Substances. It can be concluded from the Society's record that it has succeeded remarkably well in its objectives up till the present time. However, progress can be maintained only if there is an influx of new members and of new ideas. That is why we invite new members, and collaboration with other learned societies. The IHSS does not regard itself as a competitor to any Society, and for that reason our Society is eager to collaborate in any venture which will advance knowledge of, and research in Humic Substances.

INTERNATIONAL HUMIC SUBSTANCE SOCIETY

MINUTES OF BOARD MEETING - CHAPEL HILL NC 5/22/92

Dr. Mel Suffet, Secretary

The meeting began at 8:30 AM.

The following board members were present:

President - Dr. Russ Christman
Past President - Dr. Roger Swift
Vice President - Dr. Mike Hayes
Treasurer - Dr. Pat MacCarthy
Secretary - Dr. Mel Suffet

The board formally thanks Dr. Russ Christman and his staff at the University of North Carolina for the special "southern hospitality" extended to the board during their stay in Chapel Hill.

AGENDA

1. Treasurer Report
2. Honorary Membership
3. 6th IHSS Meeting in Bari Italy
4. Newsletter
5. Publication of the IHSS Meetings and Humic Substance Papers
6. National Chapters of the IHSS
7. Advertisement For IHSS Society Membership and Sales of the Humic Substances Standards/ Reference Collection
8. IHSS Membership and Dues
9. Logo for IHSS
10. Newsletter
11. Standards and Reference Collection
12. Election of Officers for Board of Directors
13. Next IHSS Congress 1994 Location - North America

Item # 1. Treasurer Report -

The financial health of the society is sound. Cash assets total \$47,645.00 as of 5/20/92. The fine financial health of the society is primarily due to the sale of reference/standard materials by the society. The society is indebted to the preparers of these reference standards.

Item #2. Honorary Membership -

At present there are three honorary members of the IHSS, W. Flaig (Germany), F.J. Stevenson (USA) and M. Schnitzer (Canada). The executive committee of the IHSS passed a resolution that society honorees be so noted on its letterhead. This will be done with the next stationary order.

Dr. J. P. Martin was nominated as an honoree by Dr. Senesi. The board recognizes Dr. Martin's tremendous contribution to the field of humic substances. However, policy dictates that nominees be living scientists. Therefore, the Board recommends to Dr. Senesi that Dr. Martin be honored at the up-coming Bari Meeting. A symposium or session(s) at the Bari meeting could be dedicated in his honor. Dr. Christman will write to Dr. Senesi about his nomination of Dr. Martin and make these suggestions.

It was proposed and passed by the board that the Society present future honorees with a certificate at an IHSS meeting. The bylaws should be changed to clearly state that honorary membership is for the life of the member selected.

A discussion ensued about other potential honorees for the IHSS. The discussion will continue at the Board of Directors meeting in Bari.

Item #3. 6th IHSS Meeting in Bari Italy -

Three hundred preliminary registrations including over 50 from the eastern european nations for the Bari Meeting were reported as of May 20, 1992. This meeting is being projected as the largest since the Society's inception. The board thanks Dr. Nicola Senesi for his excellent work in preparation of the Bari Meeting. The board was very pleased with the technical quality of the meeting and the progress being made by Dr. Senesi.

The board expressed its support for a session under the joint auspices of the IHSS and ISSS (International Soil Science Society) at the Bari meeting in reciprocation for a similar joint session at the last ISSS Congress in Kyoto, Japan in August of 1990.

The board noted that support for attendance at International Meetings is a matter for the local organization committee.

Item #4. Newsletter -

A newsletter is being prepared by the secretary before the Bari Meeting. It will be mailed by August 15, 1992.

Item #5. Publication of the IHSS Meetings and Humic Substance Papers -

A lively discussion ensued about the relationship between the IHSS presentations and publications from the international meetings as well as the coordination of an outlet for papers on humic substances. The following consensus was developed by the board.

First, the society has an agreement to publish papers from the 6th biannual Humic Substance Society meeting in Bari Italy in a special issue of the journal "Science of the Total Environment"

Second, The Board of Directors have reaffirmed that it is not time for the society to have a primary journal.

