

**ESF Exploratory Workshop**  
**The Prediction of the Environmental Function of the**  
**Dissolved Organic Matter (DOM) in Ecosystems**  
*Beilngries, Germany, 2-6 July 2001*

**Scientific Report**

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**Executive Summary**

An Exploratory Workshop funded by the European Science Foundation (ESF) was held from 2 to 6 July 2001 at Schloss Hirschberg in Beilngries. One of its purposes was to explore, especially on a European level, our knowledge in regards to the numerous environmental functions (*e.g.* co-transport, environmental gas production, soil stabilisation) of the dissolved organic matter (DOM) in the environment. The Workshop also had the goals to explore future research needs in this area and to determine, if it should become the basis of an ESF sponsored network or programme. DOM is a relatively small pool within ecosystems, but, similar to the biosphere, it is a very dynamic one, and, on the microscopic scale, it is even more mobile than the biosphere. Although there have been numerous publications dealing with DOM (albeit not nearly as many as those dealing with the humic acids), our understanding of *in situ* DOM functions are by no means adequate, since the required holistic interpretations have been lacking. Also, with the present knowledge there is reason to doubt that the experimental approach used was indeed suitable for the understanding of the *in situ* functions of DOM.

In order to stimulate and facilitate the exchange of expertise, the participants of the Workshop distributed among each other months in advance their key recent publications. Furthermore, during the Workshop the participants briefly described their home institutes and research activities. The bulk of the time within the Workshop, however, was utilised to present and discuss specific themes dealing with DOM research and our understanding of the results. The themes were presented and moderated by one or two theme leaders. An attempt was made to have interdisciplinary themes and participants (*e.g.* from agricultural and sylvan science, aquatic chemistry, colloidal chemistry, mathematical modelling, microbiology, and oceanography). The participants and the themes are listed in the Final Programme section of this report. The results of the theme presentations and discussions were condensed into 26 prime questions. These questions were then further sub-divided into 3 major categories: (1) experimental approaches, (2) variability and field scale effects, and (3) mechanisms and are listed in the Assessment of the Results section below. The summarised overall views for each category are given here.

**Experimental Approaches**

- There are no standard methods to obtain DOM or to preserve DOM samples. However, it is probably not desirable to have a single standard methodology. Most likely several different standard methods are required, depending on the matrix (water, soil, or saturated solid systems such as aquifers) and on the DOM functions, which are of interest (*ex.* groundwater pollution, soil stabilisation, greenhouse gas production, *etc.*).
- Numerous excellent chemical analytical tools are available, but there is a need to better link the analytical results with each other and furthermore with the prediction and quantification of the ecological functions of DOM.

- Modelling efforts have concerned themselves mainly with DOM pollutant interactions and often results are obtained with humic substances or concentrated DOM samples and are then used to explain *in situ* DOM functions. This is in most cases inappropriate. Furthermore, modelling approaches also need to be developed to describe other DOM functions.
- It would be of great value, if more of the modern, genetically based, microbiological tools could be applied to DOM research.

### **Variability and field scale effects**

- Understanding the temporal and spatial variability of DOM concentrations and quality in the ecosystem (field) is a prerequisite for modelling and predicting DOM related processes.
- Up to now studies on the DOM concentration and quality have been mainly conducted within a few forest catchments. Such studies need not be limited to forests and could be a means of following DOM and its function from “the cradle to the grave”. Obviously the choice of such catchments needs to be judiciously considered and could be a component within a possible network.
- In such studies, as mentioned above, it is important that structural DOM analyses are better linked to the appropriate DOM functions.
- It is postulated, and has in some cases been experimentally shown, that DOM plays a role and is itself altered within the field and super-regional scale effects of podzolisation, deforestation, greenhouse gas increase, and carbon sequestration. Similarly DOM may also be involved with and function as an indicator for management attempts to improve the physical structure of deteriorated soils. In order to better understand and to predict the impact of these effects more information is needed as to what is “normal” DOM in a given system

