

Humic substances in ecosystems HSE9

Polish Chapter of the IHSS
(Polskie Towarzystwo Substancji Humusowych)
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Polish Humic Substances Society©

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30 Years of IHSS

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The International Humic Substances Society (IHSS) was founded on September 11, 1981 in Denver, Colorado, and was officially incepted on January 1, 1982 (Fig. 1). This thirteenth anniversary marks a period of remarkable achievements. The contribution will focus on the period of the foundation, on the scientists involved and on the ongoing and current activities of today and of the future.



International Humic Substances Society

Figure 1. The official logo of the International Humic Substances Society.

HISTORY, 16TH TO 20TH CENTURY

The roots of the society are found at least more than two centuries ago. The beginning of the industrial revolution early in the 18th century is marked by a tremendous increase in science and technology. The advances in technology started to change human society and the environment. During this century the study of agriculture was a demanding issue for the increasing growth of the population. Johan Gottschalk Wallerius (1709 – 1785) (Fig. 2), a Swedish doctor of medicine and a professor for chemistry, medicine and

pharmacy at Uppsala University introduced the word *humus* in his book “*Agriculturae fundamenta chemica*” in 1761. He is regarded as the founder of agricultural chemistry, the definition and the description of the word humus is still accepted with minor revisions until today (Wallerius 1761). In the book of Brown (1944) a summary of Wallerius`s book is given.

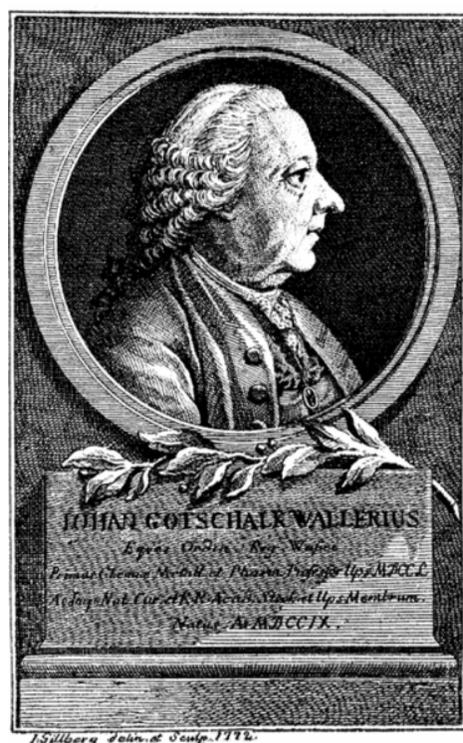


Figure 2. Johan Gottschalk Wallerius (1709 – 1785), a Swedish doctor of medicine and a professor for chemistry, medicine and pharmacy at Uppsala University

The earliest publication that regarded isolation and fractionation of the complex organic matter is due to Achard. Franz Karl Achard (1753 – 1821) was a German chemist and biologist. In 1786 he published a study, where he treated peat with potassium hydroxide. He added acid to the dark solution and obtained an amorphous dark precipitate. He obtained more precipitate by the extraction of the darker (more humified) layer, than from the less humified residues in the upper layers (Fig. 3).

Many famous scientists from the 18th century until now are involved in the research of soil humic substances. The literature reviews are highly recommended, as introduced by the textbooks of Kononova (1961), Schnitzer and Khan (1972), and Stevenson (1982).



Figure 3. Achard. Franz Karl Achard (1753 – 1821), a German chemist and biologist.

A review on selected pioneering works on humus in soils and sediments during the 20th century was presented by Feller and co-workers recently (Feller et al. 2010).



Figure 4. Jöns Jakob Berzelius (1779 – 1848), a Swedish chemist and a professor of medicine and pharmacy.

The study of soil humic substances is much older than the study of aquatic humic substances. Jöns Jakob Berzelius (1779 – 1848), a Swedish chemist and a professor of medicine and pharmacy, was the first who introduced aquatic humic substances. In 1806 he extracted humic substances from a spring in Sweden (Fig. 4). He called these acids *crenic* and *aprocrenic* acids, which means „organic acids from springs“ (Berzelius 1806).

After Berzelius few literature is available dealing with aquatic humic substances. The issue of the origin of the color in water came up in 1919. Oden (1919) named the yellow acids *fulvic acids* (fulvus, the latin name for golden, yellow). An interesting publication was given by Waksman (1938). He studied the formation of humus in water and he distinguished between humus from sea water, rivers and lakes. This was done according to chemical analysis. In 1974, Rook published that chlorination of colored waters led to the formation of mutagenic chlorinated hydrocarbons.

20TH CENTURY, UP TO 1981

During the centuries humic substances have received attention from scientists in a wide variety of disciplines: chemistry, biology, soil chemistry, environmental chemistry, limnology, hydrology, engineering and others. Although the scientists from the different disciplines were working in small network groups, a international organized platform was missing.

The need to bring together scientists from the different disciplines was most obvious: The variability in humic substances resulting from differences in source materials and extraction and fractionation techniques made the interlaboratory comparison of the experimental results of various researchers very difficult. For many scientists this situation was undesirable and therefore several people addressed these problems on an international scope. Efforts to establish an international reference collection of humic substances started in the early 1970s. Patrick MacCarthy, professor from the Colorado School of Mines, USA, and Ronald Malcolm, professor at the US Geological Survey (USGS) brought the ideas into reality. In 1976, Patrick MacCarthy, published a manuscript in *Geoderma* (MacCarthy 1976). The publication showed the potential benefits by establishing a reference collection of humic material for interlaboratory comparison. The initiative met with a very disappointing response from the editor in chief: Dr. Simonson: ...*“Proposals for establishing a collection of humic materials for interlaboratory comparison have been made in the past....but have never really gotten off the ground. Prospects for yours do not*

look good“. ... *“To get further than promising reference collection, I think you will have to get some organization to push it“.*..(MacCarthy 2002).

However, MacCarthy, Malcolm and other colleagues involved submitted the idea to other colleagues, and committees, and they presented the idea on national and international meetings. In 1978 Malcolm and MacCarthy introduced to the soil humic scientists that an initiative had started to introduce humic substances as reference samples during the International Soil Science Society Meeting in Edmonton (MacCarthy and Malcolm 1979). There a special working group was set up to study the possibility of establishing an international standard collection of humic substances. Patrick MacCarthy was the chairman of the committee, and Ronald Malcolm acted as secretary.

Two meetings implemented the issue and the need to organize a platform for humic substances in 1981. Egil Gjessing, professor from the Norwegian Institute for Water Research (NIVA), Norway and Russ Christman, professor at Chapel Hill, North Carolina, USA, chaired the first-ever international humic substances meeting at the University of North Carolina. The meeting was sponsored by NIVA and the US Environmental Protection Agency (EPA). One important result of the meeting was the book “Aquatic and Terrestrial Humic Substances in the Environment” (Christman and Gjessing 1983).

A subsequent meeting was initiated in September 1981 at the US Geological Survey (USGS) from the committee which was established in 1978 in Edmonton. Designated persons from the soil and from the water field presented the state-of-the-art information about various aspects of humic substances science. This meeting had the aim to establish an international standard collection of humic substances. The persons acting in the international committee, and other scientists involved in humic studies in soil and water, are named in Table 1.

During this meeting the group set up a strategic plan for generating a suite of standard humic substances which could be available to researchers world wide. The committee decided on the following items which had to be reached for the years 1982 to 1983:

- **To collect, to extract and to purify humic and fulvic acids from soil, Leonardite, peat, and from aquatic sources by controlled extraction procedures,**
- **and to distribute and to maintain standard samples.**

Table 1. The persons acting in the international committee at the US Geological Survey (USGS), September 1981.

International Committee	Country, affiliation
Francis Andreux	France
Egil T. Gjessing	Norway
Michael H.B. Hayes	England
Shozo Kuwatsuka	Japan
Patrick MacCarthy	USA
Ronald R. Malcolm	USA
Morris Schnitzer	Canada
Paulo Sequi	Italy
Frank J. Stevenson	USA
Roger S. Swift	New Zealand
Invited guests	
Jerry A. Leenheer, Robert W. Wershaw, Georg Aiken, E. Michael Thurman, Robert C. Averett, Hal Stuber	USGS, Denver, USA
David Reckhow	University of North Carolina, USA
Paul Ringhand	US EPA, Cincinnati, USA
Robert Steward	President American Society of Agronomy (ASA), USA
Matthias Stelly	ASA, Madison, USA

The persons responsible for collecting and isolating the samples were:

1. Bulk Sample Collecting:

- Soil: *F. J. Stevenson*
- Leonardite: *R. L. Malcolm*
- Peat: *R. L. Malcolm*
- Aquatic Samples: *R. L. Malcolm, G. R. Aiken, W. L. Campbell, C. Bowles, P. MacCarthy*

2. Extraction/Isolation of Humic Substances (HA and FA):

- Soil: *R. S. Swift*
- Leonardite: *M. Schnitzer*
- Peat: *M. H. B. Hayes*
- Water: *R. M. Malcolm, G. R. Aiken, W. L. Campbell, C. Bowles, P. MacCarthy*

For the extraction of the IHSS soil standard samples dilute sodium hydroxide was chosen, followed by precipitation of humic acid at low pH and a series of desalting steps involving cation exchange, dialysis, etc. to obtain fulvic acid. Roger Swift outlined the procedure, which is still in practise.

The state-of-the-art method for isolation of humic substances from natural waters was the XAD-8 resin adsorption method. In this method, the dissolved organic matter (DOM)

was fractionated through adsorption of the hydrophobic fraction on the XAD-8 resin. Subsequently, the hydrophobic fraction was eluted from the resin by alkaline extraction with aqueous sodium hydroxide, followed by precipitation of humic acid at low pH and a desalting step involving cation exchange to obtain fulvic acid.

Finally during the last days of the meeting, the decision was made to establish a new society. The maintenance and the distribution of reference samples was one stimulus of the foundation. But it was decided that the focus of the society should be much broader and that the society has to deal with all fundamental and applied aspects in the field of humic substances. This was summed up in the motto of the new society:

“to bring together scientists in the coal, soil and water science with interest in humic substances, and to advance the knowledge and the research of humic substances”.

The last part of the sentence has been changed about 10 years ago. It was the intention to broaden the aspects. The revised version is ***“...and to advance the knowledge and the research of natural organic matter in soil and water”.***

The founding members of the society are shown in Figure 6. Professor Michael Hayes, and Professor Frank Stevenson are not present in the group-photography.



Figure 6. Photography of the founding members of the Society.

The first officers were elected at that meeting and the first bylaws were drawn up in the upcoming months. The members of the first IHSS board are presented in Figure 7. According to the updated bylaws, the members of the board increased. Today the board consists of six board members (president, vice president, past president, secretary, and two board members). All members are elected by the members of the society. The treasurer and the chairperson of the samples collection are appointed by the board and are associated to the board. The acting board members are presented in Figure 8. A review of the officers and board members of IHSS since its inception in 1982 is shown in Figure 9.

IHSS Board 1981/1982 to 1985/1986

President	Ronald Malcolm , USGS, USA
Vice-President	Roger Swift , Canterbury College, New Zealand
Board Members	Paulo Sequi , University of Bologna, Italy Shozo Kuwatsuka , Nagoa University, Japan
Treasurer /Secretary	Patrick MacCarthy , Colorado School of Mines, USA



Figure 7. The members of the first IHSS board.

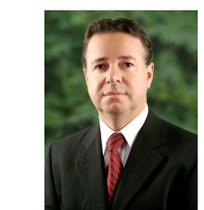
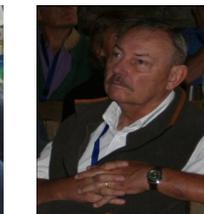
IHSS Board June 2010 to September 2012

President	Ladislau Martin-Neto , Brazil
Past President	Jerzy Weber , Poland
Vice President	Teodoro Miano , Italy
Secretary	Gudrun Abbt-Braun , Germany
Member	Claudio Ciavatta , Italy Irina Perminova , Russia
Samples Collection	
Chairman	Paul Bloom , USA
Treasurer	Raymond Hozalski , USA
Associate Treasurer	C. Edward Clapp , USA



Figure 8. The acting board members of the IHSS.

President		
1983 - 1986	Ronald L. Malcolm	USA
1987 - 1989	Roger S. Swift	New Zealand
1990 - 1992	Russell F. Christman	USA
1993 - 1995	Michael H. B. Hayes	England
1996 - 1997	Nicola Senesi	Italy
1998 - 1999	James J. Alberts	USA
2000 - 2001	Fritz H. Frimmel	Germany
2002 - 2003	Yona Chen	Israel
2004 - 2005	Maria De Nobili	Italy
2006 - 2007	Paul Bloom	USA
2008 - 2009	Jerzy Weber	Poland
	Ladislau Martin-Neto	Brazil
2010 - 2011		
2012 - 2013	Teodoro M. Miano	Italy
Secretary		
1982 - 1987	Patrick MacCarthy	USA
1987 - 1990	Simon A. Visser	Canada
1991 - 1994	I. H. (Mel) Suffet	USA
1995 - 2003	Theodore M. Miano	Italy
2004 - 2012	Gudrun Abbt-Braun	Germany
Treasurer		
1987 - 1993	Patrick MacCarthy	USA
1993 - 2002	C. Edward Clapp	USA
	C. Edward Clapp	
2006 - 2010	(Ray Hozalski)	USA
	Ray Hozalski (C. Edward Clapp)	
2010 - 2014	Edward Clapp)	USA
Samples Collection Chair		
1981 - 1997	Patrick MacCarthy	USA
1997 - now	Paul Bloom	USA
Board members		
1984 - 1985	Paolo Sequi	Italy
1984 - 1987	Shozo Kuwatsuka	Japan
1986 - 1988	Hamish A. Anderson	Scotland
1989 - 1992	Ryoshi Ishiwatari	Japan
1991 - 1994	Edward Tipping	England
1993 - 1997	Egil Gjessing	Norway
1995 - 1999	E. Michael Perdue	USA
1997 - 2001	Jean-Philippe Croué	France
2000 - 2002	Maria De Nobili	Italy
2002 - 2004	Gudrun Abbt-Braun	Germany
	Ladislau Martin-Neto	Brazil
2002 - 2005		
2004 - 2012	Claudio Ciavatta	Italy
2006 - 2010	Etelka Tombacz	Hungary
2011 - 2013	Irina Perminova	Russia



Figures 9. Presidents, officers and board members of IHSS since 1982.

MEMBERS AND CHAPTERS

During the 30 years, the society grew up to almost 700 members (Fig. 10). Members are spread all over the globe. The IHSS has three types of membership: regular, student, retired. The fees are divided for high and low income countries.

According to the bylaws each member belongs to national or regional chapters. In 2009/2010 the members have been organized in 20 chapters. The list of the chapters and the responsible chapter coordinators in 2010 are listed in Table 2. Today there are about two hundred members in North and South America. The highest numbers are counted in Central Europe. lower numbers for the eastern part of the globe, whereas there are almost no members from Africa.

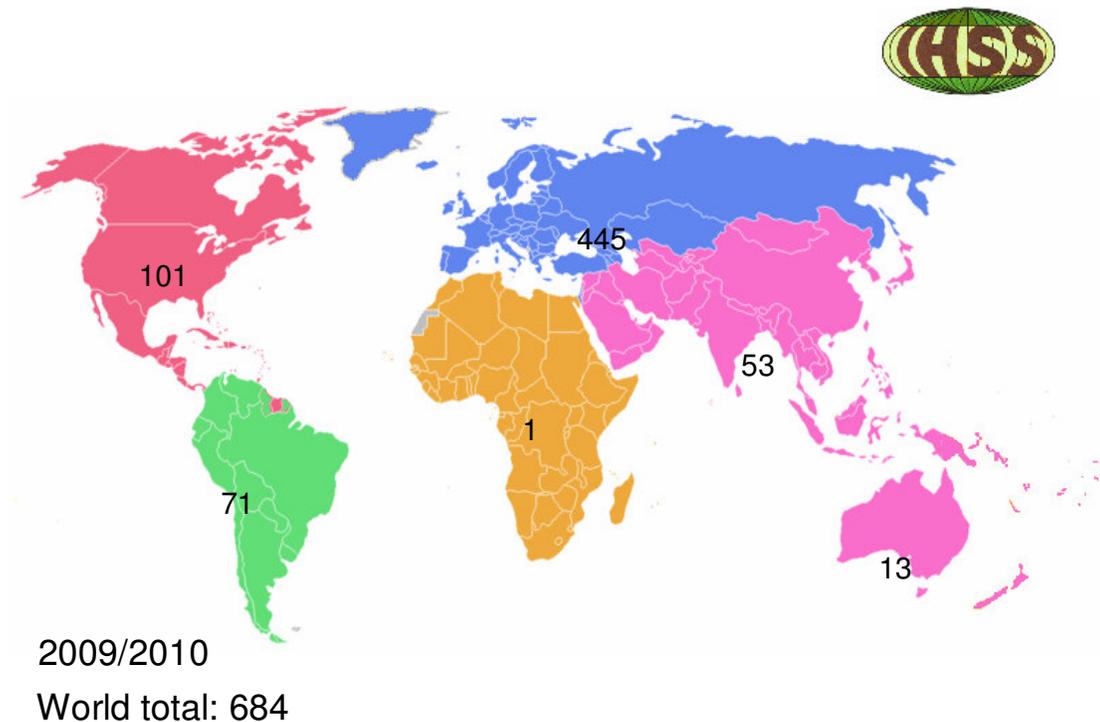


Figure 10. Number of IHSS members.

The chapter of the Independent States (CIS) and the US chapter show the highest numbers, followed by Poland, Italy and Brazil. A unique situation is given for the northern European countries. They decided to build up the Nordic-Baltic Chapter, including Denmark, Estonia, Finland, Latvia, Lithuania, Norway and Sweden. Countries which can not build up a regional chapter belong to the ROW chapter (rest of the world chapter).

Chapters with a high number of members have set up their own bylaws and initiate chapter meeting which occur annually or biannually.

Table 2. The list of the chapters and the responsible chapter coordinators in 2010 (IHSS, 2010: General assembly, held during the 15th IHSS Meeting, Puerto de la Cruz 2010).

Regional/national chapter	number of members	chapter coordinator
CIS (chapter of independent states) Belarus, Kazakhstan, Kyrgyz Republic, Russia, Ukraine, Uzbekistan	124	Irina Perminova
US Chapter	100	Daniel Olk
Poland	70	Jerzy Drozd
Italy	69	Teodoro Miano
Brazil	63	Deborah Pinheiro Dick
Bulgaria	35	Ekaterina Filcheva-Konisheva
Nordic-Baltic Chapter Denmark, Estonia, Finland, Latvia, Lithuania, Norway, Sweden	26	Dag Olav Andersen
Germany	24	Gudrun Abbt-Braun
Japan	22	Masakazu Aoyama
China	18	Jianming Xu
Hungary	17	Etelka Tombacz
France	17	Marc Benedetti
Australia & New Zealand	13	Kaye Spark
Czech Republic	15	Miloslav Pekar
Ireland	11	Corinna Byrne
Slovakia	10	Gabriela Barancikova
Spain	8	Jose Gonzalez-Peres
Argentina	7	Marcelo Avena
Greece	7	Yannis Deligiannakis
Israel	7	Yona Chen
RoW Chapter Belgium, Canada, Chile, India, Iran, Netherlands, South Africa, Switzerland, Turkey, United Kingdom	21	Gudrun Abbt-Braun

Members are informed by the IHSS newsletter which is spread out to inform about board decisions und guidelines, upcoming events, reports on past meetings, new books, abstracts of PhD thesis and other business.

STANDARD AND REFERENCE COLLECTION

One important column of the IHSS is the collection of the standard and reference samples. According to the bylaws:..."*This committee shall be responsible for the oversight of the maintenance and sales of the Standard and Reference Collection of humic substances and natural organic matter. The Standard and Reference Collection Committee*

Chair shall be the custodian of the Collection and be responsible for sales of Standard and Reference samples.” (IHSS 2011).

The unique features of the collection are:

- **it is accessible to researchers worldwide,**
- **all materials originated from carefully chosen and specified locations,**
- **all samples have been isolated by carefully controlled and supervised procedures that are fully documented,**
- **all materials (both the isolated humic substances and the bulk solids) have been thoroughly homogenized,**
- **availability of the three bulk solids allows the comparison of different extraction methods.**

The procedures used to isolate standard and reference humic and fulvic acids are the methods which were chosen by a working group of scientists in 1981. On the basis of information that was available at that time, these methods were considered as being most suitable for the specific purpose of establishing a collection of standard and reference samples from the selected bulk source materials. IHSS does not endorse or recommend these methods as the best methods for extracting humic substances.

By definition, a IHSS standard sample must satisfy all four of the following criteria (IHSS 2011):

1. The sample must have come from a site specifically designated by the IHSS for this purpose.
2. The sample must have been prepared according to a specific procedure designated by the IHSS.
3. The operations involved in (1) and (2) must have been conducted under the direct supervision of the IHSS.
4. The sample must be designated as a standard by the IHSS.

Upon depletion of the existing supply of a standard humic or fulvic acid, another batch of that standard will be prepared from the existing stock of bulk soil, peat, or leonardite, or from the Suwannee River. Successive batches of a standard material are expected to be very similar but not necessarily identical.

Sources of the standard samples are:

- Suwannee River, rises in the Okefenokee Swamp in south Georgia and flows southwest to the Gulf of Mexico, peat area, brown water source,

- Elliott Soil, fertile prairie soils of the US states of Indiana, Illinois, and Iowa,
- Pahokee Peat, agricultural peat soil of the Florida Everglades,
- Leonardite, a low-grade coal.

A detailed description of the sources of the standard samples is given on the webpage of the society (IHSS 2011).

By definition, an IHSS reference sample does not satisfy at least one of the criteria for standard humic substances, but does meet both of the following conditions:

- The sample must have been prepared from a clearly designated source material, and its preparation must be described in detail.
- The material must have been homogenized by the IHSS and must be distributed by the IHSS.

Sources of the reference samples are:

- Suwannee River NOM, same sampling site was used for the standard and reference samples, Pahokee Peat, same sampling site was used for the standard and reference samples, Hellrudmyra, reference Nordic humic acid and fulvic acid, small tarn,
- Summit Hill Soil, tussock grass area, South Island of New Zealand,
- Waskish Peat, sphagnum bog peat typical of northern temperate regions,
- Nordic Reservoir NOM, drinking water reservoir at Vallsjøen, Skarnes, Norway,
- Pony Lake NOM, zero terrestrial input end-member of aquatic NOM, Antarctica.

A detailed description of the origin of the reference samples is given on the webpage of the IHSS (IHSS 2011).

The list of standard and reference samples available today are shown in Table 3. Since establishing the standard and reference collection several additional samples are available, varying both in origin and in the isolation procedure. In the late 1990's, IHSS has employed reverse osmosis to concentrate natural organic matter (NOM) from selected water sources. These reference NOM samples contain not only the hydrophobic and hydrophilic acids but also other soluble organic solutes that are present in natural waters. For the future efforts are taken to enlarge the sample collection by introducing an additional aqueous water sample, originating from a river with a low organic carbon content and a moderate alkalinity, and a tropical soil sample.