Third, the IHSS would like to see some coordination of published papers on the study of humic substances short of beginning a new journal at this time. The society would like to develop a relationship with a journal that can benefit the journal and IHSS, as well. A relationship of the IHSS with an existing journal could help the journal by enhancing its advertising, circulation, lowering the journal's costs and above all having quality papers submitted to it. This could facilitate the journal's ability to offer discount subscriptions to members of IHSS. The journal and IHSS members would mutually develop a place for refereed publications of high technical merit on humic substances in a respected journal. The journal should be broad enough to publish any good paper that relates to humic substance research.

The board suggested that several possibilities exist for the future, including special issues of humic substances papers with a journal. The journals, "Organic Geochemistry", (Pergamon) and "Geoderma" (Elsevier), were suggested as possibilities to coordinate IHSS activities. Environmentally oriented, Ann Arbor Science, Lewis Pub'l, and CRC Press were also suggested as publishers to contact for ideas. The IHSS linkage to the journal's editorship will foster review of humic substance articles. Dr. Mel Suffet will undertake an information gathering effort and report back at the Bari meeting.

Item #6. National Chapters of the IHSS -

A historic discussion ensued on the formation of Chapters of the IHSS to foster the society goals, stay in touch with society growth objectives, and make services and benefits of the IHSS more accessible to the membership. Local chapters will help develop more cooperation among members, encourage membership input into IHSS, do better service to the society and develop consensus and enthusiasm for society efforts.

A form to petition the board of directors of the IHSS to form a society chapter is being developed by the IHSS President, Dr. Russ Christman in cooperation with the Board of Directors and will be sent to the appropriate people interested in forming a chapter by IHSS Vice President Dr. Mike Hayes. A member of a chapter of IHSS must be a member of the IHSS. People can join the IHSS without being a member of a regional chapter but not vice versa. Each chapter must propose by-laws to form a chapter. As a chapter of the society, each must conform to the bylaws of the International Humic Substance Society. The individual chapter can petition the IHSS Board of directors for exceptions if necessary. The development of the chapters will follow Article 10, Sections 2 and 6 of the BYLAWS OF IHSS.

The following Chapters were identified from the excellent ground breaking work of Vice President Dr. Mike Hayes:

1. Australia and New Zealand - Dr. M. A. Wilson
2. Belgium - Dr. Maes
3. China -
4. CIS -
5. Eastern Europe -
6. France - Dr. Ewald
7. Germany - Dr. Zech
8. Holland - Dr. DeHaan
9. Israel - Dr. Chen
10. Italy - Dr. Senesi
11. Japan -
12. North America - Dr. MacCarthy
13. Nordic countries - Dr. Gjessing
14. Portugal - Dr. Amondo
15. Spain - Dr. Saiz Jimenez
16. Taiwan

17. United Kingdom - Dr. Hayes
18. Others

The names of the National Chapter and the leaders of the National Chapter are suggested only for the initiation of the individual chapters. The local chapter will develop its own leadership after it is formed. The local chapter will facilitate collection of dues for the IHSS. A local representative chosen by the Board of Directors as its agent will collect dues for IHSS

Item #7. Advertisement For IHSS Society Membership and the Humic Substances Standards/Reference Collection -

Dr. Russ Christman prepared an Advertisement for IHSS Society Membership and Sale of the Standards/Reference Collection of Humic Substances in concurrence with the Board of Directors. The Advertisement as it now stands is attached as Appendix B. The costs of the advertisement for newsletter and journals are being investigated by Russ. The following journals and newsletters will be contacted for the cost of publication by Russ except where noted:

- Agronomy News (MacCarthy)
- Division of Environmental Chemistry, ACS Newsletter (Christman)
- Environmental Science and Technology (Christman)
- Geoderma (Swift)
- International Soil Science Society Bulletin (Swift)
- EOS (MacCarthy)
- Organic Geochemistry (Christman)
- Soil Use and Management (Swift)
- Society Environmental Toxicology and Analytical Chemistry (Christman)
- The Science of the Total Environment (Christman)
- Water Research (Christman)

If there is no cost, the ad will be placed immediately.