### **Mechanisms**

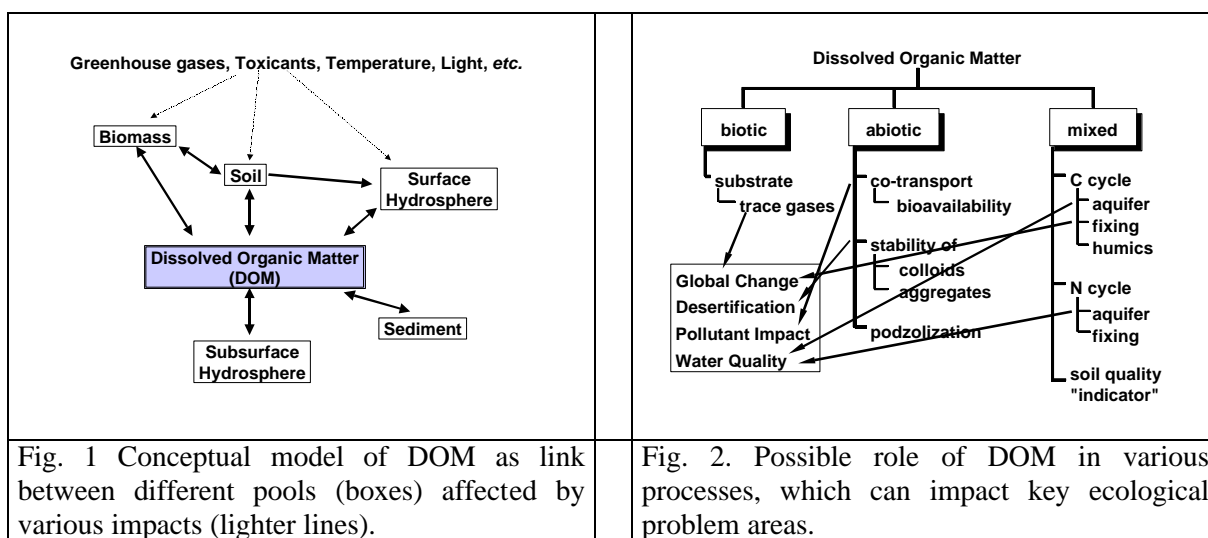
- The mechanisms by means of which DOM interacts with the environment, and how they are affected by anthropogenic and natural perturbations, can only be properly investigated within an interdisciplinary framework, including colloidal chemistry and microbiology.
- On the abiotic level the organic matter (OM) is distributed between the solid and aqueous (DOM) phases. This is presumably affected by multiple factors such as pH, clay mineralogy, concentration of specific cations, *etc.*. The *in situ* kinetics and driving factors need to be further investigated. Results based on studies with fulvic acids or DOM concentrates may often be inadequate.
- On the biotic level DOM synthesis, metabolism, and catabolism are strongly controlled by the microflora, which are in turn affected by nutrient supply, pore structure (microsites), water availability, *etc.*. Again, the *in situ* kinetics and driving factors need to be further investigated.
- Regarding the biotic/abiotic interface more investigations dealing with the interrelationship and interaction between the rhizosphere, DOM, and the bulk soil are definitely needed.
- Most of the mechanisms by means of which DOM can effect the ecological functions illustrated in Fig. 2 need to be further experimentally investigated in order to make modelling possible and to assist in the selection and application of management measures to mitigate negative processes. The abiotic and biotic kinetics of DOM concentration and quality, as indicated above, need to be considered in such efforts.

In summary it can be stated that much information and understanding in regards to DOM functions in the environment are available but that much of this understanding is only conceptual and that large experimental gaps exist. These gaps can only be closed within a multi-institutional and interdisciplinary effort. An ESF sponsored network could provide a viable framework for this. Therefore, an application in this regard will be initiated in the very near future. It was also felt that a DOM oriented ESF sponsored programme would be at present premature.

**Scientific Content**

The goal of the Workshop was to determine the state of our knowledge for the prediction of the environmental function of the dissolved organic matter (DOM) in ecosystems. DOM comprises a relatively small fraction of the total organic matter (OM). Typical concentrations for aquatic system are less than 50 mg dissolved carbon (DOC) per litre. In soils and sediments this DOM pool amounts to less than 1 % of the OM . However, DOM is potentially very mobile and can move from one ecosystem component to another. This can conceptually be envisioned in Fig. 1. Biomass is the pool of living organic material ranging from microorganisms to the macrophytes (including their rhizosphere). It also includes non-living intact material such as straw. The heavier arrows represent mass fluxes. The lighter arrows refer to influences relatively independent of mass.

Furthermore, with the possible exception of the living biomass, the DOM pool also has the most rapid turnover of the organic pools present in a given ecosystem. Therefore, ecological impacts are relatively rapidly reflected in the characteristics of the DOM. For example, the co-ordinator has found that an increase in atmospheric CO<sub>2</sub> in an Alpine grassland resulted in changes in the characteristics of the soil’s DOM. Also, the co-ordinator and others have found that drought can strongly alter the nature of DOM. These and similar results indicate that DOM can be used to monitor possible ecological impacts.



It has also been postulated or shown that DOM can participate in several important ecological processes (Fig. 2). The relatively recent damage to Doñana National Park and the recent pollution of the Tisza River in Hungary have shown that a well-founded understanding of DOM is most timely. DOM’s possible role in ecological processes include:

- DOM has an effect on the co-transport and availability of noxious compounds, both inorganic and organic. In the latter case, this is especially true when the undesirable chemicals are hydrophobic such as the polyaromatic hydrocarbons. This aspect is of importance in research aimed at mediating pollutant impacts and at improving terrestrial or aquatic remediation programmes.
- DOM generates acid water; yet due to complexation it keeps biotoxic inorganic aluminium at low concentrations. The role of this natural weak acidity in the ongoing ecosystem recovery from acid rain is clearly important, though uncertain.
- DOM influences the adsorption of heavy metals on clay compounds, since it has been found that DOM can compete for potential metal binding sites on mineral surfaces. This again is important for remediation based studies and also for improving our understanding of the fate of radioactive contaminants such as  $^{137}\text{Cs}$ .
- DOM effects the stabilisation of soil and sediment colloids and microaggregates. These are, especially for soils, critical for the maintenance of proper physical quality to prevent desertification, excessive runoff, poor plant growth, *etc.*
- DOM serves as a sink for carbon by removing it from areas of high metabolic activity.
- DOM may be a substrate for organisms not proximal to a food source, such as those in aggregates, deeper soil and sediment layers as well as in aquifers. This can be important in the co-metabolism of noxious compounds. Furthermore, DOM can control the redox conditions in microsites and also on larger scales under appropriate conditions. This in turn can have an effect on the production of environmentally relevant gases such as nitrous oxide ( $\text{N}_2\text{O}$ ) and methane ( $\text{CH}_4$ ).
- DOM participates in photochemical reactions, both in the destruction (remediation of the surface hydrosphere) and in the production (a potential problem in water purification) of noxious compounds.
- DOM can possibly also be an indicator for changing environmental conditions as was briefly discussed above.
- Furthermore, DOM can have an economical impact by influencing either through odour or colour the acceptability of drinking and bathing water. It may even produce carcinogenic compounds by reacting with disinfectants used in water treatment.