IHSS humic acids, fulvic acids, and NOM samples are stored as desalted (H^+ -saturated), freeze-dried solid powders. A summary of the properties of the standard samples is available from Averett et al. (1989) and from Thorn et al. (1989).

All samples of the original solid earth materials and the standard and reference humic substances are available from the IHSS on a cost-reimbursable basis. Today the samples can be ordered online, paying by credit card is offered.

Table 3. The list of standard and reference samples: FA - fulvic acid; HA - humic acid; NOM - natural organic matter.

Standard Samples	
Suwannee River	HA II, FA I, II
Elliott Soil	HA, FA III
Pahoee Peat	FA, HA
Leonardite	FA, HA
Reference samples	
Pahoee Peat	FA, HA
Waskish Peat	HA
Nordic Aquatic sample	FA, HA
Pony Lake (Antartica)	FA
Suwannee River	NOM isolate
Nordic Reservoir	NOM isolate
Bulk solid sources of HA and FA: Elliot silt loam, Pahoee, Leonardite	

There is an increasing demand for standard and reference samples since the establishment of the collection, sales numbers since 2001 are given in Figure 11. The samples are ordered worldwide, as shown by the breakdown of sales for the year 2009 (Fig. 12). It is quite obvious that there is an increasing demand for aqueous standard and reference samples.

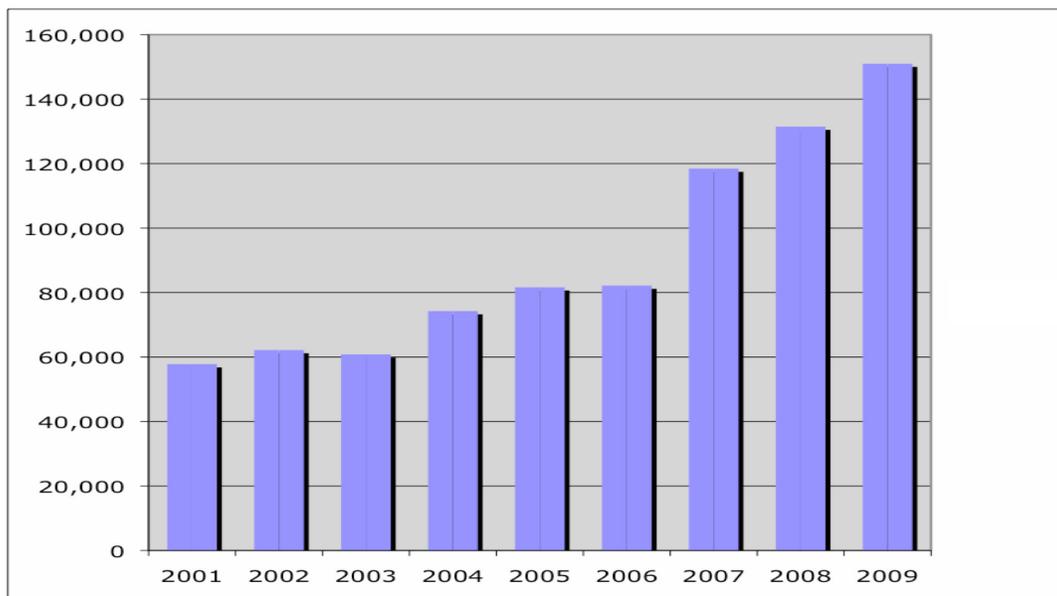


Figure 11. Sales numbers of standard and reference samples.

INTERNATIONAL MEETINGS

The IHSS holds international meetings biennially at a time and place determined by the board to discuss the results of recent scientific research on humic substances and natural organic matter (Fig. 13). It is the intension of the society to hold the meetings all over the world in order to balance not only travel time and travel costs for all our members but also attract new colleagues to discuss common interests.

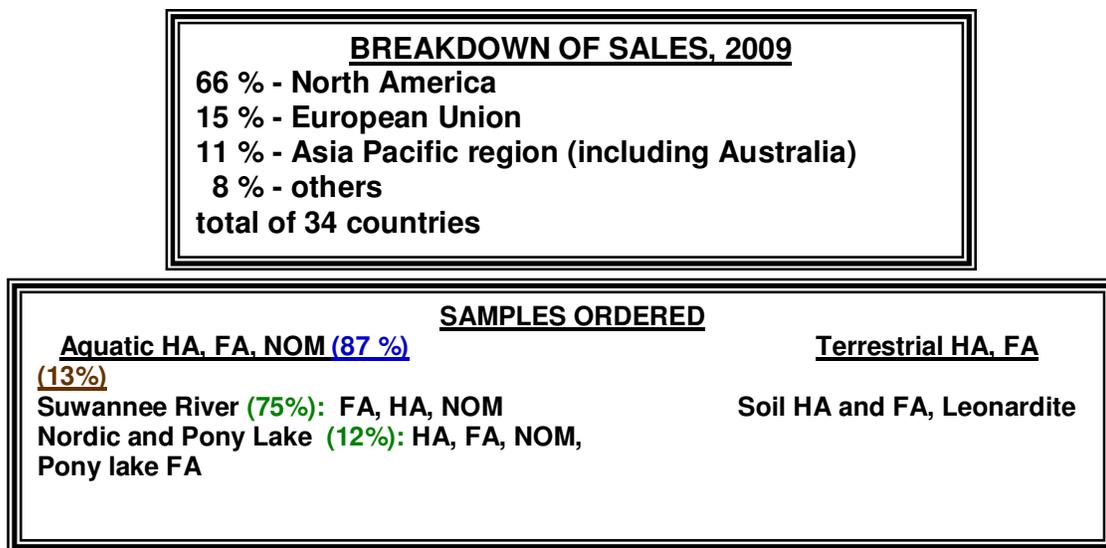


Figure 12. The breakdown of sales of samples for the year 2009.

In 1983, the first international meeting took place in Estes Park. “*Geochemistry, Isolation and Characterization of Humic Substances*“ were the main topics on the agenda of the meeting. Hayes and Aiken presented the first results about the isolation of the standard samples. The outcome of this meeting was the book “*Geochemistry, Isolation and Fractionation, and Characterization of Humic Substances*”, edited by Aiken et al. (1985). Meanwhile this book has the status of a textbook.

The second meeting took place in Birmingham one year later. The corresponding outcome was the book “*Humic Substances II: In Search of Structure*”, edited by Hayes et al. in 1989.

Several special books and extended abstracts books were the outcome of the 15 meetings so far (Tab. 4a and b). In 2012 we are approaching the 16th International meeting. It will take place in Hangzhou in China, September 2012.



Figure 13. IHSS meetings since 1983.

Table 4a. Special books and extended abstracts books of the IHSS (1983 – 1988).

International meeting, year	Publication
1983	Baker, E. W. (Ed.): Proceedings of the First Meeting of the International Humic Substances Society, Estes Park, Colorado, August 1983. Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (Eds.): Humic Substances in Soil, Sediment, and Water. Wiley-Interscience, New York, 1985.
1984	Hayes, M. H. B., Swift, R. S. (Eds.): Volunteered Papers - 2nd International Conference. International Humic Substances Society, University of Birmingham, Birmingham UK, 1984. Hayes, M. H. B., MacCarthy, P., Malcolm, R. L., Swift, R. S. (Eds.): Humic Substances II: In Search of Structure. Wiley-Interscience, New York, 1989.
1986	Becker, G., Gjessing, E. (Eds.): Abstracts of Oral and Poster Papers of the Third International Meeting of IHSS, August 4-8, 1986, Oslo, Norway, 1986. Becker, G.: Special Issue of Humic Substances Research from the Third International Meeting of IHSS, Oslo, Norway, August 4-8, 1986, The Science of the Total Environment, Elsevier Science Publishers, Amsterdam, 62: 1-505, 1987.
1988	Saiz-Jimenez, C. (Ed.): Abstracts of Oral and Poster Papers at the Fourth International Meeting of IHSS, October 3-7, 1988, Matalascanas Beach, Huelva, Spain, 1988. Saiz-Jimenez, C., Rosell, R. A., Albaiges, J.: Special Issue of Humic Substances Research from the Fourth International Meeting of IHSS, Matalascanas Beach, Huelva, Spain, October 3-7, 1988, The Science of the Total Environment, 81/82:1-723, 1989.

Table 4b. Special books and extended abstracts books of the IHSS (1990 – 2010).

International meeting, year	Publication
1990	Ishiwatari, R. (Ed.): Abstracts of Oral and Poster Papers at the Fifth International Meeting of IHSS, August 6-10, 1990, Nagoya, Japan, 1990. Ishiwatari, R., Lowe, L., McKnight, D., Shinozuka, N., Yonebayashi, K.: Special Issue: Advances in Humic Substances Research, a Collection of Papers from the Fifth International Meeting of IHSS, Nagoya, Japan, 6-11 August, 1990, The Science of the Total Environment, Elsevier Science Publishers, Amsterdam, 117/118: 1-591, 1992.
1992	Senesi, N., Miano, T. M. (Eds.): Abstracts of Oral and Poster Papers at the Sixth International Meeting of IHSS, September 20-25, 1992, Monopoli (Bari), Italy, 1992. Senesi, N., Miano, T. M. (Eds.): Humic Substances in the Global Environment and Implications for Human Health. Elsevier, Amsterdam, 1994.
1994	Clapp, C. E., Hayes, M. H. B., Senesi, N., Griffith, S. M. (Eds.): Humic Substances and Organic Matter in Soil and Water Environments: Characterization, Transformations and Interactions. Proceeding of the 7 th International Conference of the International Humic Substances Society, July 3-8, 1994, University of the West Indies, St. Augustine, Trinidad and Tobago, 493 pp., 1996.
1996	Drozd, J., Gonet, S. S., Senesi, N., Weber, J. (Eds.): The Role of Humic Substances in the Ecosystems and in Environmental Protection. PTSH-Polish Society of Humic Substances, Wroclaw, Poland, 1997.
1998	Swift, R. S., Spark, K. M. (Eds.): Understanding and Managing Organic Matter in Soils, Sediments, and Waters. International Humic Substances Society, St. Paul, MN, USA, 2001.
2000	Croué, J.-P. (Ed.) : Entering the Third Millenium with a Common Approach to Humic Substances and Organic Matter in Water, Soil and Sediments. Proceedings of the 10 th International Meeting of the International Humic Substances Society, July 24-28, 2000, Toulouse, 699 pp. (Vol. I), 1274 pp. (Vol. II), 2000.
2002	Gabbour, E. A., Davies, G. (Eds.): Humic Substances: Nature's Most Versatile Materials. Proceedings of the 11 th IHSS Conference, July 21-26, 2002, Northeastern University, Boston, MA, USA, 481 pp., 2002.
2004	Martin-Neto, L., Milori, D. M. B. P., da Silva, W. T. L. (Eds.): Humic Substances and Soil and Water Environment. Proceedings of the 12 th International Meeting of the International Humic Substances Society, July 25-30, 2004, Colina Verde Hotel, Sao Pedro, Sao Paulo, Brazil, 763 pp., 2004.
2006	Frimmel, F. H., Abbt-Braun, G. (Eds.): Humic Substances - Linking Structure to Functions. Proceedings of the 13 th Meeting of the International Humic Substances Society, July 30 to August 2, 2006, Universität Karlsruhe, 492 pp. (45-I), 623 pp. (45-II), 2006.
2008	Perminova, I. V., Kulikova, N. A. (Eds.): From Molecular Understanding to Innovative Application of Humic Substances. Proceedings of the 14 th Meeting of the International Humic Substances Society, September 24-29, 2008, Moscow - Saint Petersburg, Russia, 350 pp. (Vol. I), 746 pp. (Vol. II), 2008.
2010	González-Perez, J. A., Gonzáles-Vila, F. J., Almendros, G. (Eds.): Advances in Natural Organic Matter and Humic Substances Research 2008-2010. Proceedings Book of the Communications presented to the 15 th Meeting of the International Humic Substances Society, June 27 – July 2, 2010, Tenerife, Canary Islands, Spain, 302 pp. (Vol. I), 539 pp. (Vol. II), 429 pp. (Vol. III), 2010.

TRAVEL AWARDS

Since 1996, young students have the opportunity to join the meetings by applying for travel awards. The aim of the IHSS travel support award is to allow students to present their work and to participate in the biannual International IHSS meetings. The number and amount of the awards will be determined by the president in consultation with the treasurer and members of the travel support selection committee. Up to now 84 students have been awarded (Fig. 14).

Since 1996, the society had selected 84 persons for the travel award. A specific award out of this is the Ron Malcolm Award. The travel support selection committee is selecting the top applicant for a special award: the ***Ron Malcolm Award***. This individual will receive a certificate and an additional cash award in addition to the regular travel support. 6 persons have been selected to the Ron Malcolm award, since



Figure14. The IHSS Travel Awards and Ron Malcolm Awards.

IHSS TRAINING AWARDS

Since 2005, the society decided to support young researcher in particular. By this the IHSS provides limited support for training awards. Training awards enable students and young scientists to spend 1 to 3 months in training/research at leading laboratories. The intension of offering the awards is to:

- have access to sophisticated facilities and training in research laboratories where humic substances are investigated,
- establish new collaborative links and the exchange of knowledge between laboratories,
- test innovative ideas that may develop into potential collaborative research projects.

The possibility is offered each two years. The IHSS has sponsored 37 young researchers since 2005, and the young researchers are spread from all over the world (Argentina (1), Australia (1), Brazil (3), Germany (2) , Greece (2), Hungary (1), India (1), Iran (1), Ireland (3), Israel (3), Italy (8), Morocco (3), Poland (3), Slovakia (1), Russia (3), USA (1)).

HONORARY AND DISTINGUISHED SERVICE MEMBERS

Members who have made exceptional contributions to the society are conferred as honorary members and distinguished service member for lifetime. In Figure 15 the members honoured during the 30 years are listed. In particular, the society has a deep dediction to the honorary members Wolfgang Flaig and Ronald Malcolm. Wolfgang Flaig (1912 - 2009) became worldwide renowned for its modern approach to the biochemistry of soil, and on the formation, structure and function of humic and fulvic acids, including their physiological effects on plants. Ronald Malcolm (1937 – 1998) was a founding father of IHSS and its first president. His name is associated with his untiring support of humic substances research, his involvement in the establishment of the standard and reference samples, especially in the aquatic humic substances isolation, and in his systematic approach in the characterization of fulvic and humic acids, especially by ¹³C-NMR.

ONGOING AND FUTURE ACTIVITIES

New improvement was reached by working on the tools with web-based online elections, online-payment of fees, online ordering of IHSS samples. The board recently decided to work on the implementation of a strategic plan for the upcoming years. Aspects to be considered are science, society organization, and finances. The expected results

should strengthen the society and to improve the visibility between other scientific communities. By the engagement of the activities the membership numbers are expected to increase.

<u>Honorary Members</u>	
Wolfgang Flaig †	1984
Morris Schnitzer	1986
Frank J. Stevenson	1989
Ronald L. Malcolm †	1992
Michael H. B. Hayes	1998
Egil T. Gjessing	1999
Russell F. Christman	2001
Konrad Haider	2001
Roger Swift	2008
Nicola Senesi	2009
Fritz H. Frimmel	2010
<u>Distinguished Service Member</u>	
C. Edward Clapp	2006



Wolfgang Flaig
1912 - 2009



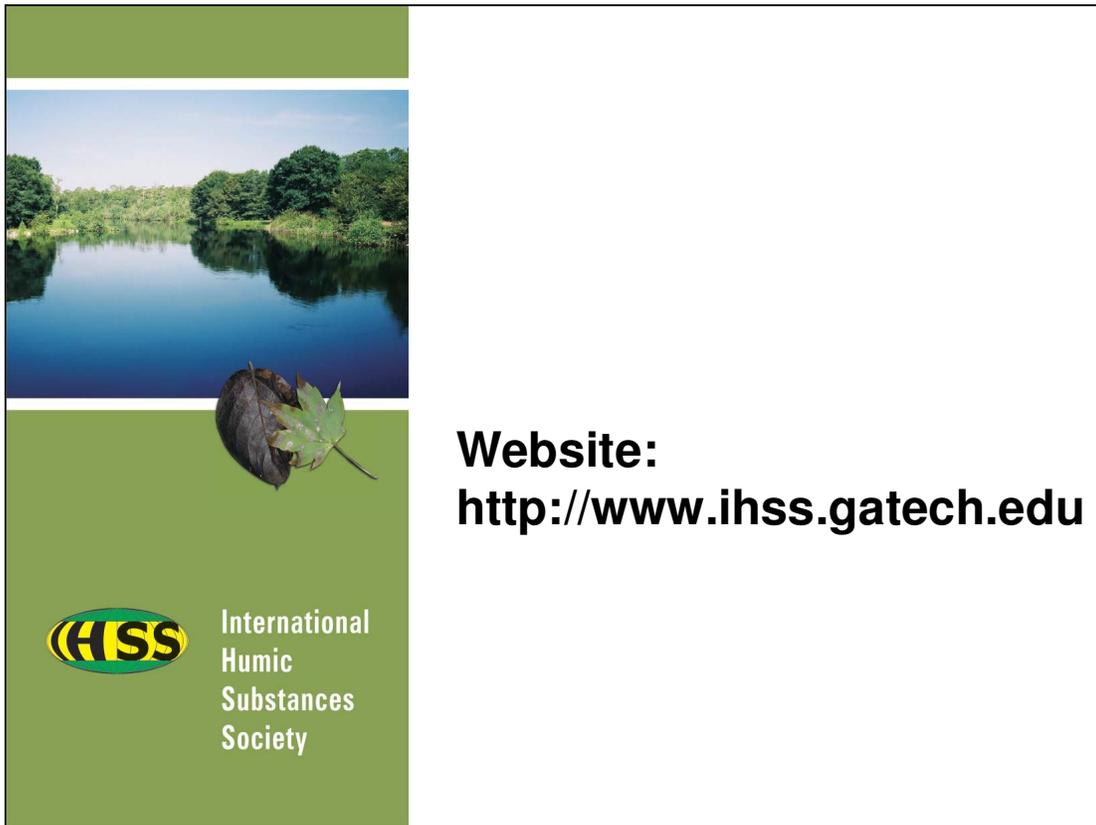
Ronald L. Malcolm
1937 - 1998

Figure 15. Honorary and Distinguished Service Members of the IHSS.

Due to the encouragement and effort of many scientists, the society has reached important achievements and international attention by conducting a high level of research, by providing standard and reference samples, which are used worldwide, and by organizing national and international meetings all over the world. Thanks to the pioneers who started the society and thanks to the those who continue to contribute to maintain and advance the IHSS society.

HOW TO BECOME MEMBER OF IHSS

Online application is possible via website access of <http://www.ihss.gatech.edu> (Fig. 16) or via contact through the secretary of the society Gudrun.Abbt-Braun@kit.edu



The graphic is a vertical rectangular invitation. The left side features a green background with a photograph of a calm river reflecting a dense line of green trees under a blue sky. Below the photo is a single leaf, partially brown and partially green. At the bottom left is the IHSS logo, which consists of the letters 'IHSS' in a stylized, bold font with a green and yellow gradient, set within a green oval. To the right of the logo, the text 'International Humic Substances Society' is written in a white, sans-serif font, stacked in four lines. The right side of the graphic is a plain white background with the text 'Website: http://www.ihss.gatech.edu' in a bold, black, sans-serif font.

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

Figure 16. Invitation to official IHSS website.

Humic Substances and Soil Structure: Dispersing Agents or Stabilizers?

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Summary

A wide array of organic compounds, including HS, PS, amino acids, peptides, proteins and aliphatics are adsorbed to the soil's mineral components, clay and hydroxides in particular, to varying degrees, thereby playing an important role in the determination of aggregate stability.

Organic substances of microbial and plant origin cement the soil particles together to form macro- and micro-aggregates. Plant residues and PS play a dominant role in determining the stability of macro-aggregates while HS including humin are more important when micro-aggregates are of concern. Integrating all these effects influences the physical properties of soils.

Coating of micro-aggregates or sand particles with DOM, HS or charcoaled material, under slow air drying can induce water repellency which, although considered a problem creating property of soils, will stabilize soil aggregates. However, in certain conditions the presence of organic components with negatively charged macromolecules such as HA, FA and anionic polysaccharides can have a negative effect on the formation and stability of soil aggregates. The most important factors are pH and cation type (monovalent or multivalent). When irrigated with TWW, which usually contains relatively high concentrations of sodium, organic matter can result in clay dispersion and destruction of soil structure.

The organic matter contained in the TWW may produce a temporary effect of hydrophobicity that changes the characteristics of water movement in the soil, causing damage to agriculture and the environment as well.

INTRODUCTION

Most arable soils contain 0.1 to 5% organic matter (OM) by weight, with sandy soils of arid zones having the lowest percentage and clayey soils in temperate zones having the highest.

Increasing soil organic matter (SOM) content usually increases the soil's total porosity and decreases its bulk density. Over a wide range of 10 to 60 g organic C per kg soil, a curvilinear decrease in bulk density from 1.7 to 0.8 Mg /m³ has been observed (Franzluebbers et al., 2001). Friability of soils, namely, their tendency to form clods that easily crumble into their constituent natural aggregates is significantly related to OM content as well as aggregate stability and bulk density (Macks et al., 1996).

Soil mineral particles usually aggregate into granular structures. The stability of soil is an important indicator of soil quality since it determines soil porosity and hydraulic conductivity. The degree to which soil is organized into water-stable aggregates influences many of its agricultural and ecosystem properties (Tisdall and Oades, 1982). Cropping systems or soil management that promotes SOM accumulation (e.g. no-till) also promotes soil aggregation, but sometimes natural or anthropogenic organic matter can induce instability of soil aggregates. A number of soil properties contribute to the formation and stabilization of aggregates including: SOM, clay mineralogy, soil texture, exchangeable cations and salt content, CaCO₃ content, and Fe and Al oxides.

Soil aggregates vary in size from microaggregates (0.02 to 0.25 mm in diameter) to macroaggregates (up to 10 mm in diameter) with the larger aggregates probably comprised of clusters of smaller aggregates.

The interaction of OM with clay has a multitude of consequences that are reflected in the physical, chemical and biological properties of the matrix. These interactions often form "organo-mineral" complexes in soils. Most of these complexes serve to bridge soil particles together, thereby forming stable aggregates (Stevenson, 1994).

Although soil organic matter is attributed to a positive and central role in the formation and stabilization of soil structure, there are cases in which the presence of certain organic components has negative effects.

SOIL AND WATER-BORNE ORGANIC MATTER

As organic materials in the soil decay, macromolecules of a mixed aliphatic and aromatic nature are formed. The term humus is often synonymous for SOM (e.g. Stevenson, 1994). An important term is natural organic matter (NOM or DOM; the latter

referring to water-borne or dissolved organic matter). Some authors distinguish between the total organic matter in a soil and humus. The latter includes the total NOM in the soil, excluding identifiable plant and animal tissues and living biomass. Humic substances (HS), including humic acids (HAs), fulvic acids (FAs) and humin, comprise soil humus. Defined biochemicals are not considered to be a component of the various HS fractions.