Item #8. IHSS Membership and Dues -

The subscription rate for members is \$20 per year, \$10 for students. The subscription rate for the next year will be special for Developing Countries and Eastern Europe at \$10 per year, \$5 for students. The subscription rate for CIS is set at 20 rubels for 1993.

The dues are for a one-year basis beginning January 1 of each year.

The board of directors concurred that dues will be now collected annually, only because of the awkwardness of multi-year dues collection. Members who, at present, have multi-year subscriptions will be exempt until their present subscription expires.

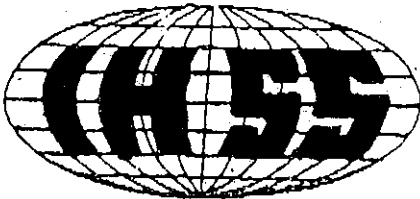
To develop an incentive for membership, new members will have a free membership until December 30, 1992, if

they sign up and pay dues for calendar year 1993. A dues collection form is being prepared by President Russ Christman.

The annual subscription notices will be sent out by the secretary on November 1, 1992 with a Newsletter after the 6th International IHSS Meeting in Bari Italy. Dr. Christman will provide the secretary with the present computer mailing list of the membership on disk with a hard copy.

Item #9. - Logo for IHSS -

The following logo design was selected from those suggested by the membership. This logo will appear on all future IHSS stationary.



Item # 10 Newsletter-

After the August 1992 newsletter, a second newsletter is due November 1, 1992 with the dues notices to members. Student help will be used by the secretary to facilitate the production of the newsletters.

Item # 11 Standards and Reference Collection (Minutes Taken in Cooperation with Patrick MacCarthy)

The Standard/Reference collection of humic substances was discussed. Sales of these materials are progressing at a steady pace. The only concern at this time is that the supply of soil fulvic acid (1S102F; 1R102F) is running out. The pros and cons of conducting another extraction of this material were considered. This is the most difficult and time-consuming of the standard/reference materials to isolate, and an extraction that yields several hundred grams of the soil humic acid provides only a few grams of the soil fulvic acid. No final decision was reached on this matter and the issue was postponed for further discussion at the Board meeting in Bari, in September 1992.

It was noted that the dollars needed to redo a standard for the reference collection would require an allocation of a minimum of \$10,000. The guideline on cost developed from past efforts is \$10,000 for a soil, \$20,000 for a water if the scientist doing the isolation donates time, labor, supplies and equipment. The true cost is three to four times the value. A reserve should be developed in the IHSS budget for replacement and additions to the humic materials reference collection.

Item #12 Election of Officers for Board of Directors (minutes taken in cooperation with Dr. Patrick MacCarthy)

The forthcoming election for Officers and for a Board position were discussed. The following positions will be vacant at the end of the current calendar year: President-Elect, Secretary, Treasurer, and one Board position. Dr. Christman will attempt to appoint the same Nominating Committee as served for the previous election, and he will instruct the Nominating Committee to contact the membership via Dr. Mike Perdue by mail prior to the end of June 1992 seeking nominations for the four positions which are becoming vacant. These names will then be forwarded to the Chairman of the Nominating Committee. Included with this mailing will be a statement from the President including proposed changes to the by-laws (see below) which will be voted on at the time of the election.

Ballots to be sent out to membership about September 30, 1992 with a last return date of November 30, 1992 so that the offices can be taken January 1993.

The mailing protocol for the election is:

1. Nominating Committee informs Secretary of nominations and provides information for balloting
2. Secretary sends out ballot
3. Members return ballots to President
4. President informs Secretary of winners
5. Secretary informs membership

Officers to be elected are:

VP. - Hayes expires December 31, 1993

Sec. - Suffet expires December 31, 1993 and should be elected for a 2-year period, pending a change in the by-laws, which would make the office good for 4 years (this will give Suffet 3 years)

Treas. - MacCarthy expires December 31, 1993

Board Member - Ishiwatari expires December 31, 1993

The Board made some initial suggestions to the nominations committee. It was suggested that Nominating Committee be advised to run "Europeans vs. Europeans," etc., not Japanese vs. Americans, or Germans vs. English, etc.