DOM research is seriously hampered by the fact that

- Researchers and their meetings tend to be structured into specific areas such as soil science, hydrology, *etc.* DOM, however, crosses these relatively arbitrary barriers. A true intensive cooperation is needed to overcome this and to enable us to understand and to predict DOM ecology in a holistic manner.
- In the hydrosphere DOM is normally present in low concentrations, while in soils and sediments usually only very small samples of *in situ* DOM are available. Much DOM research has been done with samples that either have been concentrated from aqueous media or that have been extracted from solid matrices. In both cases relatively strong conditions tend to be used, and it is questionable to what extent the investigation of such samples is applicable to our understanding of *in situ* DOM ecology. One goal of this workshop was to seek to clarify this and to make recommendations as to how DOM should be obtained to investigate and predict its ecological function with a minimum of artefacts.
- There is a lack of standard analytical methods in DOM research. To some degree this reflects the fact that different research goals require different methodologies, but quite often the methodologies used simply differ in an arbitrary manner. Furthermore, samples that are pre-treated differently or that are analysed using different techniques often give differing results for the same physical or chemical parameter.

From a European perspective, a serious limitation is that such meetings are almost always either national or international on a world scale. In the former case, the geographical base is too small while in the latter it is too large. Also, the number of participants is often much too large to enable in depth discussion, which are needed to produce concrete results and not just an exchange of results and experiences. DOM research is perhaps most needed when there are major interactions between anthropogenic activities and the fluxes between terrestrial and aquatic environments. This is especially true in Europe with its large concentration of industrial, agricultural and municipal activities centred around its many rivers and lakes. This is also the case on other continents, but by no means to the same extent. Therefore, DOM research is most needed in Europe and can best be developed by exchanges on a European and not national or world scale.

In the past the co-ordinator was involved in a series of small interdisciplinary German DOM workshops, which were held in Bayreuth, Munich, Bochum, and Berlin. These meetings were true workshops but had no financial support and lacked the participation of established senior scientists. They were often of considerable interest, but resulted in no concerted follow up. Also at these meetings the lack of participation of scientists from other European countries with their complimentary experiences was seriously felt. It was expected that this ESF Workshop would overcome these lacks.

In general the proposed Workshop had the following goals:

- An exchange of experiences and research aims. This is in common with almost all other scientific meetings. However, specific DOM related aspects were emphasised.
- Identify or re-identify the possible ecological roles of DOM.
- Develop a better understanding of the biases, which different methods of DOM acquisition may inflict on our conception of the processes, which either are controlled by DOM or which alter DOM. Is there a single means of DOM acquisition, which would be suitable for all ecological studies? If not, what are the advantages and disadvantages of the different methods.
- Compare experiences in regards to the analytical tools, which can be used to characterise DOM and to predict a given ecological process. This covered analytical techniques such as DOC analysis, NMR, (FT)IR, UV, fluorescence, capillary electrophoreses, mathematical approaches to data analysis, *etc.*
- Exchange experiences in the use of DOM as an indicator for ecological processes.
- Identify open questions in regards to the DOM.
- Produce a written document containing the above.
- Investigate whether or not there is a need to formulate a proposal to the ESF for the initiation of a DOM Network or Programme.

In summary, DOM needs to be considered in almost all research concerned with organic material in the environment. The purpose of this Workshop was to consolidate our knowledge of DOM in the European community and to develop the most promising approaches for future studies dealing with our ability to predict and apply the environmental role of this elusive and dynamic pool of organic compounds.

## Final Programme

The final programme deviated scarcely from the preliminary programme sent out by the ESF.

1. Before the meeting participants sent to all the other participants some of their key publications dealing with DOM. This provided substantial background information, while modern electronic data exchange made this relative simple.
2. The Workshop was held at Schloss Hirschberg in Beilngries from the late afternoon of 2 July until midday of 6 July, 2001. On 1 July there was an Alpine excursion for most of the participants, who had to arrive on 30 June to take advantage of reduced air travel. This was also an opportunity to informally exchange views before the Workshop itself. Starting the Workshop on 1 July was not possible, since Schloss Hirschberg was not available on that date. Details in regards to the participants are given in the Statistical Information and List of Participants sections below.
3. Initially at the Workshop each participant gave a 5 to 10 minute presentation dealing with his institute and person. This enabled a further appreciation of the research potential of the participants to be developed.
4. Research themes were then presented and discussed for a period ranging from 1 to 2 hours, depending on the need. Some of the theme titles were minimally modified from the initial programme. Furthermore, there had to be some impromptu changes in theme leaders because of the rather sudden inability for Drs. García Novo and Parlanti to attend the Workshop. The final list of themes and their leaders are listed in the table below.