In recent decades, the use of TWW for crop irrigation as an alternative to wastewater disposal is common in water-scarce countries worldwide and has led to addition to the soil of organic matter of anthropogenic origin. Wastewater originating from municipal, industrial and agricultural sources contains OM at different levels, which is gradually removed during sewage-water treatment. The COD level in raw sewage and in TWW after the primary and secondary treatments has been reported to be 250-1000, 150-750 and 30-160 mg L⁻¹, respectively (Feigin et al., 1991). Rebhun and Manka (1971) identified 42% of the DOC in secondary effluents as HS: 25% (FA), 11% humic acid (HA) and 6% humathomelanic acid. According to Manka and Rebhun (1982), HS were the largest organic group in a municipal sewage treatment plant after different treatment steps, with proteins next in order. The total HS were 35.9% of the soluble COD after a secondary treatment by oxidation ponds, and they decreased to 21.6% after a lime clarifier and to 16.7% after a polishing pond (Manka and Rebhun, 1982). In another study, the HS content in TWW was found to be 45% of the DOC, and it increased by 40% during a further degradation process (Namour and Müller, 1998). Amy et al. (1987) reported HS content of 54 to 58% after an activated sludge treatment. The hydrophilic fractions (Leenheer, 1981; Stevenson, 1994) (such as low-MW polysaccharides, carbohydrates, proteins, peptides and amino acids, which are widespread in sewage water) were degraded during the aerobic wastewater treatment, resulting in a relative increase in aromatic and aliphatic compounds (Chefetz et al., 1998).

STRUCTURAL MODELS FOR AGGREGATE FORMATION

Several structural models for aggregate formation have been proposed by soil investigators over the years. Russell (1933) presented a theory of crumb formation after clay particles were held together by oriented molecules of water around cations, through dipole-cation-dipole links. The Emerson's model (1959) is an extension of Russell's model and introduced the bonding between organic and inorganic colloids with ionic and hydrogen bonding between carboxyl groups in the organic matter and clay. The organic bond theory (Greenland, 1965) proposed that soil organic matter forms ionic bonds

between soil particles. According to Edwards and Bremner (1967), organometallic complexes are an essential component in the formation of microaggregates (< 250 μm) and also participate in the bounding to macroaggregates (> 250 μm). According to Tisdall and Oades (1982) the various fractions are formed as a result of the action of the following stabilizing constituents: <0.2 μm —oxides and organic polymers sorbed on clay surfaces via electrostatic bonding and flocculation; 0.2 to 2 μm —microbial and fungal debris (refractory organics) encrusted with inorganics, often clay minerals; 2 to 20 μm —plant and fungal debris encrusted with clay minerals; 20 to 200 μm —roots and hyphae (moderately stable organics); and 200 to 2000 μm —larger mineral particles such as sand size quartz surface covered with oxides and often associated through plant residues; these are strongly management-dependent. Elliot (1986) suggested that this model is valid for soils at a pH range of 6.9 to 7.5, OM levels of 1 to 2%, and relatively high contents of silt, CaCO_3 and smectites. Other researchers have suggested different particle sizes for microaggregates (e.g. Hamblin, 1977), but the grouping proposed by Tisdall and Oades (1982) is widely accepted. Many publications have supported the hypothesis that OM bound to Ca^{2+} ions and clays forms stable complexes that are important to the formation of stable aggregates (McKeague, 1971; Watson and Parsons, 1974; Tate and Churchman, 1978; Tiessen and Stewart, 1983; Muneer and Oades, 1989; Stevenson, 1994). Hamblin and Davies (1977) found a positive correlation between the OM content in the 20- to 50- μm fraction and aggregate stability.

The common denominator of all the above models is the presence of organic matter as an integral part in the formation and stabilization of aggregates.

EFFECTS OF POLYSACCHARIDES AND HUMIC SUBSTANCES ON AGGREGATE STABILITY

Several investigators have focused their studies on the effects on soil structure of both HAs and FAs. Dell'Agnola and Ferrari (1971) found that aggregate stability increases with molecular weight (MW) of soil HS enclaved in the aggregate. Turchenek and Oades (1979) found that the HS were more aliphatic for the very fine clay fraction (<0.1 μm), than for those found in the larger particle sizes. Tarchitzky et al. (1993) provided explanations for the interactive mechanisms involved in clay-HS flocculation and aggregation, and showed that Ca-HS interactions result in flocculation of montmorillonite suspensions. Chaney and Swift (1984) reported that the total organic carbon of soils which they studied exhibited a positive and high correlation with aggregate stability. Both

polysaccharides (PS) and extractable HS levels correlated positively with aggregate stability although the degrees of correlation varied between various soil groups. A significant and positive correlation between aggregate stability and the concentrations of HA or FA or their mixtures was also reported by Piccolo and Mbagwu (1990).

Many microorganisms produce extracellular polysaccharides (EPS) which can be bound to their cell walls or occur in slimes that diffuse into the surrounding medium. The special distribution in soil, chemical composition, interaction with clay minerals and effects on the physico-chemical properties of soils have been investigated by many researchers (e.g. Foster, 1981; Chenu, 1993; Puget et al., 1999; Tarchitzky et al., 1993; Tarchitzky and Chen, 2002b; Dontsova and Bigham, 2005). A number of investigators found that the amount of PS is positively correlated with aggregate stability (Tisdall and Oades, 1982; Anger and Mehuys, 1989; Haynes and Francis, 1993; Tisdall, 1994). Others claimed that aggregate stability decreases with increasing levels of PS (e.g. Degens and Sparling, 1996).

Since sorption is clearly one of the important mechanisms involved in soil structure formation in the presence of OM, interactions of clays with PS were investigated by a number of researchers (e.g. Tarchitzky et al., 1993; 1998; Dontsova and Bigham, 2005).

In field studies on effects of HS on soil structure, Mgbagwu and Piccolo (1989) found that following the application of four rates of HS (up to 10 g Kg⁻¹) to a series of soils representing a wide range of physical properties, soil aggregation had greatly improved. Aggregate stability was found to increase with increasing rates of HA application. The higher application rates induced stabilities that were significantly higher than those found for the controls. Soils originally exhibiting low aggregate stability were improved to a greater extent in response to HA additions. Although the authors attributed much of the formation of stable aggregates to hydrophobic coating of aggregates by the HS, no data were provided to support this hypothesis.

The long term effectiveness of HS as an aggregate stabilizer could also be affected by wetting and drying cycles (WD) as suggested by Piccolo et al (1997). Amending the soils with 100-200 kg HS/ha improved aggregate stability in the three soils studied and also reduced the WD effect.

Swift (1991) concluded that PS are capable of producing stable aggregates, but their effect is transient and declines as the PS are decomposed. Adsorbed HS also produce stable aggregates and the effect is more persistent. The most stable and persistent reformed aggregates were produced by the combined action of PS and HS. According to Swift

(1991) there is no doubt that the increased persistence is due to the relative resistance of HS to biological decomposition in the soil compared to PS. In all instances, the involvement of soil microorganisms is an essential ingredient of the aggregate formation and stabilization process.

Short term effect and mechanism were investigated by Muneer and Oades (1989), who showed that a serial addition of glucose after WD cycles led to substantial aggregation of soils. Glucose plus Ca further amplified this process. In contrast, treating soils with Na₄P₂O₇ which is a powerful extractant of HS (Stevenson, 1994) caused dispersion of most of the clay but did not disrupt large aggregates, probably because their main binding constituents were PS. Muneer and Oades (1989) demonstrated the combined effects of Ca and OM on the bridging of clay aggregates to OM in a series of illustrations, which although hypothetical in nature, help their readers in assessing processes of aggregate formation.

According to research presented above, components of soil organic matter play an important role in the formation of stable aggregates. However, in certain conditions it was found that these components can induce instability of the soil structure.

Kaolinite dominated soils or pure clay-sand mixture as well as the effects of HS and/or Ca on them were also investigated by Yamaguchi et al. (2004). Calcium alone induced microaggregate formation yet the addition of HS further amplified this effect. These effects were not observed in Na dominated clay-quartz systems. The mechanisms inducing these observations were unfortunately not discussed by Yamaguchi et al. (2004) even though they were earlier explained in detail by Tarchitzky et al. (1993).

Narkis et al. (1968) investigated surface waters containing clay and OM and reported an increase in suspension stability relative to suspensions of reference clays. In coagulation experiments, Gibbs (1983) found that natural organic coatings on a mixture of minerals suspended in river water (consisting of kaolinite, illite, chlorite, and montmorillonite) increased the flocculation value (FV) of the clay four-fold compared with uncoated samples. Bloomfield (1954, 1956, 1957) described deflocculation and reflocculation of kaolinite by aqueous leaf extracts of various plant species and Gillman (1974) explained changes in water-dispersible clay in basaltic soils in terms of the variation in the point of zero charge (PZC) of the clay edge. Shanmunagathan and Oades (1983) found that, increasing the concentrations of some anions in the soil solution resulted in the dispersion of clay fractions, because of the fact that adsorbed anions lowered clay PZC.

Similarly, HA was reported to disperse montmorillonitetactoid in suspension (Narkis et al., 1970) as well as soil particles from a humicgleysol (Visser and Caillier, 1988).

Goldberg et al. (1990) reported that removal of OM from arid soils causes a decrease in clay dispersivity. This suggests that at the clay-particle level, negative charges of organic anions enhance clay dispersion. Goldberg and Foster (1990) found lower critical coagulation concentrations for reference clays than for soil clays, suggesting that the content of OM and that of Al and Fe oxides influences soil-clay dispersion. The natural abundance of soil humus may be sufficient to impart a high degree of dispersion to soil-clay fractions (Frenkel et al (1992). Moreover, results reported by Kretzschmar et al. (1993) support the hypothesis that naturally occurring HS increase the colloidal stability of kaolinitic fine clays in aqueous suspensions. These authors suggested that a combination of electrostatic and steric stabilization is responsible for this effect. Kretzschmar et al. (1997, 1998) studied the effect of additions of small amounts of HA to kaolinite suspensions and found that at low pH, flocculation was inhibited because of charge reversal from positive to negative. Similarly, Jekel (1986) reported that HS stabilize dispersed silica and kaolinite particles in suspension. Supportive evidence for potential dispersive properties of organic molecules was also reported by Gu and Doner (1993) who studied the influence of organic polyanions on soil properties (a soil HA, a soil polysaccharide, and a commercial anionic polysaccharide) and found that they serve as effective dispersing agents for Na-clay soils. These investigators did not describe in detail the mechanism involved in clay dispersion, although they suggested that organic polyanions are adsorbed on the clay edges and steric interferences are involved.

The dispersive effect of Na-humate on clay suspensions was explained by Zhang et al. (1991) whose interpretation involved adsorption of humicpolyanions onto the edges of clay particles resulting in a reduced attractive force between the particles. Van Olphen (1977), Frey and Lagaly (1979), and Tombácz et al. (1984) proposed a similar mechanism. The effect of HS on the stability of Na-Montmorillonite suspensions was explained by interactions between negatively charged HS molecules and the edge charge of the clay. These interactions are affected by pH and by the charge and configuration of the HS macromolecule. In pure clay systems, at pH values below the PZC of edge sites, edge-edge (E-E) and edge-face (E-F) interactions among clay platelets are dominant flocculation mechanisms. At pH values above the PZC of the edge sites, only F-F associations occur. In the presence of HS, at pH values below the PZC, negative HS molecules are adsorbed to positive edge sites causing edge-charge reversal (from positive to negative). Consequently,

increased electrolyte concentrations are required for flocculation relative to Na-montmorillonite suspensions without HS. The second flocculation mechanism proposed is based on a random distribution of HS macromolecules among the montmorillonitetactoids. The FV of such a mixture is higher than the FV of montmorillonite suspensions. The term mutual flocculation (heteroflocculation) has been suggested to describe this mechanism (Tarchitzky et al., 1993). Similar results were obtained with polygalactouronic acid (PGA) (Tarchitzky and Chen, 2002b).

According to Majzic and Tombácz (2007) the dispersion/aggregation of montmorillonite particles in aqueous suspensions at $\text{pH} \approx 6.5$ is a question of the presence and concentration of HA and Ca^{2+} . HA addition can disperse clay particles by adsorption on edges, but Ca^{2+} bridges between them forming aggregates. Insufficient Ca^{2+} to bind organic anions to the surface and then to bridge the organic-coated clay platelets can avoid strengthening in the clay network.

The results obtained in flocculation experiments (Tarchitzky et al., 1993) were confirmed by rheological studies (Tarchitzky and Chen, 2002a and b). In these studies, the rheological properties of montmorillonite suspensions in the presence of HS or PGA show a decrease in the differential viscosity at all the pH values tested. These results can be explained by the edge-charge reversal mechanism. An additional mechanism influences the differential viscosity of the suspensions. This mechanism is possibly associated with the formation of mixed micelles of HA (or FA or PGA) with clay platelets. Repulsion forces within these mixtures are higher than those existing between the clay platelets and therefore the suspension flow curves become Newtonian or dilatant. Similarly, Ramos-Tejada et al. (2001) concluded that adsorption of Ha on montmorillonite particle edges transforms suspensions from approximately solid-like when no HA is adsorbed, to almost liquid-like when the HA concentration is in the range of 50–100 mg/l.

ANTHROPOGENIC ORGANIC MATTER EFFECTS ON AGGREGATE STABILITY

Treated wastewater (TWW) is an important source of irrigation water in arid and semi-arid regions. Its use for irrigation is expanding in many areas in the world with different climatic and soil characteristics. Wastewater effluents generally contain high concentrations of dissolved solids, both organic and inorganic. The properties of the DOM present in the treated wastewater (solubility, high aromaticity and functional group content) and HS extracted from sewage sludge (recently-formed humic macromolecules with a high

concentration of aliphatic and carbohydrate moieties), are of major importance to clay-organic matter interactions, both in the wastewater itself and to soils irrigated with it (Tarchitzky et al., 1998). In a study on the effects of humic-like substances originating from treated wastewater, on clay dispersion and hydraulic conductivity of soils, maximum FV values were exhibited by Na-montmorillonite at the highest DOM concentration. Soil packed in columns and treated with wastewater effluent exhibited a sharp decrease in hydraulic conductivity (HC) to only 20% of its initial value. The reduction in HC is likely the result of decreased soil-pore size which reflects two processes: (i) retention of part of the DOM during water percolation; and (ii) a change in pore-size distribution due to swelling and dispersion of clay particles. The latter could result from a higher percentage of adsorbed Na⁺ combined with the presence of HS originating from the wastewater effluent. In addition, these researchers tested the interactions of homo-ionic DOM originating from wastewaters and sewage sludge (SS) with montmorillonite and a clay fraction of soils (dark brown clayey grumosol and sandy loam hamra). Both HA and FA were isolated from the SS and purified (SSHA and SSFA, respectively). The Na saturated DOM isolated from the wastewater caused dispersion of Na-montmorillonite and of the sandy loam clay fraction, but did not affect the clay fraction of the clayey grumosol. The SSHA saturated with Na⁺ did not affect the stability of Na-montmorillonite suspensions. In contrast, the Na-SSFA stabilized the Na-montmorillonite suspension and an increase in the FV was observed (a dispersive effect). The Ca²⁺ saturated DOM reduced the FV of Ca-montmorillonite and that of the clay fraction of the clayey soil. The soil HA however, had a very small dispersive effect on Ca-montmorillonite.

Several processes can cause the reduction in hydraulic conductivity—physical, biological or chemical. Among the physical mechanisms, Vandevivere and Baveye (1992) include the release of entrapped air bubbles, filtration activity of solid particles suspended in the percolating liquid, and a progressive disintegration of soil aggregates. Clogging of the soil surface layer following TWW irrigation has also been reported to result from the accumulation of suspended solids (de Vries, 1972; Rice, 1974; Metzger et al., 1983). According to Vinten et al. (1983), at least with respect to sandy and sandy loam soils, the coarse fraction of the effluent is responsible for most of the decrease in hydraulic conductivity. Balks et al. (1997) presented a microbial response and the formation of a semi-continuous film on the soil surface consisting of polysaccharide slime as the main factor reducing permeability in soils following the application of meat-processing effluent. The effect of TWW on decreasing soil hydraulic conductivity was connected to blockage

of soil pores by microbial growth and extracellular carbohydrate production. According to some investigators, only high carbon concentrations and C/N ratios in the wastewater are able to cause a change in hydraulic conductivity (Magesan et al., 1999, 2000).

Levy et al. (1999) concluded that in TWW with a high OM load, the OM fraction determines the hydraulic conductivity of the soils, whereas in low-OM-load TWW, it is the electrolyte concentration and composition in the water that appear to determine the hazard to the soil's hydraulic properties. In contrast, in a soil with low clay content and no carbonate, elevated SOM content from TWW irrigation did not prevent a reduction in aggregate stability which resulted in lower infiltration rates compared to a FW-irrigated plot (Lado et al., 2005). However, Agassi et al. (2003), in laboratory and field studies, did not find an increased influence of raindrop impact on aggregate disintegration, sealing processes, runoff or soil erosion in TWW-irrigated soils in comparison to FW-irrigated ones.

Farmers utilizing TWW in northern Israel reported a unique type of water distribution in drip-irrigated soils, consisting of: (i) limited wetted area on the soil surface, and (ii) small saturated areas around and below the dripper in TWW-irrigated soil, as opposed to the even, onion-like wet profile formed under FW irrigation. Following these observations in the field, it was hypothesized that TWW irrigation introduces water-repellent organic constituents into the soil (Chen et al., 2003; Tarchitzky et al., 2007). Tests characterizing the water distribution showed the diameter of the saturated area on the soil surface and its water content (at a depth of 0-10 cm) to be smaller with TWW than with FW irrigation. TWW accumulated on the soil surface in small lenses and then flowed rapidly into the ground. The repellency of soils irrigated with FW and TWW was measured using the water-drop penetration time test, among others. Soils irrigated with FW were wettable whereas those irrigated with TWW exhibited water repellency.

The condition of water-repellency (nonwettability, hydrophobicity) due to coating of sand grains by OM is a well-known phenomenon that has been observed most frequently in citrus groves, burned-over areas of forest soils, and turf (Stevenson, 1994). Often, repellency has been associated with coarse-textured sandy soil, but peat based soils and clay textured soils were also reported to exhibit water repellency (Ritsema and Dekker, 2003; Bachmann et al., 2006; Arye et al., 2006; Arye et al., 2007; Tarchitzky et al., 2007). Recently, water repellency was found in an orchard on a clayey soil, irrigated with TWW. Smaller wetted surface areas were recorded around the drippers in comparison with FW drippers. OM extraction from the different plots exhibited differences in quantity and

quality of organic substances between TWW- and FW-irrigated soils, with a higher quantity of hydrophobic substances in the TWW-irrigated soil extract (Nadav et al., 2011).

In a factorial experiment on the influence of water quality (OM content) and clay content (different Specific Surface Area - SSA), it was found that the highest degree of repellency was exhibited by sandy soil treated with the lowest quality TWW (highest OM content). The lowest degree of water repellency was consistently exhibited by the soil with the highest SSA with the highest quality TWW (lowest OM content). Water quality, rather than SSA was the dominant factor in determining the degree of repellency induced by TWW irrigation (Nadav et al., 2012).

The nonwettable conditions of sandy soils are most commonly attributed to the aliphatic components of SOM, mostly fats and waxes. Most commonly, the evidence provided is circumstantial. Chen and Schnitzer (1978) however, demonstrated a strong surfactant effect of both HAs and FAs. It has also been demonstrated by these investigations that this effect was both pH and concentration dependent, namely, decreased with pH increase and HS concentration decrease. FTIR and ¹³C-NMR analyses of organic components extracted from the soils using organic solvents indicated differences in composition only at a depth of 0-2 cm (Chen et al., 2003; Lerner, 2003; Lerner et al., 2003; Tarchitzky et al., 2007). It was also shown by Chen's group (Tarchitzky et al., 2007) that aliphatic components originating from the TWW are the reason for the induction of soil hydrophobicity in TWW-irrigated soils. Soil repellency could be eliminated by solvent extraction of aliphatic carbon compounds. These were identified by FTIR, and a prominent ¹³C-NMR peak at 32 ppm (a definitive peak of aliphatic carbon atoms).

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REFERENCES

- Agassi, M., J. Tarchitzky, R. Keren, Y. Chen, D. Goldstein, and E. Fizik. 2003. Effects of prolonged irrigation with treated municipal effluent on runoff rate. *J. Environ. Qual.* 32, 1053-1057.
- Amy, G.L., C.W. Bryant, and M. Belyani. 1987. Molecular weight distributions of soluble organic matter in various secondary and tertiary effluents. *Wat. Sci. Tech.* 19, 529-538.

- Angers, D.A. and Mehuys, G.R. 1989. Effect of cropping on carbohydrate content and water-stable aggregation of a clay soil. *Canadian Journal of Soil Science*, 69, 373-380.
- Arye, G., Bachmann, J., Woche, S.K. and Chen, Y. 2006. Applicability of interfacial theories of surface tension to water-repellent soils. *Soil Science Society of America Journal*, 70, 1417-1429.
- Arye, G., Nadav, I. and Chen, Y. 2007. Short-term reestablishment of soil water repellency after wetting: effect on capillary pressure-saturation relationship. *Soil Science Society of America Journal*, 71, 692-702.
- Bachmann, J., Arye, G., Deurer, M., Woche, S.K., Horton, R. Hartge, K.H. and Chen, Y. 2006. Universality of a surface tension---contact-angle relation for hydrophobic soils of different texture. *Journal of Plant Nutrition and Soil Science*, 169, 745-753.
- Balks, M.R., C.D.A. McLay, and C.G. Harfoot. 1997. Determination of the progression in soil microbiological response, changes in soil permeability, following application of meat processing effluent to soil. *Appl. Soil Ecol.* 6,109-116.
- Bloomfield, C. 1954. The deflocculation of kaolin by tree leaf leachates. In *Trans. 5th Int. Cong. Soil Sci. Leopoldville, Congo. 16-21 Aug. 1954. Societe Belge de Pedologie, Gent, Belgium* 2, 280-283.
- Bloomfield, C. 1956. The deflocculation of kaolinite by aqueous leaf extracts. The role of certain constituents of the extracts. In *6th Trans. Int. Cong. Soil Sci. Paris. 1956. Laboureur. Paris.*
- Bloomfield, C. 1957. The possible significance of polyphenols in soil formation. *J. Sci. Food Agric.* 8, 389-392.
- Chaney, K. and Swift, R.S. 1984. The influence of organic matter stability in some British soils. *Journal of Soil Science*, 35, 223-230.
- Chefetz, B., J. Tarchitzky, N. Benny, P. Hatcher, J. Bortiatynski, and Y. Chen. 1998. Characterization and properties of humic substances originating from an activated sludge wastewater treatment plant. p. 69-78. In: G. Davies and E. Gabbour (Eds.) *Humic Substances: Structure, Properties and Uses*. The Royal Society of Chemistry, Cambridge, UK.
- Chen, Y. and Schnitzer, M. 1978. The surface tension of aqueous solutions of soil humic substances. *Soil Science*, 125, 7-15.
- Chen, Y., Lerner, O. and Tarchitzky, J. 2003. Hydraulic conductivity and soil hydrophobicity: effect of irrigation with reclaimed wastewater. In: *9th Nordic IHSS Symposium on abundance and functions of natural organic matter species in soil and water* (ed. U. Kundstrom), p. 19. Mid-Sweden University, Sundsvall, Sweden.
- Chenu, C. 1993. Clay- or sand- polysaccharide associations as models for the interface between micro-organisms and soil: water related properties and microstructure. *Geoderma*, 56, 145-156.
- Degens, B.P. and Sparling, G. 1996. Changes in aggregation do not correspond with changes in labile organic C fractions in soil amended with C-14-glucose. *Soil Biology and Biochemistry*, 57, 1071-1076.