Items 12 Suggested Changes to IHSS Bylaws (Minutes taken in cooperation with Dr. Patrick MacCarthy)

A discussion was held concerning various possible changes to the bylaws. These suggested amendments will be distributed to the membership by the President for voting. The suggested amendments are as follows, where square brackets [] indicate text that is being deleted, and underlining indicates newly-added text.

ARTICLE V. OFFICERS AND DUTIES

Section 1. The officers of the Society shall be President [.] and Vice President/President Elect [and Secretary all]

~~both~~ of whom shall serve for two (2) years and ~~Secretary and Treasurer [who] both of whom~~ shall serve for four (4) years beginning January 1 following the ballot election ~~[and their election shall be announced at the annual International Meeting]~~. The said term of office shall terminate on December 31 of the final year or when their successors have assumed office.

This proposed amendment to Article V is suggested because the Board of Directors now believes that two years is too short of a term for the Secretary to operate effectively in the best interests of the Society. It is intended that this change would take effect with the 1994 elections, so that the four-year terms of the Secretary and Treasurer would be staggered.

ARTICLE VI. NOMINATIONS AND ELECTION

Section 2. Election. The ballot shall be sent by the Secretary by first class mail to all members [at least ninety (90) days prior to the International Meeting of the Society] no later than October 1 of the election year. Within sixty (60) days after the date of the mailing, the ballots shall be returned to the [Chairperson of the Nominating Committee] President. The ballots shall be opened and tabulated [in the presence of at least one member of the Nominating Committee and at least one member of the Board of Directors, then reported to the President prior to the International Meeting of the Society] by the President in the presence of an impartial observer chosen by the President. The [names of the] candidates who received the highest number of votes for each position will be [announced at the subsequent International Meeting of the Society and the President shall declare those persons duly elected] declared duly elected by the President. The President shall forward the names of the elected candidates to the Secretary, and the Secretary shall inform the membership of those names. In the event of a tie, the retiring Board of Directors shall, by ballot, select the winner.

The reason for the proposed changes to Article VI is the present requirement that the ballots be tabulated in the presence of at least one Board member is impractical, and is not being adhered to. The proposed revised procedure provides a workable alternative for tabulating the ballots and reporting the results to the membership.

ARTICLE VII. BOARD OF DIRECTORS

Section 1. There shall be a Board of Directors comprised of [seven (7)] eight (8) persons including the President, Vice President/President Elect, Secretary, Treasurer, the immediate Past President, [and] an additional (2) members elected by the membership designated as Board Positions, and the Chairman of the Standard and

Reference Humic Substances Committee as an ex-officio member.

The reason for this proposed amendment is to accommodate the proposed change in Article IX below.

ARTICLE IX. COMMITTEES

Section 1.

D. Standard and Reference Collection of Humic Substances Committee

To the end of this paragraph add:

The chairman shall be an ex-officio member of the Board of Directors.

The reason for this suggested change is that the Board of Directors considers this position to be very important to the affairs of the Society, because of the key role played by the standard/reference collection among Society activities, and because the standard/reference collection provides the basis for the majority of the Society income.

Item 13 - Next IHSS Congress 1994 (Minutes taken in cooperation with Dr. Patrick MacCarthy) -

It was mentioned that the Congress of the International Society of Soil Science (ISSS) will be held in Acapulco, Mexico in August 1994. It was suggested that the 1994 International Meeting of the Society (IHSS) be held in North America immediately before or after the ISSS Congress. It was suggested that Dr. Suffet might consider hosting the meeting at UCLA or that Dr. Sposito might consider hosting the meeting at Berkeley in 1994.

The meeting adjourned at 5:30 PM.