No.	Theme	Theme Leader(s)
1	What are the potentials for international co-operation on DOM?	Gjessing
2	What is theoretically DOM? What are its potential functions? Definitions.	Zsolnay
3	How do we obtain it? Aqueous extractions, resins, RO? Factors (soil drying, <i>pH</i> , <i>etc.</i> ), which influence its extraction. Artefacts.	Croué / Marschner
4	To what extent can DOM be colloidal?	Tombác
5	“Simple” (optical, biotests, <i>etc.</i> ) analytical approaches. <i>In situ</i> measurements. Humification indices.	Blaser / Miano
6	“Complicated” (NMR, CE, MS, <i>etc.</i> ) analytical approaches.	Kretzschmar
7	The possible composition of DOM in general? How much is “natural”? How important is the distinction?	Frimmel / Gjessing
8	DOM in aqueous systems.	Miano / Pempkowiak
9	DOM in forests.	Gallardo
10	DOM in fields.	Kalbitz / Zsolnay
11	DOM’s interaction with metals and nutrients.	Römkens
12	DOM’s interaction with organic pollutants.	Szabó
13	Modelling DOM interactions.	Benedetti
14	DOM’s interaction with microbes. Can DOM be toxic?	Baldi / Smolders
15	Application of modern microbial methods to DOM research.	Baldi / Krsek
16	DOM and environmental gas (CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O) production.	Zsolnay
17	DOM’s interaction with higher organisms, including the rhizosphere.	Zsolnay
18	Geochemistry of DOM, including podzoloisation.	Kalbitz
19	Experiences with large DOM projects.	Frimmel / Vogt

5. Toward the end of the Workshop a detailed discussions were held to attempt to synopsis the theme presentation results.
6. During one evening a mid-Workshop excursion to the city of Regensburg was held.

## Assessment of the Results

These results of the theme presentations and discussions were condensed into 26 prime questions. In many cases a consensus was possible, but in many cases experimental results were lacking to confirm the views of the participants. Frequently, as is certainly appropriate for a workshop, unpublished results were used as a discussion basis. These questions were then further sub-divided into 3 major categories: (1) experimental approaches, (2) variability and field scale effects, and (3) mechanisms. One must keep in mind that these categories are certainly not mutually exclusive. The questions, our ability to answer them, and the gaps or needs in their regard are presented below.

### **Experimental Approaches** (summarised by R. Kretzschmar)

#### *X1. How should DOM samples be stored and exchanged for analysis?*

DOM is comprised of an extremely complex mixture of organic compounds. Some components of DOM may be rather resistant to microbial degradation, while others are readily degraded by bacteria or fungi. Thus, DOM samples must either be analysed immediately after sampling or microbial degradation must be prevented by cooling, freezing, freeze drying, or some other means. The method to be used will also depend on the objectives of the work (*e.g.* metal complexation, biodegradation). Direct analysis is often not possible, especially if samples need to be shipped to other laboratories. Treatments such as drying may affect certain DOM properties and functions, while leaving other properties or functions intact. Very little is currently known about such effects. This needs to be clarified in order to develop optimised sampling and storage protocols used in international DOM research, for example, within the planned DOM network.

#### *X2. Are DOM functions preserved after physical extractions?*

DOM concentrations in natural waters are frequently much lower than required for chemical and spectroscopic analysis. Therefore, it is common practice to concentrate DOM by various techniques, including membrane ultrafiltration, reverse osmosis, and resin column techniques. All methods have their advantages and disadvantages and usually a combination of techniques must be used to achieve full recovery. The greatest concern is that certain fractions of DOM may be lost during these procedures, especially the low molecular weight and/or highly polar DOM fractions, thereby changing the overall composition of DOM as compared to the natural state. Another important aspect is to which extent the isolated DOM needs to be purified. In many analytical techniques, contamination of DOM samples with inorganics can cause interferences. Isolation and purification procedures may also affect DOM functions, which often depend on specific compounds, for example, biologically active molecules or strong complexing ligands. It is currently not clear which method is best suitable for extracting or concentrating DOM while preserving various DOM functions.

#### *X3. Which extracts should be used for which functions?*

DOM is defined by the means with which it is extracted. Which extracts should be used for which functions? Each of the available techniques preferentially isolate a given category of DOM. The method to be used will depend on the objective of the research work. Fractionation can be based on size (membrane filtration, size exclusion chromatography), on polarity (non ionic resin such as XAD) or charge (anionic and cationic exchange resins).

X4. *How should DOM be characterised in order to understand and predicts its functional behaviour?*

A large variety of physical, chemical, and spectroscopic techniques are available to characterise natural organic matter. However, all of these methods yield specific information on only one property, such as elemental composition, molecular weight, or functional group contents. Thus, a combination of many different techniques would be required to fully characterise DOM composition, which is very cost and labour intensive and can only be achieved in collaborative efforts, such as the planned DOM network. Another problem arises from the fact, that most methods yield “average” information on DOM composition instead of very specific, structural information. Such “average” properties may not be directly related to DOM functions. For example, some biological functions may depend on trace quantities of specific chemical compounds, which are not detected by spectroscopic techniques such as FTIR or NMR. Thus, two DOM samples with apparently similar “average” chemical composition may behave differently in terms of a particular biological function. Currently, there is a clear lack of studies that link physico-chemical and structural DOM-properties to certain DOM-functions, *e.g.*, its biodegradability, metal complexation ability and carrier function for hydrophobic xenobiotics or metal cations. In this context, there is also a need for reproducible standard methods for quantifying DOM functions (*e.g.*, biodegradability, colloid stabilisation, enhancement of root growth).