- Dell'Agnola, G. and Ferrari, G. 1971. Molecular sizes and functional groups of humic substances extracted by 0.1M pyrophosphate from soil aggregates of different stability. *Journal of Soil Science*, 22, 342-349.
- deVries, J. 1972. Soil filtration of wastewater effluent and the mechanism of soil clogging. *J. Water Pollut. Control Fed.* 44, 565-573.
- Dontsova, K.M. and Bingham, J.M. 2005. Anionic polysaccharide sorption by clay minerals. *Soil Science Society of America Journal*, 69, 1026-1035.
- Elliot, E.T. 1986. Aggregate structure and carbon, nitrogen and phosphorus in native and cultivated soils. *Soil Science Society of America Journal*, 50, 627-633.
- Edwards, A.P., and J.M. Bremner. 1967. Microaggregates in soils. *J. Soil Sci.* 18, 64-73.
- Feigin, A., I. Ravina, and J. Shalhevet. 1991. Irrigation with sewage effluent. *Advanced Series in Agricultural Sci. Vol. 17.* Springer-Verlag, Berlin.
- Foster, R.C. 1981. Localization of organic materials in situ in ultrathin sections of natural soil fabrics using cytochemical techniques. In: E.B.A. Bisdorf (Editor), *Int. Working Group on Submicroscopy*, Wageningen, The Netherlands, pp. 309-319.
- Franzluebbers, A.J., Steudemann, J.A. and Wilkinson, S.R. 2001. Bermudagrass management in the Southern Piedmont of the U.S.A: I. Soil and surface residue carbon and sulfur. *Soil Sci. Soc. Am. J.* 65:8334-8341.
- Frenkel, H., M. V. Fey, and G. J. Levy. 1992. Organic and inorganic anion effects on reference and soil clay critical flocculation concentration. *Soil Sci. Soc. Am. J.* 56, 1762-1766.
- Frey, E., and G. Lagaly. 1979. Selective coagulation in mixed colloidal suspensions. *J. Colloid Interface Sci.* 70, 46-55.
- Gibbs, R.J. 1983. Effect of natural organic coatings on the coagulation of particles. *Env. Sci. Technol.* 17, 237-240.
- Gillman, G.P. 1974. The influence of net charge on water dispersible clay and sorbed sulfate. *Aust. J. Soil Res.* 12, 173-176.
- Goldberg, S., and H. S. Foster. 1990. Flocculation of reference clays and arid-zone soil clays. *Soil Sci. Soc. Am. J.* 54, 714-718.
- Goldberg, S., B. S. Kapoor, and J. D. Rhoades. 1990. Effect of aluminum and iron oxides and organic matter on flocculation and dispersion of arid soils. *Soil Sci.* 150, 588-593.
- Greenland, D.J. 1965. Interaction between clays and organic compounds in soils. I. Mechanism of interaction between clays and defined organic compounds. *Soils and Fertilizers* 28, 415-425.
- Gu, B., and H. E. Doner. 1993. Dispersion and aggregation of soils as influenced by organic and inorganic polymers. *Soil Sci. Soc. Am. J.* 57, 709-716.
- Hamblin, A.P. 1977. Structural features of aggregates in some East Anglian silt soils. *Journal of Soil Science*, 28, 23-28.
- Hamblin, A.P. and Davies, D.B. 1977. Influence of organic matter on the physical properties of some East Anglian soils of high silt content. *Journal of Soil Science*, 28, 11-22.

- Haynes, R.J. and Francis, G.S. 1993. Changes in microbial biomass C, soil carbohydrate composition and aggregate stability induced by growth of selected crop and forage species under field conditions. *Journal of Soil Science*, 44, 665-675.
- Jekel, M. R. 1986. The stabilization of dispersed mineral particles by adsorption of humic substances. *Water Res.* 20, 1543-1554.
- Kretzschmar, R., W. P. Robarge, and S.T. Weed. 1993. Flocculation of kaolinitic soil clays: effects of humic substances and iron oxides. *Soil Sci. Soc. Am. J.* 57, 1277-1283.
- Kretzschmar, R., D. Hesterberg, and H. Sticher. 1997. Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. *Soil Sci. Soc. Am. J.* 61, 101-108.
- Kretzschmar, R., D. Hesterberg, and H. Sticher. 1998. Influence of pH and humic acid on coagulation kinetics of Kaolinite: a dynamic light scattering study. *J. Colloidal and Interface Science* 202, 95-103.
- Lado, M., M. Ben-Hur, and S. Assouline. 2005. Effects of effluent irrigation on seal formation, infiltration, and soil loss during rainfall. *Soil Sci. Soc. Am. J.* 69, 1432-1439.
- Lerner, O. 2003. Hydraulic conductivity and soil hydrophobicity: effect of irrigation with reclaimed wastewater. (M.Sc. thesis). Ben Gurion University (in Hebrew with English abstract).
- Lerner, O., Y. Chen, U. Shani, J. Tarchitzky, G. Arye, and A. Lowengart-Aycicegi. 2003. Changes in soil water distribution in soils irrigated with effluents. *Wat. Irrig.* 437, 22-28 (in Hebrew with English abstract).
- Levy, G.J., A. Rosenthal, J. Tarchitzky, I. Shainberg, and Y. Chen. 1999. Soil hydraulic conductivity changes caused by irrigation with reclaimed wastewater. *J. Environ. Qual.* 28, 1658-1664.
- Macks, S.P., Murphy, B.W., Cresswell, H.P. and Koen, T.B.. 1996. Soil friability in relation to management history and suitability for direct drilling. *Australian Journal of Soil Research*, 34, 343-360.
- Magesan, G.N., J.C. Williamson, G.P. Sparling, L.A. Schipper, and A.Rh.Llood-Jones. 1999. Hydraulic conductivity in soils irrigated with wastewaters of differing strengths: field and laboratory studies. *Aust. J. Soil Res.* 37, 391-402.
- Magesan, G.N., J.C. Williamson, G.W. Yeates, and A.Rh.Llood-Jones. 2000. Wastewater C:N ratio effects on soil hydraulic conductivity and potential mechanisms for recovery. *Biores. Technol.* 71, 21-27.
- Majzik, A. and E. Tombáč. 2007. Interaction between humic acid and montmorillonite in the presence of calcium ions II. Colloidal interactions: Charge state, dispersing and/or aggregation of particles in suspension. *Organic Geochemistry* 38, 1330-1340.
- Manka, J., and M. Rebhun. 1982. Organic groups and molecular weight distribution in tertiary effluents and renovated waters. *Wat. Res.* 16, 399-403.
- Mbagwu, J.S.C. and Piccolo, A. 1989. Changes in aggregate stability induced by amendment with humic substances. *Soil Technology*, 2, 49-57.
- McKeague, J.A. 1971. Organic matter in particle-size and specific gravity fractions of some Ah horizons. *Canadian Journal of Soil Science*, 51, 499-505.

- Metzger, L., B. Yaron, and U. Mingelgrin. 1983. Soil hydraulic conductivity as affected by physical and chemical properties of effluents. *Agronomie (Paris)* 3, 771-778.
- Muneer, M. and Oades, J.M. 1989. The Role of Ca-Organic Interactions in Soil Aggregate Stability. III. Mechanisms and Models. *Australian Journal of Soil Research*, 27, 411-423.
- Nadav, I., A. Lowengart-Aycicegi, J. Tarchitzky, and Y. Chen. 2011. Soil surface water repellency induced by wastewater irrigation: physic-chemical characterization and quantification. *Irrigation Sci.* Published online: 12 June 2011.
- Nadav, I., J. Tarchitzky, and Y. Chen. 2011. Induction of soil water repellency following irrigation with treated wastewater: effects of irrigation water quality and soil texture. *Irrigation Sci.* Published online: 16 December 2011.
- Namour, Ph., and M.C. Müller. 1998. Fractionation of organic matter from wastewater treatment plants before and after a 21-day biodegradability test: a physical-chemical method for measurement of the refractory part of effluents. *Wat.Res.* 32, 2224-2231.
- Narkis, N., M. Rebhun, N. Lahav, and A. Banin. 1970. An optical-transmission study of the interaction between montmorillonite and humic acids. *Isr. J. Chem.* 8, 383-389.
- Piccolo, A. and Mbagwu, J.S.C. 1990. Effects of different organic waste amendments on soil microaggregates stability and molecule sizes of humic substances. *Plant and Soil*, 123, 27-37.
- Piccolo, A., Pietramellara, G. and Mbagwu, J.S.C. 1997. Use of humic substances as soil conditioners to increase aggregate stability. *Geoderma*, 75, 265-277.
- Puget, P., Angers, D.A. and Chenu, C. 1999. Nature of carbohydrates associated with water-stable aggregates of two cultivated soils. *Soil Biology and Biochemistry*, 31, 55-63.
- Ramos-Tejada, M.M., J. de Vicente, A. Ontiveros, and J.D.G. Durán. 2001. Effect of humic acid adsorption on the rheological properties of sodium montmorillonite suspensions. *Journal of Rheology* 45, 1159-1172.
- Rebhun, M., and J. Manka. 1971. Classification of organics in secondary effluents. *Environ. Sci. Tech.* 5, 606-609.
- Rice, R.C. 1974. Soil clogging during infiltration of secondary effluent. *J. Wat. Pollut. Control Fed.* 46, 708-716.
- Ritsema C.J. and Dekker, L.W. 2003. Soil water repellency: occurrence, consequences and amelioration. *Elisiever, London*, 352pp.
- Russell, E.W. 1933. The binding forces between clay particles in a soil crumb. *Trans. 3rd Int. Cong. Soil Sci.* 1, 26-29 (seen in Warkentin, 2008).
- Shanmunagathan, R.T., and J.M. Oades. 1983. Influence on anions on dispersion and physical properties of the A horizon of a Red-brown earth. *Geoderma* 29, 257-277.
- Stevenson, F.J. 1994. *Humus Chemistry. Genesis, composition and reactions.* Wiley, New York, 496 pp.
- Swift, R.S. 1991. Organic matter characterization. P. 1011-1069. In D.L. Sparks et al. (ed.). *Methods of Soil Analysis. Part 3. Chemical Methods – SSSA Book Series no. 5.*

- Tarchitzky, J., Chen, Y. and Banin, A. 1993. Humic substances and pH effects on sodium- and calcium-montmorillonite flocculation and dispersion. *Soil Science Society of America Journal*, 57, 367-372.
- Tarchitzky, J., Golobati, Y., Keren, R. and Chen, Y. 1998. Reclaimed wastewater effects on flocculation value of clay suspensions and hydraulic properties of a sandy soil. *Soil Science Society of America Journal*, 63, 554-560.
- Tarchitzky, J., and Y. Chen. 2002a. Rheology of montmorillonite suspensions in the presence of humic substances. *Soil Science Society of America Journal*, 66, 406-412.
- Tarchitzky, J. and Chen, Y. 2002b. Polysaccharides and pH effects on sodium-montmorillonite: flocculation, dispersion and rheological properties. *Soil Science*, 167, 791-801.
- Tarchitzky, J., Lerner, O, Shani, U., Arye, G., Lowengart-Aycicegi, A, Brenner, A. and Chen, Y. 2007. Water distribution pattern in treated wastewater irrigated soils: hydrophobicity effect. *European Journal of Soil Science* 58, 573-588.
- Tate, K.R. and Churchman, G.J. 1978. Organo-mineral fractions of a climosequence of soils in New Zealand Tussock grasslands. *Journal of Soil Science*, 29, 331-339.
- Tiessen, H. and Stewart, J.W.B. 1983. Particle size fractions and their use in studies of soil organic matter: II. Cultivation effects on organic matter composition in size fractions. *Soil Science Society of America Journal*, 47, 509-513.
- Tisdall, J.M. and Oades, J.M. 1982. Organic matter and water-stable aggregates in soils. *Soil Science Society of America Journal*, 33, 141-163.
- Tisdall, J.M. 1994. Possible role of soil microorganisms in aggregation in soils. *Plant and Soil*, 159, 115-121.
- Tombácz, E., M. Gilde, and F. Szanto. 1984. The effects of Na-salicylate and Na-fulvate on the stability and rheological properties of Na-montmorillonite suspensions. *Acta Phys. Chem.* 30, 165-174.
- Turchenek, L.W. and Oades, J.M. 1979. Fractionation of organo-mineral complexes by sedimentation and density techniques. *Geoderma*, 21, 311-343.
- Van Olphen, H. 1977. *An Introduction to Clay Colloid Chemistry*, 2nd ed. Interscience, New York.
- Vandevivere, P., and P. Baveye. 1992. Saturated hydraulic conductivity reduction caused by aerobic bacteria in sand columns. *Soil Sci. Soc. Am. J.* 56, 1-13.
- Vinten, A.J.A., U. Milgenrin, and B. Yaron. 1983. The effect of suspended solids in wastewater and soil hydraulic conductivity: II. Vertical distribution of suspended solids. *Soil Sci. Soc. Am. J.* 47, 408-412.
- Visser, S. A., and M. Caillier. 1988. Observations on the dispersion and aggregation of clays by humic substances. I. Dispersive effects of humic acids. *Geoderma* 42, 331-337.
- Warkentin, B.P. 2008. Soil Structure: A History from tith to habitat. *Advances in Agronomy* 97, 239-272.
- Watson, J.R. and Parsons, J.W. 1974. Studies of soil organo-mineral fractions: I. Isolation by ultrasonic dispersion. *Journal of Soil Science*, 25, 1-8.

- Yamaguchi, T., Takei, T., Yazawa, Y., Wong, M.T.F., Gilkes, R.J. and Swift, R.S.
2004. Effect of humic acid, sodium, and calcium additions on the formation of water-stable aggregates in Western Australian wheatbelt soils. *Australian Journal of Soil Research*, 42, 435-439.
- Zhang, Y., H. Gan, and P. F. Low. 1991. Effect of sodium-humate on the rheological characteristics of montmorillonite suspensions. *Soil Sci. Soc. Am. J.* 55, 989-993.

Catching the Functionality of Refractory Organic Matter (ROM)

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INTRODUCTION

Humic water presents itself in manifold forms in nature (1-6). As left over of the living world, humic matter is at the same time the store for new life. This includes a major impact on the energy balance for man and nature and on the global climate change (7,8). Moderate to poor reactivity dominate the physical, chemical and biological properties of humic matter which can be found mainly in soil and aquatic systems of the environment. However, the application of powerful analytical methods has shown that some of the reactions and transformations especially in aqueous phase are quite fast. At a first glance this looks like a contradiction to the all overall refractory character of humic substances. In detail, their fairly complex chemical structure reveals specific features which have turned out to be essential for the integrative functionality of the earth.

This chapter aims to catch examples of functionality of dissolved refractory organic matter (DROM) suited for the assessment of structure-effect relations. The focus will be on elemental composition, acidic groups, delocalised electrons and various interactions with common water constituents and solid phases. Of special interest are the interdependences of the analytical parameters concerned and the resulting functional consequences with all their power and limitations.

ELEMENTAL COMPOSITION

Determination of elements and quantification of their amounts belong to the most powerful and precise results for identification of substances and their purity. In case of environmental samples like DROM, the results are highly dependent on the operation of sampling and isolation. The need of representative samples is crucial and hard to fulfil. Well defined procedures of sample isolation like the IHSS methods for gaining fulvic acids (FA) and humic acids (HA) might help to get fairly reproducible results (9). Their interpretation with respect to the relevance for gross environmental systems however remains questionable. A possible way out of this problem can start at a total material balance and may proceed to the characterisation of the “rest”.

Table 1 shows the elemental composition of typical FA samples of different origin. Besides the general uniformity in the decreasing amount from C to S, there is obviously a reflection of the availability of oxygen in the environment the samples are from.

Table 1. Elemental composition (%-weight) of isolated fulvic acids from different aqueous samples (10,11).

Sample	C	O	H	N	S	ash, Me
Soil FA (11)	41 – 51	40 – 50	3.8 – 7.0	0.9.-3.3	0.1 – 3.6	-
Aqueous FA n = 33	36 – 54	23 – 40	3 – 5	0.8 – 3.8	0.1 – 1.7	-
Ground water (FG1 FA)	56	31.9	4.9	1.4	1.6	4.6
Soil water (BS1 FA)	53	41.8	3.6	0.7	0.3	0.3
Waste water (ABV2 FA)	51	33.2	5.0	2.9	2.8	5.2
Brown water (HO10 FA)	53	41.5	3.7	0.7	0.7	0.7
IHSS (FA)	<55	<52	<5	<2.9	<2.8	-

This is underlined by the van Krevelen diagram which shows the H/C vs O/C values of the samples (Fig. 1). FA samples isolated from groundwater and secondary effluent have relatively low oxygen content.

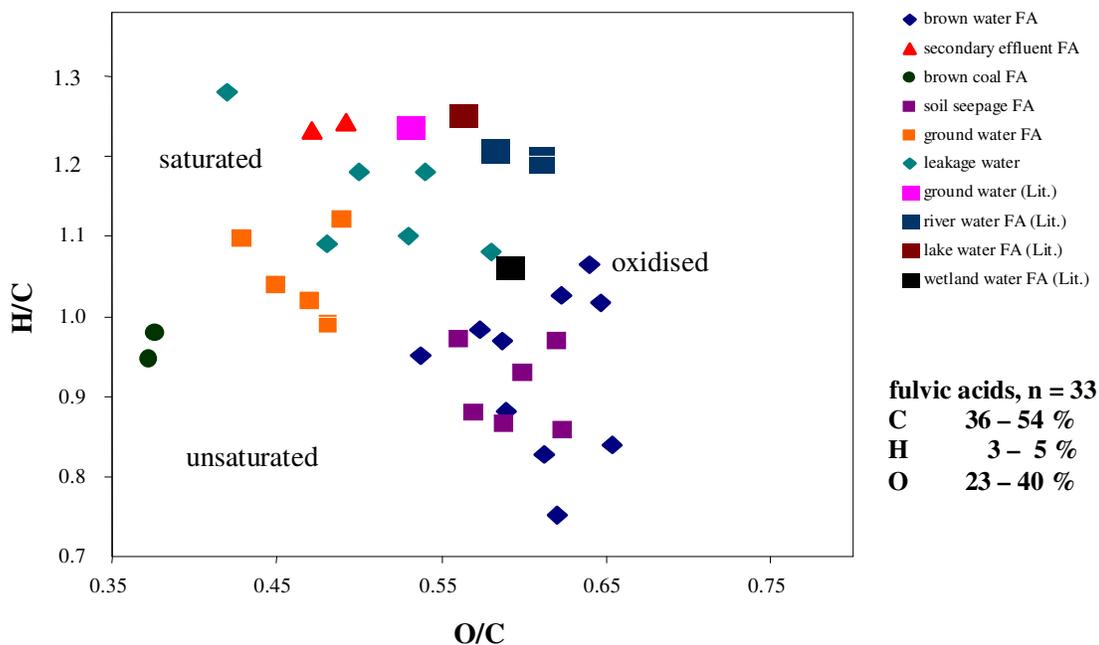


Figure 1. van Krevelen diagram for isolated fulvic acids from different origin (10).

STRUCTURAL ASSIGNMENT

Many different approaches have been used to characterize HS. However, the heterogeneous and high molecular structure of HS in its manifold appearances makes it impossible to identify the chemical structure in the classical sense. Numerous reviews and detailed studies have been published on methods and approaches applied to the structural characterization of HS (1,2,12). Although the elemental composition of HS is known, information about structures and functionality is still insufficient due to the complexity of these substances. The complexity can be partly resolved by quantifying some typical structure units and their physico-chemical properties. ^{13}C solid phase NMR is a powerful tool for that. Fig. 2 shows spectra of the FA and HA fractions of the organic matter isolated from a brown water lake (Lake Hohloh, Black Forrest, Germany). Besides aromatic and aliphatic regions, the occurrence of carboxylic and O-alkylic functional groups is obvious. There are significant differences in the relative abundances of these structural features for the two samples (14).

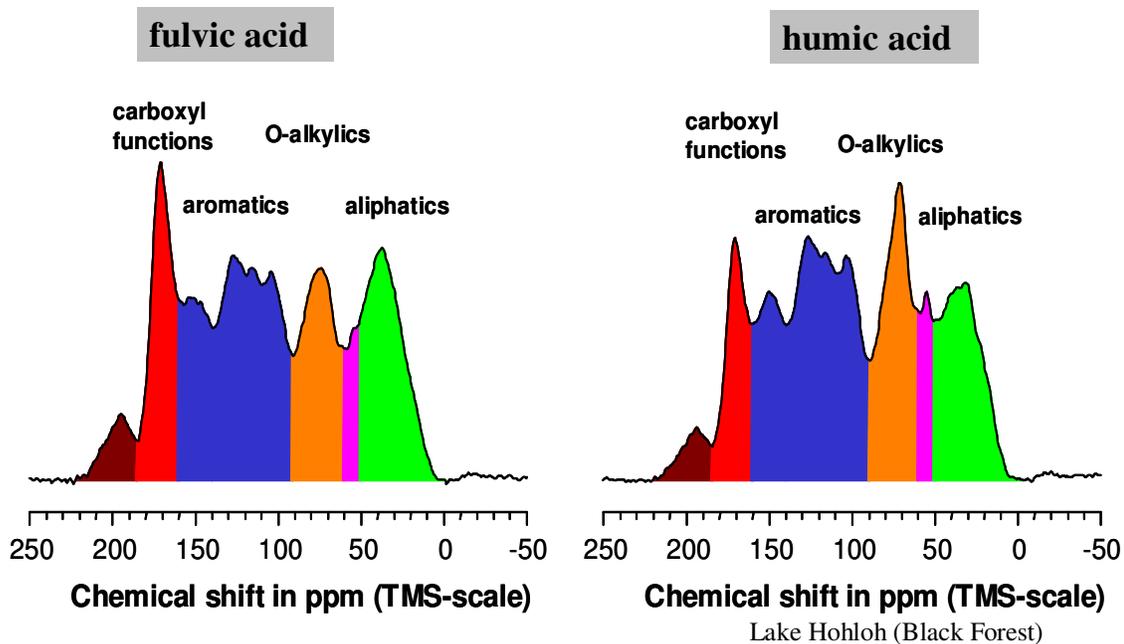


Figure 2. ^{13}C -CP-NMR spectra for isolates from a bog lake water sample (13).

ADSORBABILITY

The distribution of water constituents in heterogeneous systems strongly depends on adsorption phenomena. They occur in the aquatic environment as well as in technical systems e. g. for water treatment. The thermodynamic equilibrium of the adsorption is determined by the kind of adsorbent, its pore structure and specific surface at the one side and the hydrophobic/hydrophilic character of the sorbates and their molecular size at the other side. A typical example for the adsorption of dissolved organic matter (DOM) from a brown water on powdered activated carbon (PAC) as revealed by size exclusion chromatography (SEC) with UV and organic carbon (OC) detection (15) is shown in Fig.