HUMIC SUBSTANCES SOCIETY NEWS

11/25/91

Third International Nordic Symposium on Humic Substances

August 21-23, 1991 - Turku/ Abo Finland

Mel Suffet, UCLA

The Third International Nordic Symposium on Humic Substances was successfully held on August (21-23) 1991 at the Paasikivi Institute in Turku/ Abo Finland. The meeting was graciously hosted by Dr. Kalevi Pihlaja of the Department of Chemistry, Turku University. The organizing committee did an excellent job of developing a pleasant setting for fruitful scientific exchanges. Invited theme lectures set the tone for each symposium area and provided a springboard for informative discussions after each paper. Invited themes included lectures by :

Derek Vaughan, Scotland: Humic Substances and Biological Activity

Anders Grimvall, Sweden: Natural Halogenation of Organic Macromolecules

Bruce LaZerte, Canada: Binding of Metals to Humic Substances: The Importance to Metal Transport

Kalevi Pihlaja, Finland: Isolation, Fractionation and Characterization of Humic Substances

Mel Suffet, U.S.A.: Binding of Organic Pollutants to Humic Substances

A well attended poster session continued the themes of the presentations -including work presented by Maris Klavins and U. Clnis on Humic Substances in Latvian Inland Waters which won the best poster award. It was heartwarming that new work from Russia was being presented during some very turbulent times. Poster presentations included:

Ludmila Shirshova, USSR: Polydispersity of Soil Humic Substances: Effect of Extraction and Separation Conditions

Olga Trubetskaya and O.A. Trubetskoj, USSR: Electrophoresis in Paag in the Presence of Denaturing Agents: A New Method for Fractionation, Isolation and Characterization of Soil Humic Matter

The lecture by Anders Grimvall on "Natural Halogenation of Organic Macromolecules" illustrated a different perspective that the relative amounts of Adsorbable Organic Halogen (AOX) from natural environmental activities are much greater than one thought. His pre-

sentation insisted that one ask questions about the origin of the AOX in rainwater and the relationship between anthropogenic and natural organic halogens.

The relative youthful audience of researchers present indicated to this observer that the field of humic substances remains in its infancy of development with renewed interest. The discussions of how to approach the study of humic substances also indicates the youthful nature of the subject. The work of the analytical - isolation, fractionation and characterization of humic substances presented by Kalevi Pihlaja indicates that there is a controversy related to studies that isolate a molecular structure of humic substances vs his opinion "...to understand better the operational function of (water) humus in nature...". This once again, brings up the question of studying the function of humic substances in their most natural state (as possible for laboratory investigation) or in nature itself, vs isolating the humic substance in an artificial laboratory environment, and reconstituting the humic substances for study. This brings my prejudices to the fore as I always suggested the former approach if at all possible, since isolation and reconstitution of humic substances can lead to artifacts. The study presented by Egon Gjessing of the Humex-Humic Lake Acidification Experiment goes directly to the side of the natural environment approach.

The Nordic Humic Conference was well done. Regional meetings are helpful in bringing researchers and students together to focus on regional concerns. The next IHSS meeting of a world-wide nature at Bari, Italy this September will continue from this type of regional dialogue and focus on issues within the world wide community to enable the broadest understanding of humic substance research and developments. I personally would thank the meeting organizers and relay the general message of the participants who said to me - I enjoyed the meeting. Bravo.

HUMIC SUBSTANCES AND THEIR INFLUENCE ON ENVIRONMENTAL PROCESSES

Patrick MacCarthy
Dept. of Chemistry and Geochemistry
Environmental Sci. and Eng. Program
Colorado School of Mines
and
I.H. (Mel) Suffet
UCLA, School of Public Health
Golden, CO 80401
Los Angeles, CA 90024

The term *humic substances* refers to organic material in the environment that results from the decomposition of plant and animal residues, but that does not fall into any of the discrete classes of compounds such as proteins, polysaccharide, and polynucleotides. Humic substances are ubiquitous, being found in all soils, sediments, and waters. Although these materials are known to result from the decomposition of biological tissue, the precise biochemical and chemical pathways by which they are formed have not been elucidated.

An endeavor to establish such pathways is a formidable task because humic substances consist of an extraordinarily complex mixture of compounds. As an indication of the molecular heterogeneity and complexity of humic substances, these materials have defied all attempts at separation into discrete components. Virtually every separation technique that has been developed by chemists and biochemists has been applied to humic substances. Many of these attempts at fractionation have succeeded in diminishing the degree of heterogeneity of the samples, but none of them comes close to isolating a material that could be referred to as a *pure* humic substance in the classical meaning of the term *pure* chemical or even a *pure* group of chemicals. In this regard, humic substances represent a unique category of natural products in which the essence of the material appears to be heterogeneity per se.