X5. *Is it possible to have a “standard” forest or should one use a multivariate approach to define forest DOM?*

This question is to some degree philosophical, but it is an important key issue in any kind of environmental and ecosystem research. Of course, there is no such thing as a “standard forest”. The real question is, which types of forest sites should be studied to gain as much generalisable information as possible? To answer this question, it would be necessary to fully understand the influence of various factors on DOM dynamics and composition, such as climate, vegetation, soil nutrient status, soil water regime, *etc.* However, these interactions are currently poorly understood, at least on a quantitative basis. Thus, site selection will have to be made based upon best judgement and experience of researchers. A multivariate approach with several study sites may help to quantify the influence of main factors on DOM dynamics and composition in forest soils.

X6. *Is it possible to have a “standard” agricultural field or should one use a multivariate approach to define agricultural field DOM?*

The answer to this question is similar to X4. However, since agricultural fields are very intensively managed ecosystems, several additional factors may play an important role in DOM dynamics and composition. Multivariate approaches, among other more process oriented approaches, could be used even at one site to study the influence of fertilisation, crop rotation, soil tillage, and crop residue management on DOM.

X7. *What parameters are needed to model DOM functions?*

To illustrate this question, let us take metal complexation as an example. To model metal complexation by DOM, comprehensive experimental data is required to calibrate competitive ion binding models. At present time, a fairly large data base of metal ion interactions with humic substances is available, although data for some important metal ions like Al and Fe are still rare. Fe and Al are important in many geochemical processes, like podzolisation or weathering, where DOM plays a key role.



Another important question that needs to be answered is the influence of DOM composition and molecular size on metal complexation. Humic substances, polyacids, or mixtures of simple organic acids are often used as analogues for DOM with respect to metal binding, but it is unclear how good these analogues really are. Also DOM composition can change with time. For example, in the environment metal-DOM complexes are expected to age. It has to be verified that models calibrated with freshly interacted DOM and metal ions would still give a reasonable description of the fate of those metal ions during sorption and desorption processes. For other DOM functions, the answer to this question is of similar complexity and a detailed discussion would be beyond the scope of this report.

X8. *To what extent can microbial tools be used in DOM research?*

Microbes like final degraders of all organic matter in natural environment are in an intimate mutual relationship with DOM. Microbial populations in direct contact with dead organic matter degrade this matter to satisfy their own C and energy needs and release furthermore DOM, which then can be transported into less accessible sites, where it can be used by local microflora. This means that if we want to understand DOM dynamics, microbial population must be taken into account. Because of the high mobility of DOM the biggest challenge is to find that part of the microbial population, which is responsible for major changes in DOM composition. Part of this population could be isolated together with some of the DOM extraction techniques. To gain information about the total microbial population at a given site, R/DNA can be extracted either directly from a water or soil sample from that site or indirectly where microbes are first concentrated using different techniques for isolation of microbial populations (dispersion, filtration, gradient centrifugation, etc). Once R/DNA from the population of interest is extracted, several molecular techniques can be used. Total composition of microbial population can be studied by some of the fingerprinting methods using universal 16/18S rDNA primers, followed by T/DGGE, RFLP, SSCP, etc. To study the active part of the population, the same techniques can be used, but the starting point will be the RNA instead of the DNA followed by RT-PCR. To study specific metabolic activities, primers targeting relevant genes can be used. Also different hybridisation methods can give us valuable information. Another promising techniques are gene libraries which enable us to examine influence of microbial life on DOM in a more complex way.

To investigate microbial activity *in situ* fluorescent molecular probes can be applied. This technique allows us to localise a certain enzymatic activity, a polysaccharide production (capsules, biofilms, surfactants) or even a microbial species in action. Today hundreds of fluorescence molecular probes are available and with the use of scanning confocal laser microscopy (SCLM) the determination of microbial activity *in situ* has increased exponentially. Hence, is it possible to study DOM formation or/and transformation in ecosystems with this approach using molecular probes and SCLM? In principle yes! However a protocol should be defined. Certainly with FISH (fluorescence *in situ* hybridisation) it is possible to localise microbial species by using 16S rDNA conjugated with a fluorochrome versus a specific fragment of 16s rRNA (in ribosomes), but we need to link the presence of certain species with their catalytic activity, as for example for cellulose degradation. So in this case, the use endoglucanases and sugars production *in situ* will be important to understand the role of bacteria in DOM in relation to nutrient uptake and phosphate recycling. All this activity can be checked by using different and specific non-genetic molecular probes.