3.

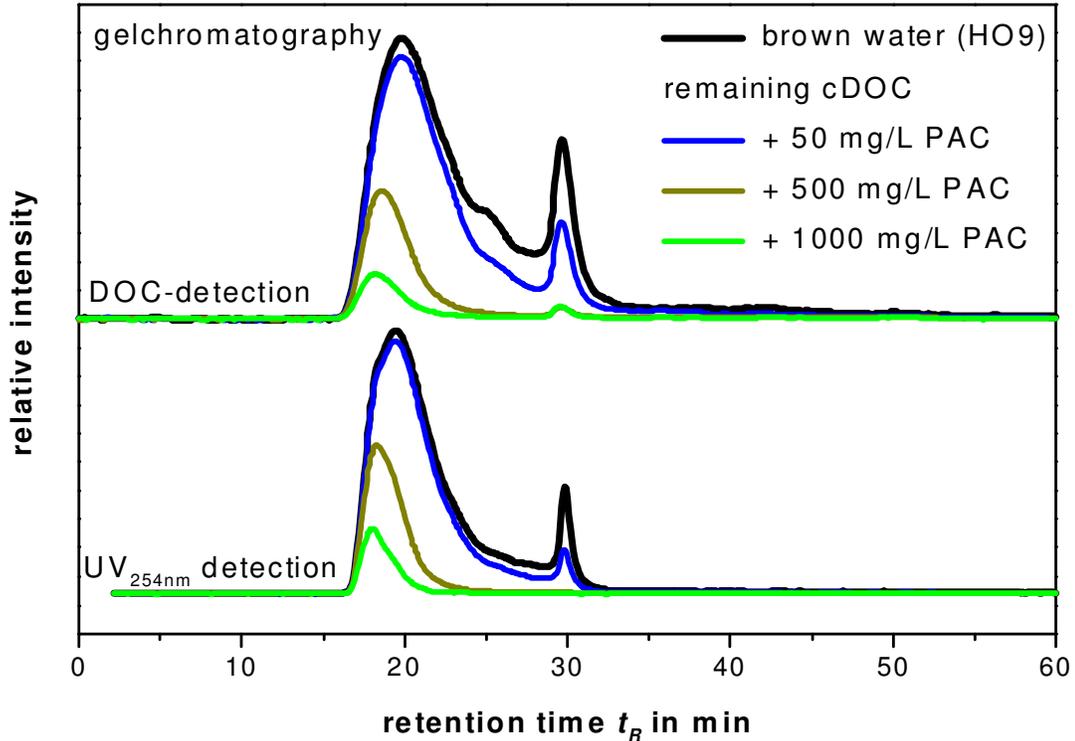


Figure 3. OC and UV traces of SEC for brown water organic matter which remains unadsorbed in solution of different powered activated carbon (PAC) suspensions; experimental conditions: 60 h reaction time, $\text{CaCl}_2/\text{NaHCO}_3$ 10^{-3} M buffer at pH 7, 20°C (16).

It can be seen that the removal of organic matter (OM) from solution increases with increasing addition of powered activated carbon (PAC). It is obvious that the chromatograms obtained by OC detection are quite similar to the ones with UV detection. Since in SEC the molecular size of the DOM correlates well with the retention times of the fractions (15) it can be deduced from Fig. 3 that the high molecular OM was less preferable removed by adsorption than the lower molecular size molecules. The limited availability of PAC pore sizes large enough for the adsorption of macromolecules can explain these results. The adsorptivity of ROM on activated carbon (AC) can be best described by FREUNDLICH adsorption isotherms (17) (eq. 1).

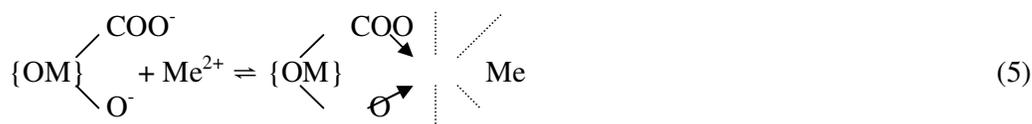
$$q = K_F \cdot \rho^n \quad (1)$$

with q load of AC in (mg/g); K_F Freundlich coefficient; ρ DOC (DROM) concentration (in mg/L) and n Freundlich exponent.

In addition to the adsorptivity also mobility and reactivity of ROM can be expected to be dependent on its molecular size. This is important for the transport of DROM in porous media and through membranes and for the ROM degradation, transformation and dissolution.

ACIDIC FUNCTIONAL GROUPS

Carboxylic and some hydroxyl groups of ROM as revealed by NMR spectroscopy and/or by acid/base titration (10) can lead to pH dependent metal complexation and even chelation (19,20,21). Thermodynamic equilibria are given in equation 2 to 5.



The acidity of DROM and the stability of the coordination compounds formed with metal ions are given in the pK_a values and the stability constant K_{stab} values respectively (eqs. 6 and 7).

$$pK_a = pH - \log \frac{c(\{OM\} - O^-)}{c(\{OM\} - OH)} \quad (6)$$

$$K_{stab} = \frac{a(\{OM\}Me)}{a(\{OM\}^{2-})a(Me^{2+})} \quad (7)$$

The stabilities for DROM complexes of common Me^{2+} decrease from Cu^{2+} to Ca^{2+} (22,23) (eq. 8).

$$K_{stab} : Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Ca^{2+} \quad (8)$$

This sequence can change in case of functional groups with other e⁻-donor atoms like {OM} S⁻ or {OM} N:→ as they occur in ROM from anoxic systems or from waste water treatment effluents. These coordinative interactions lead to significant influences on the gross effects based on e. g. adsorbability, solubility, mobility and coagulation. Typical proton capacities (H⁺/DROM) and metal to DROM ratios of up to 17 and 4 μmol/mg respectively have been observed (10).

COLOUR, UV-ABSORBANCE AND LUMINESCENCE

Unsaturated, aromatic and lone pair electron systems lead to the typical DROM colour, luminescence and UV-spectra. The yellowish brown colour for DROM led to the assignment as “Gelbstoff” in the literature (24). Quantification uses platinum numbers and/or spectral absorbance (SAK) at λ = 436 nm (Fig. 4).

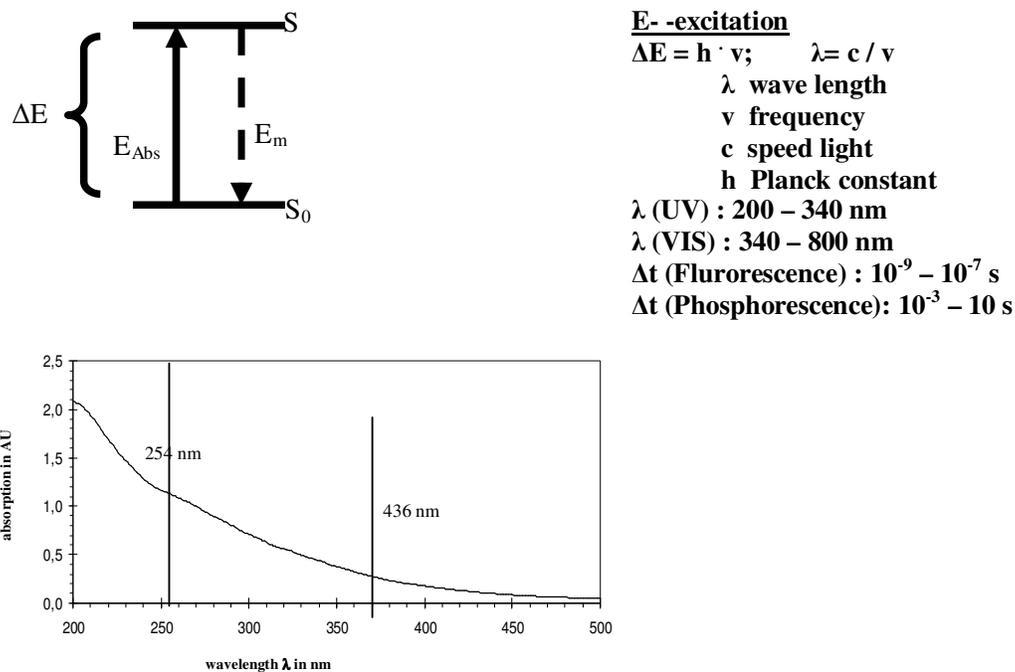


Figure 4. Principle of e⁻-excitation and UV-vis spectrum of DROM

The specific UV-absorbance (SUVA) which relates the spectral absorption (A) at λ = 254 nm to the mass concentration (mg/L) of DROM has become a widely used parameter for characterisation. Typical A(254) / A(436) ratios range from 12 to 20, and SUVA values (A(254)/DOC) reach up to 4.5 L/(mg·m) (10).

Recently 2D-fluorescence spectra have been used to characterise DROM and to distinguish the humic matter from other biogenic fluorophores, e. g. in algae bacteria and pollutants (Fig. 5) (25).

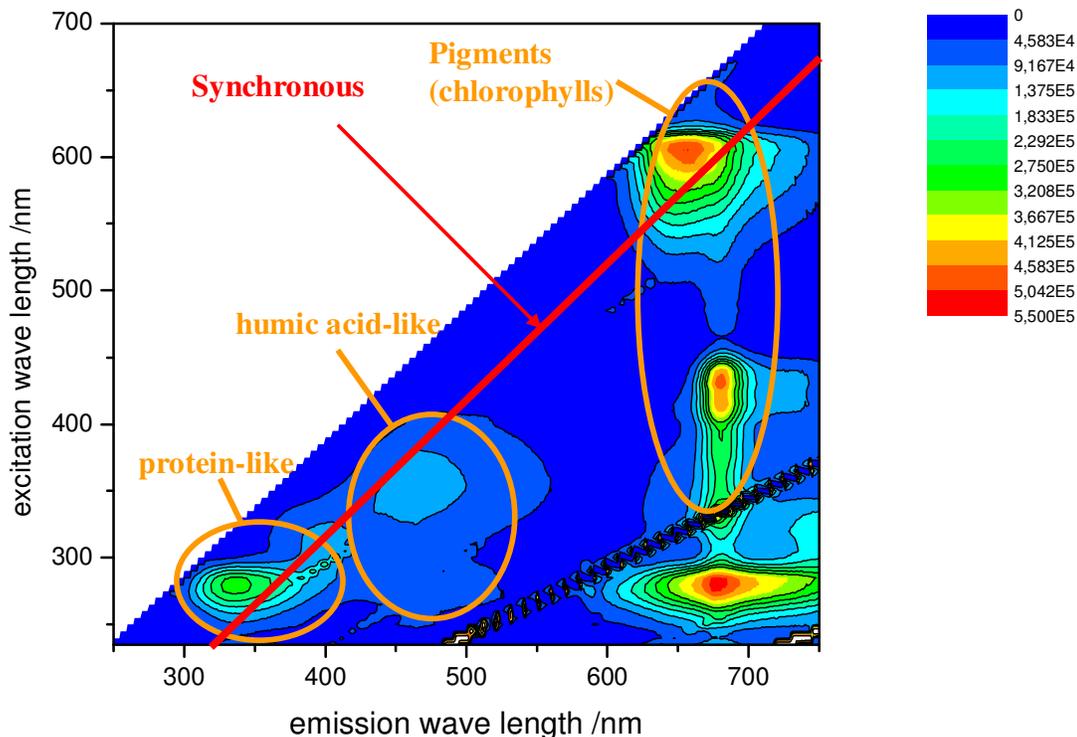


Figure 5. Excitation-emission matrix of a lab cell culture of *Microcystis aeruginosa* after $t = 38$ day of growth (25) and assignment of the fluorescent spots.

Time resolved luminescence and investigations on luminescence quenching have been used to obtain insight into molecular interactions of DROM with itself and/or other water constituents, e. g. paramagnetic metal ions (26,27).

OXIDATIVE TRANSFORMATION AND DEGRADATION

Oxidation reactions of DROM often lead to changes in the electron system with the effect of bleaching, to a decrease of molecular size with the consequence of increased biodegradability and finally to CO_2 formation. In the environment, abiotic oxidation reactions can be closely connected to photolysis or catalytic processes which involve OH-radicals. One of the well-known mechanisms of ozone oxidation is the ozonolysis of double bonds according to Criegee (Fig. 6).

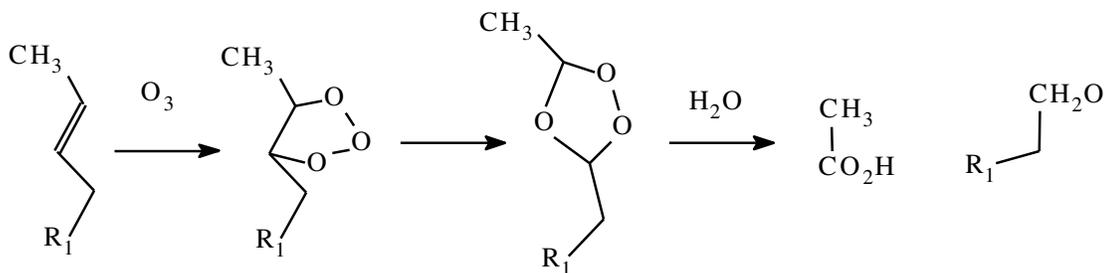


Figure 6. Ozone reaction with organic double bonds according to the Criegee mechanism.

The initial olefinic compounds get degraded via ozonids to smaller fragments of higher oxidation state. These products are normally better biodegradable. This can be demonstrated by growth curves of microorganisms (28) exposed to the organic matter under defined starting conditions. The growth curves result from turbidity measurement over time. The turbidity (12 ° forward scattering) is caused by microorganisms and is directly correlated with their number. The growth rate of the population increases with the availability of assimilable matter; the better assimilable the substances, the steeper the growth curve. Often there is a lag time during which the microorganisms adapt to the matrix of the specific starting conditions and/or an excess of added oxidants.

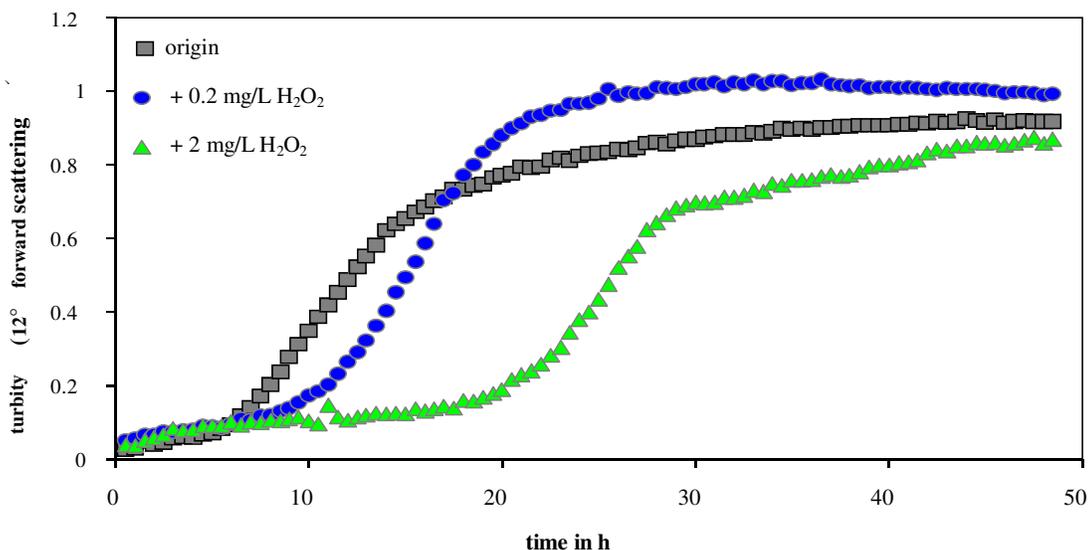


Figure 7. Growth curves for Lake Constance water without and after addition of different H₂O₂ –concentrations (0.2 mg/L; 2 mg/L) (28).

Fig. 7 shows the growth curves of ROM in original Lake Constance water and after addition of two different amounts of H₂O₂ as oxidant. In case of the first addition of H₂O₂

resulting in an initial concentration of 0.2 mg/L, there is a slightly larger lag time, a higher yield and a steeper growth curve. The curve for the sample with the highest initial H_2O_2 concentration (2 mg/L) clearly shows the longest lag time and modest gradual increase of the turbidity at the end (> 30 min) of the growth curve.

As an example of the application of advanced oxidation (AOP) of ROM, TiO_2 was used as photocatalyst. The remaining dissolved organic matter after ROM adsorption onto TiO_2 and degradation at increasing irradiation time is shown in Fig. 8. The size exclusion chromatograms show a gradual decrease of high molecular matter and an increase of low molecular size substances which finally get mineralised. For ease of comparison the chromatograms are given for the beginning (grey) and the end (black) of each irradiation period of 60 min.

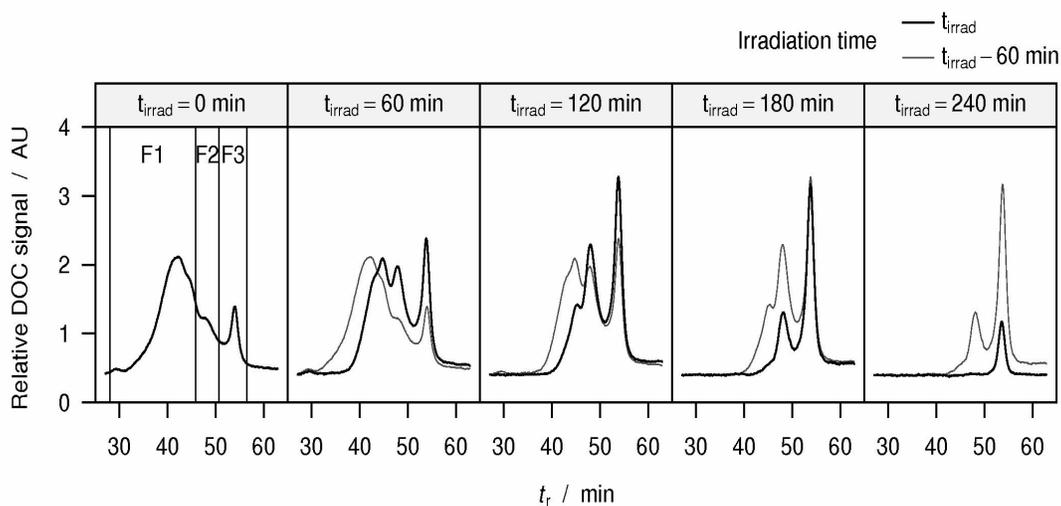


Figure 8. Photocatalytic degradation of brown water ROM in TiO_2 suspension, $m(\text{TiO}_2) = 0.5 \text{ g/L}$ (29).

In the low molecular size fractions, several small organic acids were identified with liquid chromatography / mass spectrometry (GC/MS) (30). Fig. 9 shows the different acids and their photocatalytic formation with increased irradiation time. It is interesting to note that the relative amounts formed over the irradiation time are highest for the smallest acids (1C acid > 2C acid > 3C acid). This suggests that photocatalytic degradation of ROM followed by biodegradation might be significant in the turn over of aquatic organic matter. Similar results were obtained for the plain photolysis of ROM (30,31) which underlines the importance of the photic zone of aquatic systems for the dynamics of the global C-cycle. It also opens the door for applications in water treatment processes (16).

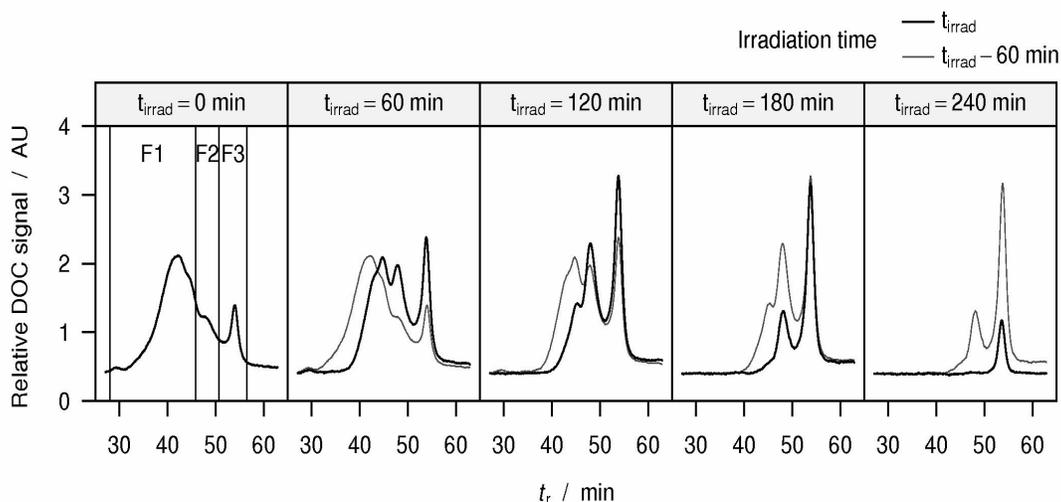


Figure 9. Small organic acids formed in photo(cata)lytic degradation of ROM (31,32,33).

In public water supply, ubiquitous ROM has gained attention due to its readiness to react with chlorine, the most common chemical disinfectant world wide. A whole suite of halogenated disinfection by-products (DBP) has been identified (34,35). Amongst them are highly mutagenic compounds like MX (3-chloro-4-(dichloromethyl)-5hydroxy-2(5H)-furanone). Chloroform and halogenated acetic acids have found their way into international drinking water legislation (36-38).

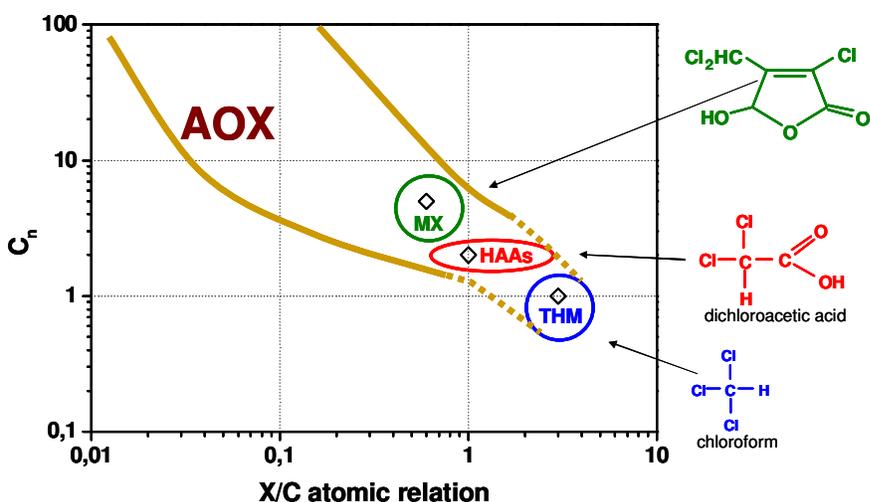


Figure 10. Formation of disinfection by-products (DBP) from chlorination of ROM (39).