Because of the poorly defined nature of humic substances, compared to the more discrete types of materials that most chemists and biochemists are familiar with handling, it might appear that any fundamental study of humic substances would be a rather futile endeavor. Adoption of such a viewpoint might be further provoked by the realization that there is, in fact, no analytical method for uniquely assaying humic substances. How could one develop a quantitative chemical analysis for a material that is so complex and ill-defined that researchers must be satisfied with a rather vague operational defi-

nition? However, it should not be surprising that a material that occurs in all soils, sediments, and waters exerts significant influences on many agricultural, geochemical, environmental and pollutant-treatment processes.

Development of new technologies for the isolation of reasonable quantities of humic substances from natural waters (Aiken, 1985) has helped to promote research on these aquatic materials. However, many workers like to study the interaction of humic substances in the environment without concentrating the samples, to observe their effect in a more natural state. This approach has become possible because of the ability to analyze nanogram-per-liter to microgram-per-liter concentrations of chemicals that the humic substances interact with by modern analytical chemical techniques. The obvious difference in the approaches is determined by the end objectives of the particular study.

Isolation of Humic Substances

Humic substances do not occur alone in the environment. Rather, they are mixed with, or chemically or physically associated with, other classes of materials. For example, in the dissolved state in natural waters, humic substances are mixed with amino acids, sugars, various aliphatic and aromatic acids, and a host of other organic compounds. In soils and sediments, and in suspension in aquatic systems, humic substances are frequently bound to the mineral components. Of course, the ultimate objective in the present context is to understand the role of humic substances in the real environment, where all of these other substances and interactions occur. Consequently, some researchers choose to work with whole water or with unextracted soil and sediment samples when evaluating the environmental impact of humic substances. Other investigators believe that all studies should actually be conducted *in situ* without removing the substrate from its natural location.

Most researchers isolate the humic substances from the nonhumic materials and independently evaluate the characteristics and behavior of the isolated materials. These researchers believe that a part is simpler than the whole, and that the chemistry of these materials can be evaluated more rigorously in the controlled conditions of a laboratory. In this regard, humic-substance researchers generally devote considerable effort to obtaining low-ash samples. These efforts can be contrasted with those of researchers whose primary focus is on the mineral constituents of soils and sediments and who make correspondingly intense efforts to isolate the mineral constituents with as little organic "contamination" as possible. These approaches focus upon two extremes of the true situation, and are largely a manifestation of the research interests of the individual investigators. Ideally, in the long run the data from both approaches can be merged to provide a more meaningful picture of the true environmental situation.

Over the years, many subfractions of humic sub-

stances have been isolated and given special names. Of these, only three fractions have stood the test of time as being generally useful, namely, humic acid, fulvic acid and humin. Because of the difficulty in establishing a uniform set of definitions that is applicable to a complicated mixture that can be isolated from a solid substrate (e.g. soil) and a nominally dissolved substrate (natural waters), these three fractions are operationally defined as follows (Aiken et al., 1985):

- **Humic acid:** the fraction of humic substance that is not soluble in water under acidic conditions (pH < 2.0) but is soluble at higher pH values
- **Fulvic acid:** the fraction of humic substances that is soluble in water under all pH conditions.
- **Humin:** the fraction of humic substances that is not soluble in water at any pH value.

These definitions reflect the methods of isolating the various fractions from the original substrate. Although there are literally hundreds of variations of the extraction techniques for humic substances, the essential features embodied in all of these techniques are based upon these definitions.

Composition of Humic Substances

Despite the limitations in our knowledge of the chemical nature of humic substances, a great deal is known about the occurrence and composition of these materials. This compositional information affords a basis for understanding many of the environmental and geochemical effects of humic substances. Humic substances vary in composition, depending on their source, method of extraction, and other parameters. Overall, however, the similarities between different humic substances are more pronounced than their differences.