To summarise, molecular techniques can give us new insights into complex processes of DOM "behaviour" but to be able to use their potential, closer collaboration between DOM experts, microbiologist, and molecular ecologists must be established

### **Variability and field scale effects** (summarised by R. Vogt)

#### *V1. How different is DOM over space and time?*

The main sources of the DOM in the most terrestrial ecosystems are the plant litter and the decomposition products of soil organic matter. The litter supply as well as the microbial activity is subject to seasonal variation as well as to the site conditions (type of vegetation and soil *etc.*). A range of physical, chemical and biological processes then fractionates or transforms the produced DOM. The relative importance of the different processes is governed by the nature of the soil- and water matrix and water chemistry. These processes result in that only a small portion of DOM remains dissolved, soluble and mobile. The overall effect of this fractionation on the DOM's bio-physico-chemical characteristics and structural properties depends therefore on the nature of the soil- and water matrix (pedogenic Fe- and Al-oxides/hydroxides, clay content, amount of suspended particles) and water chemistry. Furthermore, the relative contribution of allochthonous and autochthonous DOM in aquatic systems is of relevance. Reflecting the large seasonal and spatial variation found in nature, the structure and function of especially allochthonous DOM vary considerably over time and space. Understanding this temporal and spatial variability of DOM concentrations and quality in the field (soils and waters) is a prerequisite for modelling of DOM dynamics and for the prediction of DOM-related processes, such as pollutant transport or de-nitrification. The linking and comparison of DOM results, obtained with similar methods, but over a long temporal span and large spatial area is an important function of a network.

#### *V2. How are differences in structure and function related?*

As stated above, the nature of DOM is the result of a number of interactive mechanisms (degradation, sorption, *etc.*). This implies both structural and functional, variations and differences in DOM, which depend strongly on the specific environment. Today's research challenge lies in the interpretation of our conditional parameters. Combined knowledge of both DOM's composition and physico-chemical characteristics is necessary in order to link these structural properties and the characteristics of DOM to its functions as *e.g.* substrate or as carrier for contaminants. *I.e.* bioavailability of DOM is of essential interest for ecological and ecotoxicological reasons.

Greater research progress is likely to be achieved with an integrated research approach. It is therefore imperative to join forces in an extensive characterisation of a limited number of samples using different tools. Such a linking and comparison of DOM data, obtained from the same sample, using a large range of physical, chemical and bio-assay methods is an important function of a network.

#### *V3. Is catchment research the best approach to understand DOM variability?*

Interdisciplinary integrated research as described in section V1 & V2 is best achieved and conducted by using a common set of sampling sites (case studies). Only a catchment approach allow linking the terrestrial with the aquatic environment, and thus study the processes that cause the changes in allochthonous DOM concentrations and properties during soil passage and its subsequent transformations in waters relative to the processes controlling the autochthonous DOM. Furthermore, environmental sciences in general lie open for criticism since we do not control all the factors influencing our data. As discussed above the nature and quality of the humic substance that is collected in nature is the product of a large number of factors and variables. A research network that is studying a common set of sampling sites are better able to

accumulate all necessary data (*i.e.* site characteristics (topography, biology, hydrology, geology, morphology), climatic conditions and history, (*i.e.* chemistry monitoring) than small research groups with limited project funding.

For other and more specific questions and hypothesis testing (*e.g.* requiring sample manipulation), laboratory study may be more appropriate. It is crucial that catchments are carefully selected so that they are as similar as possible, yet cover a large range in certain key explanatory variables (*e.g.* climate, catchment size, topography, pedology or % bog coverage), in order to reflect a clearly stated purpose. Ideally, the catchments have been studied before and are well characterised by other research groups, so that not all basic data has to be collected. The selection of such catchments is best conducted by a network of research groups, which establishes a program and selects the site criteria and then identifies potential sites.

V4. *How important is atmospheric input?*

Depositions of both acidic deposition as well as organic matter (OM) affect soil and water systems. Changes (in pH, ionic strength, N compounds, *etc.*) caused by acidic deposition are able to modify DOM composition and/or behaviour and therefore interactions, specific availability, *etc.* Furthermore, the influence of anthropogenic components (*e.g.* pesticides) with respect to their irreversible fixation in DOM is of fundamental importance to understand soil fertility and soil microbiology.

Atmospheric OM-inputs from atmospheric aerosol are in some European regions in the range of 10-40 kg C ha<sup>-1</sup> yr<sup>-1</sup> and are therefore similar to C outputs from many soils through seepage. An atmospheric input is the most important source in the case of some substances. However, little is known about origin and composition of this OM and its fate in soils and waters. This OM input should therefore be considered, since its contribution may be important.

V5. *What is the role of DOM in geo-chemical cycles such as carbon sequestration?*

DOM at any one sampling time is a relatively small pool, but it is constantly replenished. C-mineralisation as well as C-sequestration in deeper soil horizons and in aquatic sediments probably occurs mainly through fixation, precipitation or sorption of previously bio-available and labile DOM. Therefore, although the quantity of DOM is small, compared to the SOM pool and to C-fluxes (litter fall and respiration) in the terrestrial or global carbon cycle, it is an important bottleneck with respect to the transformation and transport of highly decomposable organic compounds to a biological stable SOM fraction. In the aquatic environment, the reaction products of photochemical reactions of DOM are also of relevance as greenhouse gases. DOM catchment studies (see question V3) have a great value in giving information as to what processes are of importance.