In case of elevated concentrations of other halides like bromide and iodide in the water matrix interhalogen exchange in the DBP has to be expected. The good deal of still

unidentified DBP are integrated in the parameter AOX (16) which quantifies the organically bound halogens after adsorption on activated carbon (Fig. 10). There are further research needs on molecular products identification as well as for investigations for reaction mechanisms and technical problem solutions.

INTERACTION WITH NANOPARTICLES

The molecular structure of ROM leads to colloid formation and coagulation dependent on pH-value and matrix of the water including geogenic particles (40,41). In addition, due to the broad application of engineered nano particles (ENP), a good part of it will find its way into the aquatic environment. There, ROM will interact with ENP resulting in a concentration dependent partial or total coating and as a consequence in a change of the original properties of the ENP. Fig. 11 shows the toxicity of several nanoparticles on microorganisms (*E. coli*). It is obvious that the concentration dependent toxic effect in case of SiO_2 is deleted in the presence of ROM (HS). This leads to the hypothesis that ENP can be camouflaged by ROM so that the inner core loses its original properties e. g. toxicity. As a consequence it can be expected that ROM cause a uniformity of the ENP's outer shell responsible for many properties in the environment.

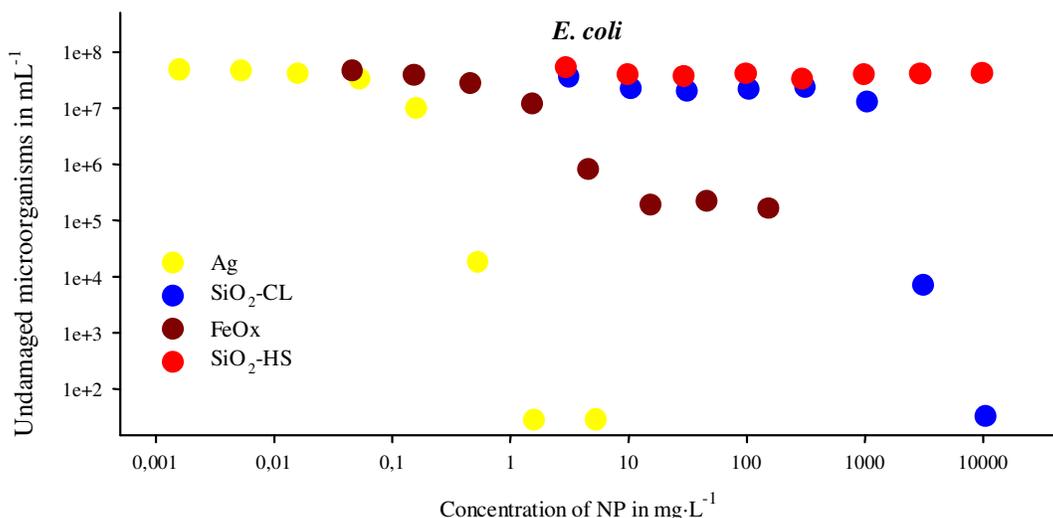


Figure 11. Concentration dependent toxicity of NP in the absence and presence (SiO_2 – HS) of ROM (42).

CONCLUSIONS

ROM have many faces and many functionalities (Fig. 12). They can partly be derived from molecular structure. However, due to the given complexity there is a need for new experimental approaches to understand the unrevealed structure – effect relations. Touching to boarders between living and non-living matter, the genesis and fate of ROM enter a new dimension of relations reaching to the basics of life. The discrepancy in ROM as a low value matter on the one hand and as a really essential good on the other seems to be broadly accepted, even without reflection.

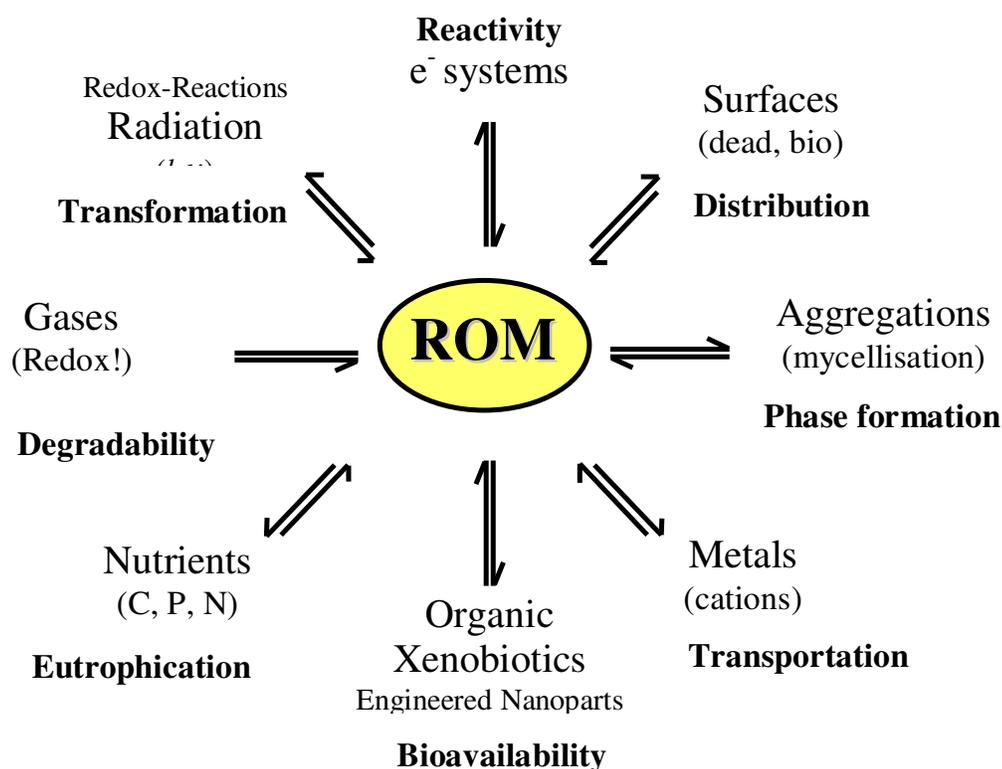


Figure 12. Interactions and functions of ROM in the environment.

Acknowledgement

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REFERENCES

- Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (eds.): Humic Substances in Soil, Sediment and Water. Wiley-Interscience, New York (1985).
- Hayes, M. H. B., MacCarthy, P., Malcolm, R. L., Swift, R. S. (eds.): Humic Substances II: In Search of Structure. John Wiley & Sons, New York (1989).
- Stevenson, F. J. : Humus Chemistry. John Wiley & Sons, New York (1982).
- Schnitzer, M., Khan, S. U. (eds.): Soil Organic Matter. Elsevier, Amsterdam (1978).
- Thurman, E. M.: Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr. W. Junk Publishers, Lancaster (1985).
- Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spiteller, M. (eds.): Refractory Organic Substances (ROS) in the Environment. Wiley-VCH, Weinheim (2002).
- Findlay, S. E. G., Sinsabaugh, R. L. (eds.): Aquatic Ecosystems – Interactivity of Dissolved Organic Matter. Academic Press, Amsterdam (2003).
- Adrews, M. E., Brimblecombe, P., Jickells, T. D., Liss, P. S.: An Introduction to Environmental Chemistry. Blackwell Science, London (1996).
- IHSS (2011): <http://www.humicsubstances.org/>
- Abbt-Braun, G., Frimmel, F. H.: The relevance of reference materials – Isolation and general characterisation. In: Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spiteller, M. (eds.): Refractory Organic Substances (ROS) in the Environment. Wiley-VCH, Weinheim, pp. 1-37 (2002).
- Steelink, C.: Implications of elemental characteristics of humic substances. In: Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (eds.): Humic Substances in Soil, Sediment, and Water. John Wiley & Sons, New York, pp. 457-476 (1985).
- Senesi, N., Xing, B., Huang, P. M. (eds.): Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems. Wiley, Hoboken, NJ (2009).
- Lankes, U., Lüdemann, H.-D., Frimmel, F. H.: Search for basic relationships between „molecular size” and “chemical structure” of aquatic natural organic matter – answers from ^{13}C and ^{15}N CPMAS NMR spectroscopy. *Wat. Res.* 42: 1051-1060 (2008).
- Lankes, U., Lüdemann, H.-D.: Structural Characterization of Refractory Organic Substances by Solid-state High-resolution ^{13}C and ^{15}N Nuclear Magnetic Resonance. In: Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spiteller, M. (eds.): Refractory Organic Substances (ROS) in the Environment. Wiley-VCH, Weinheim, pp. 96-114 (2002).
- Huber, S. A., Frimmel, F. H.: Direct gel chromatographic characterisation and quantification of marine dissolved organic carbon using high-sensitivity DOC detection. *Environ. Sci. Technol.* 28: 1194-1197 (1994).
- Frimmel, F. H., Abbt-Braun, G.: Sum parameters: potential and limitations. In: Wilderer, P. (eds.): *Treatise on Water Science*, Vol. 1. Academic Press, Oxford, pp. 3-29 (2011).

- Müller, M. B., Schmitt, D., Frimmel, F. H.: Fractionation of natural organic matter by size exclusion chromatography – Properties and stability of fractions. *Environ. Sci. Technol.* 34: 4867-4872 (2000).
- Sontheimer, H., Crittenden, J. C., Summers, R.: *Activated Carbon for Water Treatment*. 2nd Edition in English of Adsorptionsverfahren zur Wasserreinigung. DVGW-Forschungsstelle, Karlsruhe (1988).
- De Wit, J. C. M., Can Riemsdijk, W. H., Koopal, L. K.: Proton binding to humic substances. 1. Electrostatic effects. *Environmental Science and Technology* 27: 2005-2022 (1993).
- Saar, R. A., Weber, J. H.: Fulvic acid: modifier of metal-ion chemistry. *Environ. Sci. Technol.* 16: 510A-517A (1982).
- Tipping, E.: *Cation Binding by Humic Substances*. Cambridge University Press, New York (2002).
- Frimmel, F. H., Geywitz, J.: Zur koordinative Bindung von Metallionen an Gewässerhuminstoffe. *Fresenius Z. Anal. Chem.* 316: 582-588 (1983).
- Stumm, W.: *Chemistry of the Solid-Water Interface*. John Wiley & Sons, New York (1992).
- Kalle, K.: The problem of Gelbstoff in the sea. *Oceanogr. Mar. Biol. Annu. Rev.* 4: 91-104 (1938).
- Ziegmann, M., Abert, M., Müller, M., Frimmel, F. H.: Use of fluorescence fingerprints for the estimation of bloom formation and toxin production of *Microcystis aeruginosa*. *Wat. Res.* 44: 195-204 (2010).
- Kumke, M. J., Abbt-Braun, G., Frimmel, F. H.: Time-resolved fluorescence measurements of aquatic natural organic matter (NOM). *Acta hydrochim. hydrobiol.* 26: 73-81 (1998).
- Kumke, M. J., Frimmel, F. H.: Stationary and time-resolved fluorescence for refractory organic substances characterization. In: Frimmel, F. H., Abbt-Braun, G., Heumann, K. G., Hock, B., Lüdemann, H.-D., Spiteller, M. (eds.): *Refractory Organic Substances (ROS) in the Environment*. Wiley-VCH, Weinheim, pp. 215-231 (2002).
- Hamsch, B., Werner, P., Frimmel, F. H.: Bacterial growth measurements in treated waters from different origin. *Acta hydrochim. hydrobiol.* 20: 9-14 (1992).
- Tercero Espinosa, L. A., ter Haseborg, E., Weber, H., Frimmel, F. H.: Investigation of the photocatalytic degradation of brown water natural organic matter by size exclusion chromatography. *Applied Catalysis B: Environmental* 87: 56-62 (2009).
- Tercero Espinoza, L. A., Frimmel, F. H.: Formation of brominated products in irradiated titanium dioxide suspension containing bromite and dissolved organic carbon. *Wat. Res.* 42: 1778-1784 (2008).
- Brinkmann, T., Hörsch, P., Sartorius, D., Frimmel, F. H.: Photoformation of low-molecular-weight organic acids from brown water dissolved organic matter. *Environ. Sci. Technol.* 37(18): 4190-4198 (2003).
- Doll, T. E., Frimmel, F. H.: Photocatalytic degradation of carbamazepine, clofibric acid and iomeprol with P25 and Hombikat UV100 in presence of natural organic matter (NOM) and of other organic water constituents. *Water Res.* 39: 403-411 (2005).

- Tercero Espinosa, L. A., Rembor, M., Arribas Matesanz, C., Heidt, A., Frimmel, F. H.: Formation of bromoform in irradiated titanium dioxide suspensions with varying photocatalyst, dissolved organic carbon and bromid concentrations. *Wat. Res.* 43: 4143-4148 (2009).
- Richardson, S. D., Simmons, J. E., Rice, G.: DBPs: The next generation. *Environ. Sci. Technol.* 36: 198A-205A (2002).
- Frimmel, F. H., Schmiedel, U.: Pyrolysis GC/MS identification of halogenated furandiones and other products from chlorinated humic solutions. *Fresenius J. Anal. Chem.* 346: 707-710 (1993).
- Guidelines for Drinking Water Quality. Volume 2: Health Criteria and Other Supporting information, World Health Organisation, Genf (2006).
- WHO – World Health Organisation: Guidelines on Drinking Water Quality. 2nd Ed. 1993, Addendum (1998).
- Verordnung zur Novellierung der Trinkwasserverordnung vom 21. Mai 2001. BGB1. Teil I Nr. 24, pp. 959-980 (2001).
- Frimmel, F. H., Hesse, S., Kleiser, G.: Technology-related characterization of hydrophilic disinfection by-products in aqueous samples. In: Barret, S. E., Krasner, S. W., Amy, G. L. (eds.): *Natural Organic Matter and Disinfection By-Products*. University Press, Oxford, pp. 84-95 (2000).
- Frimmel, F. H., von der Kammer, F., Flemming, H.-C. (eds.): *Colloidal Transport in Porous Media*. Springer-Verlag, Berlin Heidelberg (2007).
- Frimmel, F. H., Niessner, R. (eds.): *Nanoparticles in the Water Cycle*. Springer-Verlag, Berlin Heidelberg (2010).
- Schwegmann, H., Frimmel, F. H.: Nanoparticles: Interaction with microorganisms. In: Frimmel, F. H., Niessner, R. (eds.): *Nanoparticles in the Water Cycle*. Springer-Verlag, Berlin Heidelberg, pp. 165-182 (2010).

The Importance of Humic Substances in the European Soil Protection Strategy

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INTRODUCTION

Soil is not simply the product of weathered parent material, it is the combined product of climate driven physical site factors and vegetation affecting soil properties by adding organic matter to the soil. Whilst soils have been recognised as having key roles to play in agricultural production, their importance beyond this function has been relatively little considered until relatively recently. Similarly for much of the latter part of the twentieth century, both nationally (e.g. the United Kingdom) and internationally (e.g. within the European Union), the protection of soils was not considered to be a priority area within the political agenda. In the United Kingdom in 1970 the report entitled 'Modern Farming and the Soil' (MAFF, 1970) highlighted the potential threats to the agricultural production on soils following a series of years where cultivation under adverse weather conditions, particularly in the autumn had resulted in a levelling off or even a slight decline in the curve of yield increases for cereals which had been experienced through the 1950's and early 1960's. This report stressed that if the soil productivity was to be maintained greater care needed to be taken in the timing of cultivation and (particularly in the case of sugar beet) harvesting operations, particularly as the machinery involved in these operations had grown in size quite dramatically over this time period. The report also contained a cautionary note that many soils seemed to show declines in the levels of soil organic matter and this appeared to be having an impact in reducing the robustness of the soil to withstand these agricultural actions under sub-optimal soil conditions. This decline in soil organic matter was linked with a decline in soil structural properties and a reduction in the soil's resistance to compaction. At the time there was much activity in relation to the robustness of soils, particularly amongst the soil science and agricultural advisory community, but with no similar sequences of adverse weather conditions, the concerns appeared to slip down the agenda. In the same broad time scale in 1972 soil protection was included in the Charter of the European Council with recommendations to the Member States to protect their soil (Council of Europe, 1972).

This was noted but there is little evidence that significant actions to protect soils resulted from the publication of the Charter.

Whilst there were limited actions within some of the European Member States, both generally addressing soil protection and often more specifically addressing soil contamination, there was no substantive Europe-wide initiative in this area. In 2001 part of the 6th Environmental Action Programme, established the objective to protect soils against erosion and pollution, and the Sustainable Development Strategy also of 2001, noted that soil loss and declining fertility were eroding the viability of agricultural land. The outcome of this and a number of other concerns voiced about the potential threats to soils resulted in the

Communication from the Commission to the Council, The European Parliament, 'Towards a Thematic Strategy for Soil Protection' (COM (2002) 179 final). This highlighted the recognition of soil as a valuable, non-renewable resource which must be protected. Within this document the emphasis was on soil functions and the threats to these functions. These functions and the associated threats have become the focus for a concerted drive towards a policy directive for soil protection within the European Union.

THE FIVE MAJOR SOIL FUNCTIONS

This Communication identified the five key functions that soils perform and which must form the focus of any soil protection policy. The five functions were:

- Food and other biomass production
- Storing, filtering and transformations
- Habitat and gene pool
- Physical and cultural environment for mankind
- Source of raw materials

A function not originally identified in 2002, but which has been increasingly recognised as important is the role of the soil system in the carbon cycle. The soil is now recognised as a significant carbon pool within the terrestrial carbon pool and management of the soil organic matter is seen to offer an opportunity to enhance sequestration of carbon (IPCC, 2007).

THE THREATS TO THE SUSTAINABLE USE OF SOIL

In addition to outlining the functions performed by soil, the Communication of 2002 also identified eight key threats to the sustainable use of soil:

- Erosion
- Decline in soil organic matter
- Soil contamination (local and diffuse)
- Soil sealing
- Soil compaction
- Decline in soil biodiversity
- Salinisation
- Floods and landslides

It was recognized these threats would not necessarily be prevalent in all regions within the European Union, for example salinisation rarely occurs in soils of North and Western Europe except in coastal regions.

Following internal discussions within the European Commission work, this initiative became known as the 'Soil Thematic Strategy for Soil Protection'. From these initial Europe wide discussions the European Commission produced a proposal for a Soil Framework to protect soils (European Commission, 2006a) and there were similar actions at national level by some countries within the European Union, for example Defra (2010) have produced a Soil Protection Strategy for England. This reflects the increasing recognition that soils play a key role in many aspects of our lives. Whilst soil development is a complex result involving various feedback mechanisms, the developments of soil protection strategies have increasingly recognised the key role played by the decomposition and accumulation of organic matter in determining, directly or indirectly, the ability of the soil to perform many of the functions identified. To a degree many of the soil's physical (structural development, aggregate stability, cation exchange capacity, etc.) and chemical characteristics (e.g. nutrient pools, buffering, chelation, etc.) can be seen as resulting from the quality and quantity of organic material and the manner in which it is mixed and aggregated with mineral matter. Soil organic matter is also closely linked to soil biodiversity, providing a food source for microflora and microfauna. Additionally the increasing recognition of the importance of the Soil Carbon Pool within the Terrestrial Carbon Pool has further emphasised the importance of Soil Organic Matter.

The perception of soil organic matter (SOM) is generally positive and is often considered as a major determinant of the health and quality of soil (Doran et al., 1996). When we think of soils, we generally accept that most have an organically enriched topsoil, although this enrichment varies considerably between soils. When we characterise soil in broad terms, we normally identify four components: - Mineral Matter;

Organic Matter; Air; Water. The proportions of these four vary, but on a volumetric basis in a cultivated medium textured topsoil in a moist temperate environment the proportions are likely to be of the order:

- 45% Mineral Matter
- 5% Organic Matter
- 50% Pore Space which is occupied by air and water depending upon the moisture status of the soil

The volumetric proportion of organic matter may be higher than this, and frequently, particularly under many types of intensive agriculture the proportion of organic matter may be much lower. Where soils with these low proportions of organic matter are found there is often concern about soil quality and soil health and encouragement to pursue strategies to increase the organic matter levels in the soil.

Soil organic matter is a diverse material, but may be considered to consist of different fractions:

1. Partially decayed plant residues – particulate organic matter (no longer recognisable as plant material).
2. Micro-organisms and flora involved in decomposition.
3. By-products of microbial growth and decomposition (soluble fraction and polysaccharides).
4. Humus (or colloidal OM) where the by-products have undergone humification.
5. Above ground (harvest/crop residues – recognisable leaf and needle litter and below ground necromass (dead roots) – probably not truly SOM, but of considerable importance.

The humus material usually consists of c. 50-58% Carbon, c. 4-5% Nitrogen and c. 1% Sulphur. This is the relatively stable component of the organic fraction, which may persist for a number of years within the soil, particularly when in intimate association with components of the mineral fraction.

Given the volumetrically small importance of soil organic matter, it is perhaps surprising that it is such a high priority consideration in most discussions of soil quality and its sustainable use and often features at the top or at least very high on the list of concerns on the agenda of soil protection policies. This focus is justified because the organic matter in soil firstly makes a large contribution to a wide range of soil properties (Table 1) and secondly the nature and the magnitude of this organic matter fraction is affected to a very large degree by our use of soil. For example our cropping practices will

influence the nature of the organic material added to soil and the nature and rate of the processes breaking down and altering the organic materials once incorporated in to the soil. These practices will be reflected in the soil conditions in a relatively short period of time. In addition there is a strong relationship between the nature and amount of soil organic matter and soil biodiversity.

THE POTENTIAL ROLES PLAYED BY SOM IN RELATION TO SOIL PROPERTIES

It is widely accepted that soil organic matter plays a major part in maintaining soil quality. Further it is claimed that without adequate levels of SOM the soil will not be capable of functioning optimally (see for example Oades, 1988; Paul et al., 1997; Schnitzer, 1991). In recent years there has also been widespread recognition that the soil is a major sink for carbon and that increasing the carbon held in the soil will potentially have a significant impact on the global carbon budget (see for example Smith, 2004). Table 1, broadly based on Stevenson (1994) lists some of the benefits associated with organic matter in soil. Whilst the provision of plant nutrients is recognised as an important contribution of SOM, it is clear there are many other properties, in particular related to soil physical conditions, which are influenced by the presence of SOM and may be controlled by the presence, amount and nature of this organic material. The retention and release of water, hydrophobicity and the ability to provide charged surfaces (variable with pH) where cations may be retained in a form available to plants are vitally important for the production of a good fertile soil.

The simple mixture of low bulk density organic material with the mineral fraction lowers the soil bulk density (and influences workability), but the significant effects are on the formation and stability of soil aggregates, which determine several associated pore related properties, such as aeration and water flow through soil (Tisdall and Oades, 1982). Many correlations are made between soil aggregation and SOM. Total SOM can still be considered a good parameter, but many research results suggest a distinction between active and passive fractions.

THE NATURE OF ORGANIC RESIDUES

The origin of organic matter is very diverse. In a natural carbon cycle, which for example can occur in a forest, the main source is plant residue entering the cycle; in agricultural systems the main part of the above ground biomass is exported (yield) and

there is often competition for plant residues and consequently relatively little may be recycled back in to the soil.

Table 1. Role of organic matter in soil.