Although humic substances have been studied for many years, it has only been since the early 1970s that a major research effort has been devoted to the investigation of aquatic humic substances and their environmental influences. As in the case of humic substances from other environments, one cannot assign unique compositions or formulas to aquatic humic substances. However, the compositional and other data that are available allow us to understand many of the environmental effects of these materials. Aquatic humic substance will be described as an example of the study of humic substances. The aquatic area of study represents the youngest field of humic substance evolution.

About 50% of the dissolved organic carbon in uncolored surface waters of the United States consists of humic substances. The average concentration of the humic substances in the surface waters is 2.2 mg of C/L or 4.4 mg of humic substances/L. (The humic substances are approximately 50% carbon by weight). Although the DOC of colored surface waters is extremely variable, it typically ranges from about 5 to more than 50 mg of C/L. Also, in these colored waters, the fraction of the total DOC in the form of humic substances varies considerably and can be as large as 80%. Typically 90%

of the dissolved humic substances in natural waters consists of fulvic acid, and the remaining 10% consists of humic acid. This composition is in contrast to humic substances from soils, where the humic acid is in very large excess over the fulvic acid. These data are taken from Malcolm (1985) who presents a detailed discussion of the occurrence and distribution of humic substances in streams.

Many workers use the terms DOC and humic substances interchangeably. Such usage is not correct and fails to make the appropriate distinction between humic substances and a mixture of humic substances plus nonhumic substances. With the growing awareness of the subtleties involved in humic substances research and terminology, important distinctions between terms such as *humic substances* and DOC should be more adequately accommodated in the future.

Aquatic humic acids differ from aquatic fulvic acids in elemental and functional group compositions, average molecular weights, and other characteristics. Aquatic humic and fulvic acids also differ from their corresponding soil counterparts. The major functional groups in humic substances are carboxyl, phenolic hydroxyl, and alcoholic hydroxyl. Typical number average molecular weights of aquatic fulvic acids are 800-1000 daltons, and those of aquatic humic acids are 2000-3000 daltons. In contrast, the molecular weights of soil humic acids are reported to be as large as several hundred thousand daltons (Swift, 1985 and Wershaw and Aiken, 1985).

It is not possible to integrate all of the compositional data into neat structural models for humic substances. These data are, nevertheless, very useful in accounting for many of the environmental influences of these materials. For example, materials with a greater oxygen content will have a greater concentration of functional groups. This composition will be likely to cause the material to be more hydrophilic, and consequently less effective in the uptake of nonionic organic compounds. However, the higher concentration of oxygen-containing functional groups will likely render this material more acidic and more effective in complexing metal ions.

If evaluation of the fate of potential hazardous pollutants in the environment and during treatment is concerned with how, where, in what form, and in what concentration pollutants are distributed (Suffet, 1977), then an understanding of the background DOC matrix as it directly influences the fate of pollutants must be carefully developed. At present, the understanding of the influences of humic materials is only sufficient to define site-specific effects on the pollutants. Thus, site specific investigations must be completed to define the fate of hazardous chemicals. In the future, as information is accumulated, it is hoped that a more general understanding of the effects of humic substances on hazardous chemicals will be developed to help predict effects in unknown situations.

A major problem that has confronted researchers in the area of humic substances has been the lack of

standard material through which they could objectively compare their results (MacCarthy, 1976; Malcolm and MacCarthy, 1979; and MacCarthy and Malcolm, 1979). This lack of standard material is apparently why commercial humic materials are used in research, but it has now been remedied by the International Humic Substances Society, which has established standard humic substances from water, soil, peat and Leonardite. Information relating to the nature and availability of these standard humic substances is available from the Society.

In conclusion, most researchers isolate the humic substances from the nonhumic materials and independently evaluate the characteristics and behavior of the isolate materials. However, some researchers choose to work with whole water or with unextracted soil and sediment samples when evaluating the environmental impact of humic substances. Other investigators believe that all studies should actually be conducted *in situ* without removing the substrate from its natural location. Thus, the debate over study approaches continues, but of course the ultimate objective is to understand the role of humic substances in the real environment.

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INTERNATIONAL HUMIC SUBSTANCE SOCIETY

Reference Collection

A reference collection of **Humic and Fulvic Acids** from **soil, coal and water** is maintained by IHSS for use in scientific research. For a price list and information regarding membership in the Society contact:

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