Furthermore, DOM plays an important role in the relocation of nutrients (N, P, S), metals (Al, Fe) and trace elements. Some of these processes, such as podzolisation, are well understood, while others are lacking systematic investigations. This central role of DOM makes it very suitable as an indicator. A change in DOM would mean that something different is happening. Naturally we need to know what “normal” DOM (structure and function) for a given ecosystem is. This brings us back to questions V1 and V2.

**Mechanisms** (summarised by Á. Zsolnay)

*M1. Are different DOM fractions (ex. mobile vs. non-mobile) effected differently by perturbations (e.g. drying, freezing)?*

DOM is influenced without doubt by almost all perturbation, but different DOM fractions are most likely influenced differently. It is important to understand this. For example in questions dealing with water quality, the mobile DOM and not the *in situ* DOM is of importance, while in our understanding of environmental gas production, the key DOM role is played by the *in situ* fraction. If such differences are truly present, there are several mechanisms, which could account for this. Almost all perturbations effect the micropores least, since they contain no biota and are only rarely dried out. The general consensus was that such differentiations do indeed exist, but experimental proof is definitely lacking.

*M2. Under what conditions can DOM become colloidal, flocculate out or become adsorbed to the solid matrix? Are these processes reversible? Do they result in a change in DOM function?*

Like most organic fractions in the environment, DOM tends to be anionic. Therefore lower pH and/or the presence of polyvalent cations will encourage it to enter into a less soluble or insoluble state. Such alterations probably also occur when the DOM becomes more concentrated or when it is exposed to higher ionic strengths. It was generally felt that the use of the terms micelle or pseudo-micelle formation were inappropriate to describe this. Such a change of state will logically change the functionality of DOM. For example bound DOM can no longer have a function in the co-transport of a pollutant. The general feeling was that the above processes were reversible to a limited degree. Again experimental evidence is lacking.

*M3. How is DOM's in situ behaviour altered by the presence of specific cations?*

As mentioned within M2, DOM tends to be anionic. This is also the case for most of the clay minerals (excluding the allophanes), which are present in most European soils and sediments. Although many clays may have cationic edges, DOM's binding to the immobile soil matrix is strongly influenced by the presence of polyvalent cations. Furthermore this binding is selective. That is to say not all portions of the DOM fraction are bound equally well. Therefore, the presence of specific cations will alter the composition and thus function of DOM *in situ*. Even if DOM remains in solution after binding to cations, it is to be expected that such functions as co-transport and the ability to cross biological membranes will be effected.

*M4. How is DOM's in situ behaviour altered by the presence of specific nutrients?*

It is to be expected that the presence or absence of certain nutrients will affect the microbial population, and its ability to utilise DOM. This can then result in selective alteration of DOM composition and therefore of DOM function. Presumably such processes are most dynamic in the rhizosphere. The possible processes can most likely be best investigated with the simultaneous use of both chemical and molecular biological analytical tools.

*M5. Can DOM be used as a signal for negative environmental impacts?*

Since DOM is the most dynamic, non-living soil fraction, it would be reasonable to assume that this is true. This has indeed been found to be the case in studies dealing with the effects of the clear cutting of forests and of increased CO<sub>2</sub>. Also, in some studies it has been found that DOM metabolism is inhibited in pollutant impacted soils. Increased DOM values can also be indicators of eutrophication in aquatic systems.

M6. *What are the mechanisms for DOM pollutant interactions*

- ◆ Physical?
- ◆ Covalent bonding?
- ◆ What is the possible role of cations?
- ◆ How is the bioavailability of DOM associated pollutants effected by these different interactions?

DOM, because of its water solubility, must have numerous polar components (*e.g.* carboxylic, hydroxy, and amino groups). On the other hand, it can also have hydrophobic microenvironments caused by alkyl chains, phenyl rings, *etc.* This is sufficient to explain the ability of DOM to make hydrophobic pollutants more soluble, without the need of a micelle formation theory. Chemical bonding would be more likely to occur with pollutants containing functional groups or with metals. What is often not considered is that binding is a competitive process. Therefore, one should only expect DOM-pollutant interactions only when a high affinity or irreversible binding is present, since the concentration of water and/or solid material is so much greater than that of DOM. Despite a very large quantity of publications, the occurrence and relative importance of these binding mechanisms under natural conditions have not been sufficiently clarified, since most of the research done has been under rather unnatural conditions or has used DOM, which does not reflect the function of naturally occurring DOM. For example it is rather unlikely that an alkali extracted fulvic acid, despite its water solubility, will reflect *in situ* DOM pollutant interactions. Cations can compete with metal binding and also alter the conformation of DOM in regards to hydrophobic binding. Similarly when DOM is in a more concentrated state self-interactions can be expected, which will again tend to block functional groups and perhaps therefore encourage more hydrophobic binding. In order to understand and model DOM's function in pollutant and bioavailability studies, more research dealing with the distribution coefficients between DOM and pollutants is needed.

M7. *How do microbes change the function of DOM?*

Microbes are certainly a source of much of the DOM in that their extracellular enzymes transform material into a soluble state, which they can then incorporate. This solubilised material will vary, depending on the type of microbes and on the food source. This in turn results in DOM with different functional properties. Special sources of labile DOM are the secretions or the lysis of microbial cells under stress conditions such as freezing and drying. This labile material can then fuel microbial activity in other areas. Since microbes in smaller pores are better protected than those in larger ones, one can envision a shift of microbiological activity from larger to smaller pores, where certain processes such as denitrification are presumably more likely taking place. Briefly microbes can alter DOM, resulting in a change in microbial activity. On the other hand the metabolism of DOM is presumably selective and should result in an enrichment of more refractory DOM, which is more condensed and which would have other properties in regards to pollutant interactions than the original DOM.