Property	Remarks	Effects on Soil
Colour	The typical dark colour of many soils is often caused by organic matter	May facilitate warming in spring
Soil Biodiversity	The organic fraction in soils provides a source of food for a diverse range of organisms. The diversity of the organic materials will generally be reflected in the diversity of the organisms	Many of the functions associated with soil organic matter are related to the activities of soil flora and fauna
Water Retention	Organic Matter can hold up to 20 times its weight in water	Helps prevent drying and shrinking. May significantly improve the moisture retaining properties of sandy soils. The total quantity of water may increase but not necessarily the AWC except in sandy soils
Combination with clay minerals	Cements soil particles into structural units called aggregates	Permits the exchange of gases. Stabilises structure. Increases permeability
Reduction in the Bulk Density of Mineral Soils	Organic materials normally have a low density, hence the addition of these materials 'dilutes' the mineral soil	The lower bulk density is normally associated with an increase in porosity because of the interactions between organic and inorganic fractions.
Chelation	Forms stable complexes with Cu^{2+} , Mn^{2+} and Zn^{2+} and other polyvalent cations	May enhance the availability of micronutrients to higher plants
Solubility in water	Insolubility of organic matter because of its association with clays. Also salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly soluble in water	Little organic matter is lost through leaching
Buffer action	Organic matter exhibits buffering in slightly acid, neutral and alkaline ranges	Helps to maintain uniform reaction in the soil.
Cation exchange	Total acidities of isolated fractions of organic matter range from 300 to 1400 $\text{cmol}_c \text{ kg}^{-1}$	May increase the CEC of the soil. From 20 to 70% of the CEC of many soils is associated with organic matter.
Mineralisation	Decomposition of organic matter yields CO_2 , NH_4^+ , NO_3^- , PO_3^{4-} and SO_2^{4-}	A source of nutrients for plant growth
Stabilisation of contaminants	Stabilisation of organic materials in humic substances including volatile organic compounds	Stability may depend on the persistence of the soil humus and the maintenance or increase of the carbon pools within the soil

In Europe these plant residues are described as part of the broad group of materials called exogenous materials, and together with animal manures and slurries are produced locally. Within this group of exogenous materials there are other materials which are not produced directly on the farm but which are frequently added to the soil as part of normal soil management. These will include manures from other farms, sewage sludge, and materials from urban and industrial sources, which are often composted. There is some concern whether these non-farm based exogenous materials should be acceptable as organic matter additions to agricultural land.

As stated above the organic fraction in soil is diverse, ranging from fresh clearly discernible plant material (Particulate Organic Matter) through to humus, where there are no clearly visible signs to indicate the plant, animal or other origin from which the material is derived.

The organic matter in soil is subject to decomposition (mainly a reaction of mineralization), which is a key determinant of the role of organic matter in soils. It depends on the type of organic residues (organic matter from natural vegetation, managed forest or grassland, agricultural crops or exogenous organic material), on the type and properties of the soil, on climatic conditions and land management practices.

The rate of turnover of the organic material varies considerably from less than one year to more than one thousand years (Table 2).

Table 2. Turnover times of different fractions of organic matter.

Organic Matter type	Turnover time (y)
Litter/crop residues	0.5 to 2.0
Microbial biomass	0.1 to 0.4
Macro-organisms	1 to 8
Light fraction	1 to 15
Stable humus	20 to 1000

THE ROLE OF SOIL ORGANIC MATTER IN SOIL FUNCTIONS

- **Sustaining food production and biodiversity**

SOM has a key role in maintaining the necessary physical, chemical and biological conditions for sustainable plant production. SOM makes a significant contribution to the overall nutrient (N, P and S) demands of plants, particularly in zero or low external input systems. Before the introduction of inorganic fertilisers organic residues were the only significant means of adding many nutrients, such as N, to the soil system. In many non-

cultivated soils more than 95% of the nitrogen and sulphur is found in the SOM, and more than 25% of the phosphorus.

In addition to the provision of nutrients, a contribution of SOM of particular importance is the influence on the physical environment, enabling roots to penetrate and exploit the soil volume, excess water to drain freely from the soil but for sufficient water to be retained to meet the evaporative demands of the plants, and the flux of gases through the soil to maintain a well aerated environment.

The organic fraction also provides a great diversity of habitats and food sources for the faunal and floral communities within the soil. These communities are essential for the breakdown of the organic materials and the release of plant nutrients. They are also significant contributors to maintaining the physical conditions in the soil and their presence may facilitate the plant to access nutrients from otherwise inaccessible sources.

- **SOM and the environmental functions of soils**

When considering environmental functions the interrelationships between Soil, Air and Water are key and within these interrelationships soil organic matter frequently plays a key role in maintaining the environmental quality and the capacity of the system to perform these functions.

Maintenance of water quality

SOM plays an important role both in the cycle of water (infiltration and run off) and in its quality. In soils with well developed aggregates and porosity (soil properties strongly influenced by SOM) infiltration is favoured over run off. The role in relation to water quality occurs through the adsorption of metals and organic materials added to the soil, either deliberately (e.g. pesticides and soil amendments) or accidentally as a result of spillage. SOM may however contribute to a reduction in water quality if nitrate released during mineralization is leached out of the system in to ground and surface waters.

SOM and air quality

SOM can be a significant source of greenhouse gases through the formation of CO₂, CH₄ and N₂O. It can also contribute significantly as a sink through C sequestration in to the soil organic pools.

Soil as a treatment system for organic wastes

Soil is a very efficient biological reactor system capable of mineralising organic waste materials. Historically it has been extensively used for this purpose by agriculture, industry and many urban and rural populations. With care this recycling can contribute

substantially to the SOM pool and consequently have a broader environmental contribution.

DECLINES IN SOIL ORGANIC MATTER

The results of the Soil Thematic Strategy for Soil Protection identified the decline in soil organic matter across Europe as a major threat which should be addressed as a high priority. The decline in soil organic matter was seen to occur as a result of a number of soil management actions including:

1. Conversion of grassland to arable land
2. Drainage of wetlands
3. Failure to return plant residues to cultivated soils through poor rotation management and burning of residues
4. Accelerated mineralization due to management practices, e.g. tillage
5. Deforestation.

The European Commission (2006b) have estimated that the onsite costs of the decline in Soil Organic Matter to be in excess of €2billion annually, with offsite costs due to carbon released from SOM as Soil Organic Matter declines estimated annually at between €1.4billion and €3.6billion. The total annual cost of Soil Organic Matter decline is therefore between €3.4billion and €5.6billion.

MANAGING THE DECLINE IN SOIL ORGANIC MATTER

Whilst not the sole area where soil organic matter is declining, the declines in soil organic matter levels in agricultural soils have been marked and have caused widespread concern amongst policy makers. Through appropriate management, however, the trends observed in recent decades may be reversed and there may be possibilities of enhanced organic matter levels and the additional benefit of carbon sequestration. Within the European Union there are instruments within the revised Common Agricultural Policy of 2003 which provide support for agricultural practices which maintain or increase soil organic matter levels. From 2003 direct aids to farmers were made mainly via one '**Single Payment Scheme**' (SPS) payment per year, which replaced most existing direct aids. This shift in the emphasis of CAP support towards direct aids to farmers, and away from price support, was accompanied by clearer obligations on farmers to manage their farms in sustainable ways. This approach known as '**Cross-compliance**' links direct payments to farmers to their actions to maintain environmental quality together with other requirements set

at EU and national levels. Cross-compliance was not a new concept but from 2003 it was compulsory. All farmers receiving direct payments are subject to cross-compliance. In 2003 cross compliance dealt not just with environmental rules, but also included new requirements regarding public, animal and plant health, animal welfare, and the maintenance of all agricultural land in good agricultural and environmental condition.

A key part of the cross compliance approach was the need for all farmers claiming direct payments from the Single Payment Scheme within CAP to maintain their land in Good Agricultural and Environmental Condition. Individual Member States established procedures to address and monitor land management in relation to single payments and cross compliance. The Soil Protection Review 2010 (Defra, 2009) is a component of the response to this element of cross compliance in England. The Soil Protection Review was established to tackle the degradation threats to soil and the environment where land is not maintained in Good Agricultural and Environmental Condition, with particular emphasis on soil erosion, soil organic matter and soil structure.

Table 3a. Actions in the Soil Protection Review to maintain or improve soil organic matter level and associated impacts on other soil risk.

Cropping Practice and land management action	Impacts on other risks
Cereals and combinable crops	
Where organic matter is low, apply bulky organic manures, compost or digestates.	Relieves run off and erosion, reduces wind erosion
Where organic matter is low, introduce grass leys into the rotation.	Relieves run off and erosion, reduces wind erosion
Where organic matter is low, introduce cover crops into the rotation.	Relieves run off and erosion, reduces wind erosion.
Minimum tillage and direct drilling used	Relieves run off and erosion, reduces wind erosion. Relieves compaction
Potatoes, Sugar beet, Salad crops, Vegetables and Bulbs	
On intensively cropped soils where organic matter is low, apply bulky organic manures, composts or digestates.	Relieves run off and erosion, reduces wind erosion
On intensively cropped soils where organic matter is low, introduce grass leys into the rotation	Relieves run off and erosion, reduces wind erosion
On intensively cropped soils where organic matter is low, introduce green manures into the rotation.	Relieves run off and erosion, reduces wind erosion
Use nurse crops or planted straw to prevent windblow on sandy and peaty soils.	Relieves run off and erosion, reduces wind erosion
Following harvest, sow the next crop within 10 days of having been prepared as a seedbed where weather conditions allow.	Relieves run off and erosion, reduces wind erosion

Table 3b. Actions in the Soil Protection Review to maintain or improve soil organic matter level and associated impacts on other soil risk.

Cropping Practice and land management action	Impacts on other risks
Maize and Forage Crops	
Undersow maize	Relieves run off and erosion, reduces wind erosion
Rough plough sandy and silty soils following harvest to produce a cloddy coarse surface that is less likely to cap and slump.	Relieves run off and erosion, reduces wind erosion. Reduces waterlogging and prevents poaching.
The field is sown with a temporary cover crop throughout winter	Relieves run off and erosion, reduces wind erosion. Relieves compaction and reduces waterlogging
Fruit crops, hops and vines	
Avoid planting in wet conditions	Relieves run off and erosion and compaction.
Use a mulch or straw to protect the soil between rows	Relieves runoff and erosion
Reduce row length by introducing half headlands or trackways so as to minimise excessive travelling during harvesting.	Relieves runoff and erosion
Outdoor pigs and poultry	
Plan and manage paddocks and tracks to avoid channelling of water.	Relieves run off and erosion and compaction. Reduces wind erosion and waterlogging and prevents compaction
Ensure field grass cover is well established at least 12 months before the pigs are introduced to the land (i.e. so root structure is well developed and have a good established grass sward before the pigs arrive). Choose deep rooted varieties of grass that are drought resistant.	Relieves run off and erosion and compaction. Reduces wind erosion and waterlogging and prevents compaction
Develop a rotation so that pigs and poultry can be moved on to grass and the sward can be maintained.	Relieves run off and erosion and compaction. Reduces wind erosion and waterlogging and prevents compaction
Improved Grassland	
Remove grazing livestock from the grassland when the soil is too wet and poaching occurs. Ensure there is enough shelter for livestock in areas where the soil is wet for long periods.	Relieves run off and erosion and compaction. Reduces waterlogging and prevents compaction

As stated earlier soil erosion and structural stability are also strongly influenced by soil organic matter levels, hence the maintenance and improvement of soil organic matter levels are a key component of the framework and guidance given to farmers.

The first task within the SPR is to identify soils and areas of the farm which are at risk (low organic matter, erosion risk, structural decline and compaction are the principal risks). These risks may not necessarily be determined directly but might be inferred from areas of poor crop establishment through compaction or waterlogging, evidence of off farm deposition of soil material from water or wind erosion, etc. The threat of a risk will of course be strongly influence by the soil type. Where risks are identified advice is given to assist the farmer to remove or alleviate risks. The advice recognises that different land uses will require different

strategies to address the risks. Whilst the actions to reduce risks are addressed for each risk and land use, the examples presented here are to address the risks to improvement of soil organic matter levels.

CONCLUSIONS AND OBSERVATIONS

Since the late 1990s there has been an increased awareness of the importance of soils in relation to the sustainable functioning of both managed and natural ecosystems. It is now widely recognised that a failure to protect soils will have serious environmental consequences with attendant economic consequences both nationally and across Europe. Within the soil system the decline in soil organic matter has been identified as one of the major threats to the sustainable use of soils and strategies to slow down or halt the decline in soil organic matter and where possible increase the levels of soil organic matter have become priority action areas. The revision of the Common Agricultural Policy in the early 2000s emphasised cross compliance as a key part of sustainable agricultural activity. CAP and the associated cross compliance provides the framework for managing soils to ensure organic matter levels are at satisfactory levels and where the soil organic matter levels are below those accepted as sustainable, strategies to increase these levels are presented. Whilst the manner in which cross compliance varies across the European Union, the Soil Protection Review introduced in England provides a good example of how good soil management will assist in maintaining and improving soil organic matter levels across a wide range of agricultural land uses.

REFERENCES

- Commission of the European Communities, Communication from the Commission to the Council, the European Parliament, the Economic and Social Committee of the Regions. 2002. Towards a thematic strategy for soil protection. Brussels 16.4.2002 COM (2002), 179.
- Council of Europe. 1972. European Soil Charter. Strasburg.
- Department for Environment, Food and Rural Affairs (Defra), 2009. Soil Protection Review 2010, Defra, London.
- Doran, J.W., Sarrantonio, M. and Liebig, M.A. 1996. Soil health and sustainability. *Advances in Agronomy*, 56, 1-53.
- European Commission 2006a. Proposal for a Directive of the European Parliament and Council Establishing a framework for the protection of soil and amending Directive 2004/35/EC, Brussels, 22.9.2006, COM(2006) 232 final,2006/0086 (COD).
- European Commission 2006b. Commission staff working document - Accompanying document to the Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the

- Regions - Thematic Strategy for Soil Protection - Summary of the impact assessment. {COM(2006)231 final} {SEC(2006)620}.
- IPCC 2007 Contributions of Working Groups I, II and III to the Fourth Assessment Report on the Intergovernmental Panel on Climate Change (Eds. Pachauri, R.K. and Reisinger, A.), IPCC, Geneva, Switzerland.
- Ministry of Agriculture, Fisheries and Food (MAFF) 1970. Modern farming and the soil: Report of the Agricultural Advisory Council on soil structure and soil fertility. HMSO, London.
- Oades, J.M. 1988. The retention of organic matter in soil. *Biogeochemistry*, 5(1), 35-70.
- Paul, E.A., Follett, R.F., Leavitt, S.W., Halvorson, A., Peterson, G.A. and Lyon, D.J. 1997. Radiocarbon dating for determination of soil organic matter pool sizes and dynamics. *Soil Science Society of America Journal*, 61(4), 1058-1067.
- Schnitzer, M. 1991. Soil organic matter – The next 75 years. *Soil Science*, 151(1), 41-58.
- Smith, P. 2004. Soils as carbon sinks: The global context. *Soil Use and Management*, 20 (June 2004 Supplement), 212-218.
- Stevenson, F.J. 1994. *Humus Chemistry – Genesis, Composition, reactions* (2nd Edition), John Wiley and Sons, Chichester.
- Tisdall, J.M. and Oades, J.M. 1982. Organic matter and water stable aggregates. *Journal Soil Science*, 33, 141-163.

Environmental Impact of Humic Substances through their Interaction with Solar Light

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INTRODUCTION

Humic substances (HS) are complex natural compounds produced by chemical and biological transformation of animal and plant residues (Schnitzer, 1972). Ubiquitously present in soils and surface waters, they are known to affect the fate of many organic micropollutants. An intensively studied property is their ability to promote the photodegradation of organic micropollutants through light absorption. This property is based on the numerous chromophoric moieties contained in HSs that give brown colour to soils and yellowish colour to surface waters. Following light absorption some of these chromophores generate excited states and reactive species that promote the degradation of surrounding chemicals. All HS show the capacity to sensitize the degradation of organic micropollutants, even though the intensity of the phenomenon is variable depending on their origin, nature and mode of extraction. Until now, it has not been possible to relate the occurrence of photoinduced transformation of organic contaminants to the presence of specific chromophores or structural units in the HS. However, some correlations between spectral characteristics and photochemistry have been found.

From the pioneering work of Zeep et al. (1981, 1985), a lot of studies have been undertaken to understand the behavior of HS under light excitation. Figure 1 summarizes the main proposed pathways. After light absorption, humic chromophores are promoted to singlet excited states which may react through different ways. They may undergo relaxation to lowest singlet excited state (internal conversion), deactivate without or with emission of light (fluorescence) giving back the chromophore ground state, undergo

chemical reactions, for instance photoionisation with formation with solvated electrons and radical cations, transfer their energy to neighbour molecules and undergo inter-system crossing yielding triplet excited states. Triplet excited states show a lifetime estimated to 2 μs in aerated solution (Canonica, 1995). They have thus a lifetime much longer than singlet excited state and consequently are more susceptible to react with other chemicals. In particular they can transfer their energy to oxygen yielding singlet oxygen or they can be involved in oxido-reduction reactions through electron or hydrogen transfer. Many of the humic mediated photodegradations of micropollutants are explained by an oxidation by singlet oxygen or by a direct oxidation by triplet excited state. In both cases the triplet excited state is the key intermediate. Investigating simultaneously the phototransformation of two chemicals, one reacting with the triplets and the other with singlet oxygen, Halladja et al (2007) demonstrated that the triplets which react through electron transfer are also the one generating singlet oxygen. Consequently, formation of singlet oxygen and direct reaction of micropollutants with triplet excited states are competitive pathways. Hydroxyl radicals are another type of reactive species can be also involved in the phototransformations (Vaughan and Blough, 1998). These latter species are very oxidant and are able to degrade all sorts of chemical. They also react with HS themselves $10^4 \text{ mg}^{-1} \text{ DOC L s}^{-1}$ (Goldstone et al., 2002). Due to this high reactivity, the stationary concentration of hydroxyl radicals in illuminated HS solutions is generally lower compared to that of singlet oxygen and triplet excited states by about 3 order of magnitude (El Housari et al., 2010).

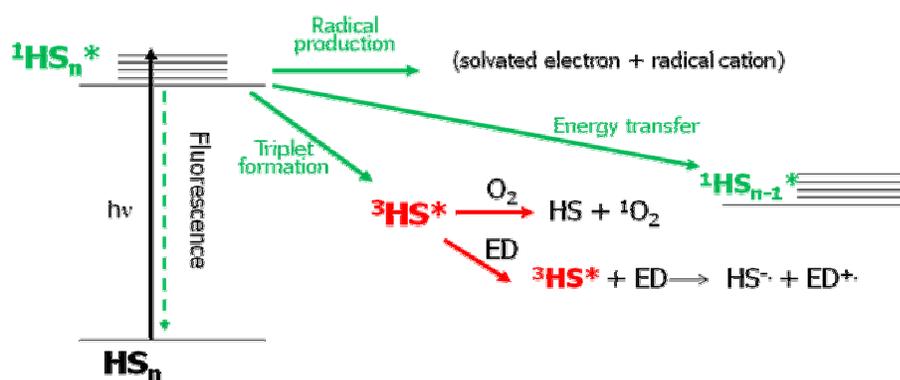


Figure 1. Scheme of HS photoreactivity. $^1\text{HS}_n^*$ and $^3\text{HS}_n$ are the singlet and the triplet excited state respectively of chromophore HS_n . ED is an electron donor molecule.

Their involvement is significant in the case where organic contaminants do not react with triplet state and with singlet oxygen and do not undergo photolysis via self light absorption. The mode of hydroxyl radical generation is not fully explained. Involvements of ferric species through photofenton reactions and of quinone moieties have been proposed (Paciolla et al, 1999; Vaughan and Blough, 1998).

In the first part of this paper, we give some examples of humic mediated micropollutants photodegradation reported in the literature focusing on the efforts made to delineate the role of each species. The second part will be devoted to the correlations found between spectral properties and photoreactivity.

1. EXAMPLES OF MICROPOLLUTANTS PHOTODEGRADATIONS

To elucidate the mechanism of phototransformation of organic micropollutants in the presence of HS from aquatic or terrestrial origin, a full set of experiments has to be conducted. First, it is necessary to check the stability of the micropollutant in the presence of HS in dark control experiments. Second, the photoreactivity of the micropollutant in the absence of HS (in pure water or in water containing buffer) must be investigated to evaluate its capacity to undergo photolysis (generally called direct photolysis). Following this, the capacity of HS to increase the rate of micropollutant photodegradation is estimated. Depending on the chosen experimental conditions, it may be necessary to correct the photodegradation rates for the screen effect (competitive absorption of photons by HS). When the rate of the micropollutant photodegradation is significantly higher in the presence than in the absence of HS, it can be concluded that HS photoinduce or photosensitize the phototransformation of the micropollutant. Photosensitization differs from photoinduction by the fact that the chromophore from which the reaction occurs is regenerated. Commonly, the term photosensitization is applied for HS although a part of the reaction corresponds to photoinduction. To delineate the role of possible reactive species ($^3\text{HS}^*$, singlet oxygen and hydroxyl radicals), specific chemical scavengers are generally used. For instance, the addition of oxygen which efficiently traps $^3\text{HS}^*$ helps to estimate the participation of these latter in the reaction. Alcohols, such as 2-propanol, are used for hydroxyl radicals trapping.

1.1 Examples of photodegradations with oxidation by $^3\text{HS}^*$ as the main pathway

$^3\text{HS}^*$ are able to react with a lot of compounds through electron transfer. In the general case, $^3\text{HS}^*$ are reduced and the micropollutant oxidized (see Figure 2). As oxygen

is necessary, it is highly probable that the radical anion of HS transfers its electron to oxygen. Given this, the humic chromophore is regenerated. The produced superoxide anion either reacts with the radical cation of the micropollutant or yields hydrogen peroxide through dismutation.

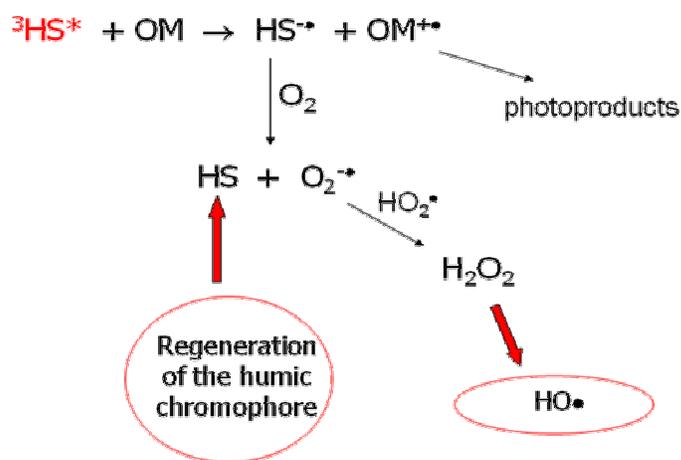
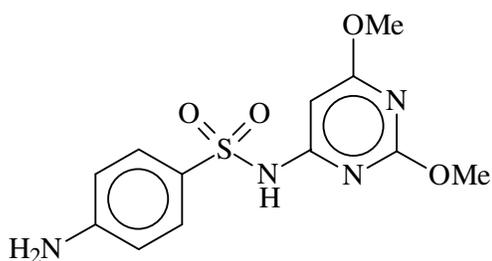


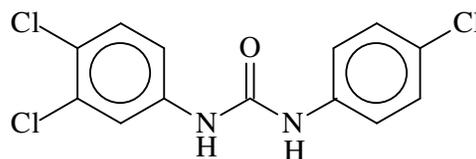
Figure 2. Reaction of ${}^3\text{HS}^*$ with organic micropollutants (OM) through electron transfer.