M8. *Is any part of DOM non-degradable or is it only protected through inclusion in micropores?*

The general feeling of the Workshop participants was that no part of the DOM was truly non-degradable. Both biochemical degradability and physical protection play a role and result in a dynamic alteration in the composition of DOM. In the former case obviously amino acids and carbohydrates would be more rapidly removed than humified material, which by definition has already been exposed to decomposition processes. In that sense it is of interest to compare DOM behaviour in aquatic, saturated, and unsaturated systems, where the influence of physical protection ranges from minimal to highly important.

*M9. Can microbial films be a source of DOM?*

This is essentially unknown, but since the films are not enclosed within a cell wall, it would be expected that they could provide a steady source of DOM. Furthermore since the films are certainly enriched in carbohydrates and perhaps in amino acids, it can also be postulated that they can be a replenishment source for this rather labile material in the DOM fraction.

*M10. What are the interactions between DOM and the rhizosphere?*

This is experimentally very difficult to investigate. How does one obtain rhizosphere DOM? Nevertheless, there have been several studies indicating that something like 5 to 10% of the carbon fixed by photosynthesis enters the soil through root processes. Furthermore, the rhizosphere is microbiologically a very dynamic area, and one would expect considerable and rapid modification of rhizoexudates. The function of the root produced DOM, and its interaction with the bulk soil organic matter is still only poorly known. Some research has indicated that DOM can improve nutrient uptake by plants.

*M11. How can we clarify the interaction between DOM and*

- ◆ *the solid soil organic matter (SOM)?*
- ◆ *the inorganic soil matrix?*

These are key questions, since DOM is a continuum. There is no sharp distinction between the dissolved (DOM) and the solid matrices. There have been adsorption studies between DOM and the solid matrices present in soils and sediments. However, it is not clear to what extent they reflect *in situ* conditions. The partitioning between phases is partially concentration driven, and the *in situ* concentration of DOM is unknown. Furthermore, microbial activity may also play an active role in such a partitioning. A large factor in this are the extracellular enzymes. The activity of which may also be influenced by the composition of SOM and the inorganic matrix. Another unknown factor is to what degree clay and oxide particles can have a heterogeneous catalytic effect on DOM. Conversely the adsorption of multifunctional organic molecules, such as DOM, can alter the surface properties of the inorganic particles. It is conceivable that DOM can also enhance the mobilisation of such inorganic particles.

*M12. By what mechanism does DOM play a role in environmental gas production?*

When DOM is catabolised, CO<sub>2</sub> is released and O<sub>2</sub> is decreased. Where oxygen is depleted denitrification is encouraged, and DOM can serve as an electron donor, resulting in the production of N<sub>2</sub>O. The complexity of this process has usually resulted in only poor correlation between DOC and environmental gas production. It must also be kept in mind that a portion of DOM is only slowly metabolised and probably does not play a role in gas production. Whether or not DOM is involved in the CH<sub>4</sub> cycle is largely unknown.

*M13. What is the role of DOM in microsite processes?*

Microsites in soils and sediments have their own environment, resulting from the constricted exchange of material between them and the bulk soil or sediment. Therefore, their unique processes can only be “fuelled” by substances capable of diffusion such as gases and DOM. As a result it can be assumed that DOM plays a crucial role here by transporting into these sites either substrates, which can be utilised for the production of trace gases in oxygen deficient environments, or by co-transporting pollutants, which may either become physically protected or broken down through fermentation type processes.

**Statistical Information**

The 19 participants came from 11 different European countries: Belgium, France, Germany, Hungary, Italy, Norway, Poland, Spain, Switzerland, The Netherlands, and United Kingdom. The two potential participants recommended by the ESF had initially intended to attend but had to cancel due to unexpected conflicting commitments.

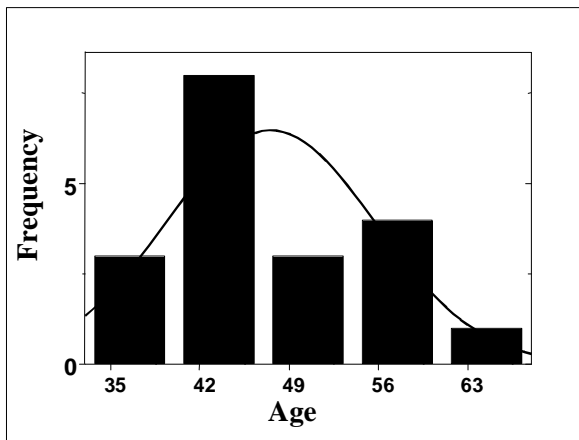


Fig. 3. The venue of the Workshop, Schloss Hirschberg.



Fig. 4. ESF-DOM-Workshop Participants

The average age was  $47 \pm 9$  years. The median was 44 years.



Four female scientists were invited. Unfortunately because of other commitments or for medical reasons, only one could attend.

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