A lot of ${}^3\text{HS}^*$ mediated micropollutants photooxidation have been reported in the literature. For instance, phenolic compounds or phenylurea are proposed to react through this pathway (Canonica et al., 1995). Other compounds belonging to family of pharmaceuticals, pesticides or additives also react by such a way.

Guerard et al. (2009) studied the effect of fulvic acids on the antibiotic sulfadimethoxime (SDM) and on the antibacterial agent tricarbzan (TCC) (see Figure 3).



sulfadimethoxime (SDM)



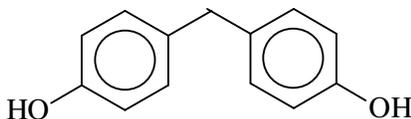
tricarbzan (TCC)

Figure 3. Chemical structures of SDM and TCC.

These micropollutants did not degrade in the dark controls over the course of the experiments. Direct photolysis accounted for > 50% of the degradation and was the dominant degradation pathway for both compounds. However, nearly all fulvic acids used in the study enhanced their photodegradation through indirect photoprocesses. Terrestrial FA showed the lowest reactivity for SDM and TCC, promoting the reactions by 19% and 28%, respectively, even though it had the greatest ability to absorb light (based upon SUVA and ¹³C-NMR analyses). In contrast, the autochthonous FA exhibited the highest reactivity toward these two compounds, although it absorbs less light than allochthonous material. To better characterize these photoprocesses and in particular to assess the role of ³HS* in the photodegradation of these two compounds, experiments were conducted in argon-saturated solutions to eliminate competitive scavenging by O₂. Measured rate constants increased by a respective 42% and 64% in the autochthonous FA, which is indicative of a ³HS* oxidation pathway. The addition of isopropanol (an effective hydroxyl radical scavenger) to SDM- autochthonous FA solutions resulted in no significant quenching. TCC, however, reacted to some degree by the hydroxyl radical pathway because isopropanol partially quenched the reaction.

This study exemplifies how the capacity of HS to photoinduce or photosensitize the phototransformation of micropollutants not only depends on the micropollutant structure and on its reactivity toward reactive species generated by HS but also on the HS origin.

Bisphenol A (BPA) which a major aquatic micropollutant can be also photodegraded by HS (Chin et al., 2004). Using 2,4,6-trimethylphenol as a humic triplet competitor, it was concluded that the reaction is partially due to reaction with humic triplets. Hydroxyl radicals also contribute to the photodegradation. Several dissolved organic matter were investigated. Contrary to the previous case, no differences in reactivity were observed.



bisphenol (BPA)

Figure 4. Chemical structure of Bisphenol A

1.2 Examples of photodegradations involving mainly singlet oxygen

Singlet oxygen is a very oxidant species, but it is specific. Highest bimolecular rate constants of reaction are observed for micropollutants bearing double bond, or S atoms for instance ($k = 7.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ for cyclopentene, $k = 2.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for 1,3-cyclopentadiene, $k = 1.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for benzylmercaptan in methanol). Many examples of photodegradation mediated by singlet oxygen are now reported in the literature. Furan derivatives are often used as chemical scavengers to measure the rate of singlet oxygen formation (see § 3). Replacement of water by D_2O is also convenient to evidence the involvement of singlet oxygen as the first order rate constant of deactivation is 10-fold faster in H_2O than in D_2O .

The first example of reaction concerns the amino acids (Boreen et al., 2008). Histidine, methionine, tyrosine and tryptophane are degraded by singlet oxygen when they are irradiated in the presence of humic material. For the three last compounds, reactive species other than singlet oxygen are involved in the phototransformation. The majority of tryptophan indirect photodegradation is due to $^3\text{HS}^*$. Methionine reacts with hydrogen peroxide and $^3\text{HS}^*$, the singlet oxygen pathway corresponding to 26 % of the whole reaction. 67 % of the tyrosine reactivity involves $^3\text{HS}^*$, through direct reaction.

Another example is that of sulfurous insecticide ethiofencarb (Vialaton and Richard, 2002). The reaction with singlet oxygen yields the sulfoxide. The formation of ethiofencarb sulfoxide is strongly enhanced in irradiated solutions containing HA and ethiofencarb.

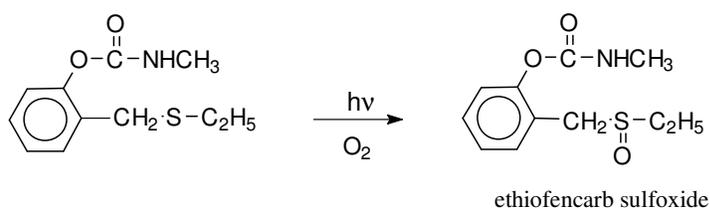


Figure 5. Chemical structure of ethiofencarb and photoproducts.

1.3 Examples of photodegradations involving mainly hydroxyl radicals

Hydroxyl radicals are able to degrade efficiently almost all the organic contaminants. Their contribution in the aquatic photodegradations is generally small because their stationary concentration is low due to both a low rate of photoformation from

HS and a fast scavenging by a lot of water constituents (HS, carbonate anions....). Nonetheless, in all the cases where reactivity of the micropollutant toward singlet oxygen and triplet humic and through direct photolysis are not important, the pathway involving reaction with hydroxyl radicals is a main degradation route. This is just the case for pharmaceutical Fluoxetine (Lam et al, 2005) (see Figure 6). FLX undergoes a direct photolysis when exposed to natural solar light. The half life in pure water is 7 ± 1 days. The rate of photodegradation is much faster in water containing dissolved natural organic matter with of half-life comprised between 5.5 and 22 hours. Scavenging experiments and rate constants measurements showed that the main contributors are hydroxyl radicals. On the other hand, phenylurea herbicide fluometuron was shown to be partly photodegraded by triplet humics (Halladja et al, 2007).

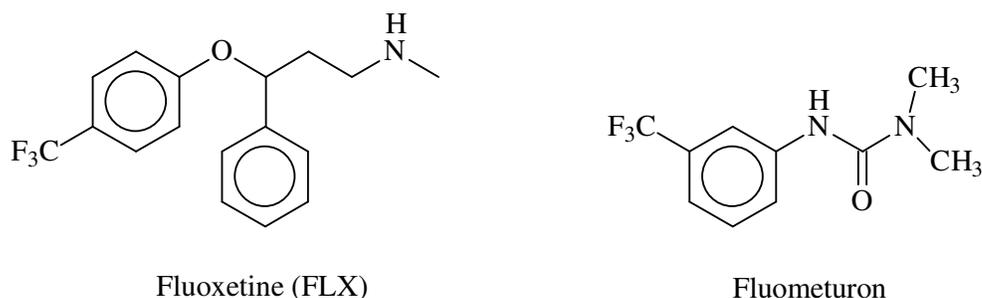


Figure 6. Chemical structure of FLX and fluometuron.

2. CORRELATIONS BETWEEN SINGLET OXYGEN PRODUCTION AND SPECTRAL PROPERTIES

As little is known regarding the nature of the reactive chromophores from which singlet oxygen is generated, finding relationships between photosensitizing properties and chemical or optical properties of HS would be useful to predict the fate of micropollutants in the environment. Attempts were made to find correlations with UV absorbance and fluorescence characteristics.

2.1 Correlations between singlet oxygen production and UV absorbance

HS show very characteristic UV-Visible absorption spectra. They are featureless and the absorbance decreases regularly as the wavelength increases from 200 to 800 nm. Only shoulders may occur below 350 nm. The UV-Visible absorption of HS is not yet

fully explained. It results from the overlapping of the absorption spectra of numerous individual constituents, but probably not only. Charge transfer complexes between hydroxyl-aromatic donors and quinoid acceptors may also exist and contribute to the long wavelength absorption (Boyle et al, 2009). Depending on the HS origins, the shape of the absorption spectrum varies, so that indicators such as spectral slope or absorbance ratios are often used to describe and compare HS. For instance, the ratio E2/E3, corresponding to the ratio of the absorbance at 254 nm and the absorbance at 365 nm, seems negatively correlated to the average molecular weight and to the aromaticity degree (Peuravuori and Pihlaja, 1997). Recently, Dalrymple et al (2010) looked for some relationship between E2/E3 and singlet oxygen photoproduction across various aquatic dissolved organic matter samples. This idea was suggested by previous results according which low molecular weight fractions of HS are more capable than high molecular weight fractions to photosensitize the phototransformation of micropollutants (Richard et al, 2004). Based on this, the ratio E2/E3 which generally increases as the average molecular weight decreases is expected to be positively correlated with the singlet oxygen photoproduction. Some dissolved organic matter were purchased from the International Humic Substances Society while others were isolated using ultrafiltration or adsorption chromatography. The method currently used for measuring the quantum yield of singlet oxygen formation is based on chemical trapping. Furfuryl alcohol is a convenient water soluble molecule for the trapping.

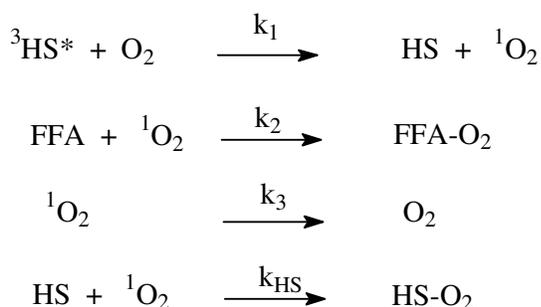


Figure 7. Reactivity of furfuryl alcohol (FFA) with singlet oxygen

The quantum yield of singlet oxygen production is obtained by dividing the rate of furfuryl alcohol consumption, r_{FFA} , by the rate of light absorption. r_{FFA} can be measured by monitoring the concentration of furfuryl alcohol in the course of the irradiation by HPLC.

However, it is necessary to check that the furfuryl alcohol disappearance through its reaction with hydroxyl radicals is negligible behind the one through reaction with singlet oxygen. This can be easily checked by measuring the effect of 2-propanol, used as a hydroxyl radical quencher. In the work of Darlympe, humic solutions were irradiated with polychromatic light, thus the rate of light absorption corresponded to that obtained by summation of the light absorbed by the HS within the wavelength range 300-400 nm. In these experimental conditions, the quantum yields of singlet oxygen production by the different natural organic matter were found between 0.5 to 4.5 % in line with those obtained by other authors (Paul et al, 2004; Frimmel et al. 1987; Haag and Hoigné, 1986) while ratios E2/E3 varied between 3 and 7. Finally, a rather good positive correlation was obtained with R^2 equaling 0.65.

As the lowering of ratio E2/E3 may be connected to a higher charge transfer complexes concentration, the authors suggested that the ability of HS to form charge transfer complexes is negatively correlated to their capacity to generate singlet oxygen. Two different mechanisms were proposed to explain the decrease of singlet oxygen formation: either singlet oxygen reacts with the organic matter itself more rapidly as E2/E3 decreases and the concentration of charge transfer complexes increases, lowering the stationary concentration of singlet oxygen, or competition reactions limit the formation of singlet oxygen precursors as E2/E3 decreases.

2.2 Correlations between singlet oxygen production and fluorescence

Another group worked on the fluorescence. They compared the singlet oxygen production and the fluorescence properties of a various set of HS which consisted of humic acids (HAs), fulvic acids (FAs) and water extractable organic matter extracted from soils. A good positive relationship was found between the rate of singlet oxygen production and the fluorescence intensity measured between 500 and 580 nm. HS were purchased from the International Humic Substances Society and from Aldrich. The other HS were extracted from soils of various origins (Ranker soil, Rendzine soil, Kursk soil, Andosol soil). Water extractable organic matters were also included in the study. They were simply extracted by agitating soils in pure water. The capacity of HS to generate singlet oxygen under irradiation was measured using furfuryl alcohol as a scavenger as described above. The role of hydroxyl radicals in the furfuryl alcohol disappearance was found negligible. At low initial concentration, furfuryl alcohol disappears by a pseudo-first order kinetics with k as a pseudo-first order rate constant.

$$r_{\text{FFA}} = k_2 [\text{FFA}] [{}^1\text{O}_2]_{\text{ss}} = k [\text{FFA}]$$

The steady-state concentration of singlet oxygen $[{}^1\text{O}_2]_{\text{ss}}$ is thus equal to the ratio k/k_2 , where k_2 is the bimolecular rate constant of reaction between furfuryl alcohol and singlet oxygen equal to $1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (Haag and Hoigné 1986). The rate of singlet oxygen production is directly linked to $[{}^1\text{O}_2]_{\text{ss}}$ by the following relationship:

$$[{}^1\text{O}_2]_{\text{ss}} \approx \frac{r_{\text{so}}}{2.5 \times 10^5 + k_{\text{HS}} \cdot [\text{HS}]}$$

In this equation, the rate constant of singlet oxygen desactivation in H_2O is taken at $2.5 \times 10^5 \text{ s}^{-1}$. The value of k_{HS} varies with the nature of HS, laying from 10 to $40 \text{ L mg}^{-1} \text{ s}^{-1}$. For $[\text{HS}] < 100 \text{ mgL}^{-1}$, the term $k_{\text{HS}}[\text{HS}]$ is generally largely lower than k_3 .

Emission spectra were recorded on a Perkin-Elmer LS-55 luminescence spectrometer and were corrected for instrumental response and the emission intensities measured for an excitation wavelength of 360 nm and normalized at an absorbance of 0.1. To reveal possible relationships between the capacity of the HS to produce singlet oxygen and their emission properties, $[{}^1\text{O}_2]_{\text{ss}}$ was plotted against the emission intensities measured at several wavelengths. For each selected emission wavelength, $[{}^1\text{O}_2]_{\text{ss}}$ increased with the emission intensity. The values of the linear regression correlation coefficient were the highest (0.76-0.84) for emission wavelengths ranging between 500 and 580 nm (see figure 8). This is important to stress that this good correlation was obtained for very different types of HS even though HAs represented the biggest pool of samples.

The parallel variations of fluorescence intensity and of singlet oxygen production would suggest that the two phenomena arise from the same chromophores or the same groups of chromophores. In such a case, the quantum yields of fluorescence and of triplet excited state formation would be related even in HS samples showing different concentrations of these chromophores. This is also important to remind that according to literature data the efficiencies of singlet oxygen production and fluorescence of HS are generally low, ranging from 0.027 to 0.06 (Paul et al., 2004) and 0.005-0.025 (Boyle et al., 2009), respectively. This means that a great part of the absorbed energy is dissipated leading neither to fluorescence emissions nor to triplet excited states production. Given this, the parallel evolution of the two properties among samples could be due to the fact

that they are both drastically affected by dissipation processes. However, it is doubtful that such an anticorrelation would rationalize our observations, because variability in the efficiencies of singlet oxygen production and fluorescence could be still important. These results strongly suggest that the fluorescence and singlet oxygen production of soil HS are to the same chromophores or to chromophores in close connection.

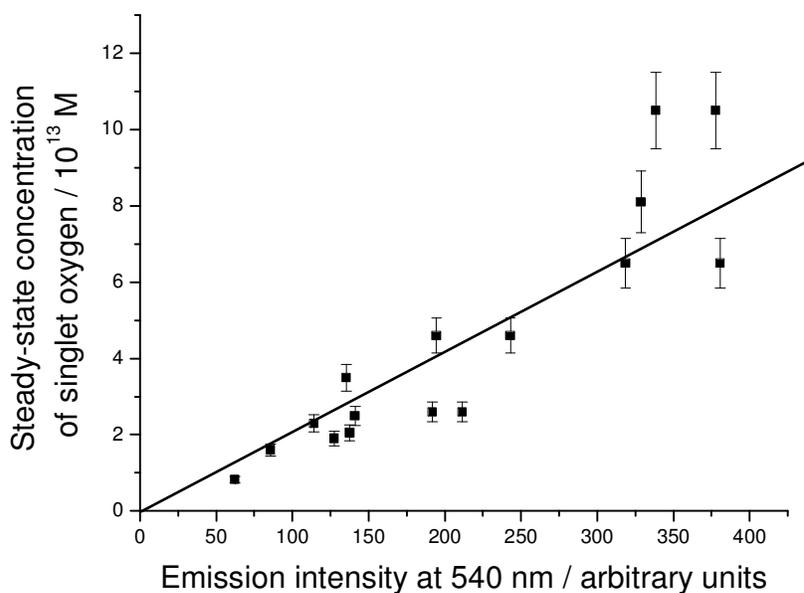


Figure 8. Plot of the intensity of fluorescence measured at 540 nm vs the stationary concentration of singlet oxygen in irradiated solutions of HS.

In conclusion, this is well established that humic substances photosensitize the photodegradation of organic micropollutants in the environment. Until now, photochemical reactions of HS have been mainly studied in aqueous solutions to mimic surface waters. Nonetheless, reactivity in solid phase would also deserve particular attention. The humic constituents from which reactive species are generated upon irradiation are not characterized. Interestingly, some correlations have been proposed between spectral properties and photochemical reactivity. They may help to predict the lifetime of micropollutants in the environment.

REFERENCES

- Al Housari F., Vione D., Chiron S., Barbati S. (2010): Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. *Photochem Photobiol Sci* 9, 78-86.
- Boyle E. S., Guerriero N., Thiallet A., Del Vecchio R., Blough N. V. (2009): Optical properties of humic substances and CDOM: Relation to structure. *Environ Sci Technol* 43, 2262-2268.
- Boreen A. L., Edhlung B. L., Cotner J. B., McNeill K. (2008): Indirect photodegradation of dissolved free amino acids: The contribution of singlet oxygen and differential reactivity of DOM from various sources. *Environ Sci Technol* 42, 5492-5498.
- Canonica S., Jans U., Stemmler K., Hoigné J. (1995): Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones. *Environ. Sci. Technol.* 29, 1822-1831.
- Cavani L., Halladja S., Ter Halle A., Guyot G., Corrado G., Ciavatta C., Boulkamh A., Richard C. (2009): Relationship between photosensitizing and emission properties of peat humic acid fractions obtained by tangential ultrafiltration. *Environ Sci Technol* 43, 4348-4354.
- Chin Y. P., Miller P. L., Zeng L., Cawley K., Weavers L. K. (2004): Photosensitized Degradation of Bisphenol A by Dissolved Organic Matter. *Environ. Sci. Technol.* 38, 5888-5894.
- Cory R. M., Cotner J. B., McNeill K. (2009): Quantifying interactions between singlet oxygen and aquatic fulvic acids. *Environ Sci Technol* 43, 718-723.
- Darlymple R., Carfagno A. Sharpless C. (2010): Correlations between Dissolved Organic Matter Optical Properties and Quantum Yields of Singlet Oxygen and Hydrogen Peroxide. *Environ. Sci. Technol.* 44, 5824-5829
- Frimmel F. H., Bauer H., Putzien J., Murasecco P., Braun A. M. (1987): Laser flash photolysis of dissolved aquatic humic material and the sensitized production of singlet oxygen. *Environ Sci Technol* 21, 541-545.
- Goldstone J. V., Pullin M. J., Bertilsson S., Voelker B. M. (2002): Reactions of hydroxyl radical with humic substances: Bleaching, mineralization, and production of bioavailable carbon substrates. *Environ. Sci. Technol.* 36, 364-372.
- Guerard J. J., Miller P. L., Trouts T. D., Chin Y.-P. (2009): The role of fulvic acid composition in the photosensitized degradation of aquatic contaminants. *Aquat. Sci.* 71, 160-169.
- Haag W. R., Hoigné J., Gassman E., Braun A. M. (1984): Singlet oxygen in surface waters - Part II: Quantum yields of its production by some natural humic materials as a function of wavelength. *Chemosphere* 13, 641-650.
- Haag W. R., Hoigné J. (1986): Singlet oxygen in surface waters. 3. Photochemical formation and steady-state concentrations in various types of waters. *Environ. Sci. Technol.* 20, 341-348

- Halladja S., Ter Halle A., Aguer J.-P., Boulkamh A., Richard C. (2007): Inhibition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol. Evidence for reactivity of the phenol with humic triplet excited states. *Environ. Sci. Technol.* 41, 6066-6073.
- Halladja S., Amine-Khodja A., ter Halle A., Boulkamh A., Richard C. (2007): Phototransformation of fluometuron in solar light. *Chemosphere* 69, 1647-1654.
- Hessler D. P., Frimmel F. H., Oliveros E., Braun A. M. (1996): Quenching of singlet oxygen by humic substances. *J. Photochem. Photobiol. B Biology* 36, 55-60.
- Latch D. E., McNeill K. (2006): Microheterogeneity of singlet oxygen distributions in irradiated humic acid solutions. *Science* 311, 1743-1747.
- Lam M., Young C.J., Mabury S.A. (2005): Aquatic photochemical reaction, kinetics and transformation of Fluoxetine. *Environ. Sci. Technol.* 39, 513-522.
- Paul A., Hackbarth S. Vogt R. D., Räder B., Burnison B. K., Steinberg C. E. W. (2004): Photogeneration of singlet oxygen by humic substances: Comparison of humic substances of aquatic and terrestrial origin. *Photochem. Photobiol. Sci.* 3, 273-280.
- Paciolla M. D., Davies G., Jansen S.A. (1999): Generation of hydroxyl radicals from metal-loaded humic acids. *Environ. Sci. Technol.* 33, 1814-1818
- Peuravuori J. and Pihlaja K. (1997): Molecular size distribution and spectroscopic properties of aquatic humic substances. *Anal. Chim. Acta* 337, 133-149
- Richard C., Trubetskaya O., Trubetskoj O., Reznikova O., Afanas'Eva G., Aguer J.-P., Guyot G. (2004) Key role of the low molecular size fraction of soil humic acids for fluorescence and photoinductive activity. *Environ. Sci. Technol.* 38, 2052-2057.
- Trubetskaya O., Trubetskoj O., Guyot G., Andreux F., Richard C. (2002): Fluorescence of soil humic acids and their fractions obtained by tandem size exclusion chromatography-polyacrylamide gel electrophoresis. *Org. Geochem.* 33, 213-220.
- Schnitzer M. and Khan S.U. *Humic Substances in the Environment*, Marcel Dekker: New York, 1972.
- Vaughan P. P., Blough N. V. (1998): Photochemical formation of hydroxyl radical by constituents of natural waters. *Environ. Sci. Technol.* 32, 2947-2953.
- Vialaton D., Richard C. (2002): Phototransformation of aromatic pollutants in solar light: Photolysis versus photosensitized reactions under natural water conditions. *Aquatic Sci.* 64, 207
- Zepp R. G., Schlotzhauer P. F., Sink R. M. (1985): Photosensitized transformations involving electronic energy transfer in natural waters: Role of humic substances. *Environ Sci Technol* 19, 74-81.
- Zepp R. G., Baughman G. L., P. F. Schlotzhauer (1981): Comparison of photochemical behaviour of various humic substances in water : Sunlight induced reactions of aquatic pollutants photosensitized by humic substances. *Chemosphere* 10, 109-117.