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**THE IMPORTANCE OF NATURAL ORGANIC
MATERIAL FOR ENVIRONMENTAL PROCESSES
IN WATERS AND SOILS**

(Technical Report)

Prepared for publication by

W. KÖRDEL¹, M. DASSENAKIS², J. LINTELMANN³ AND S. PADBERG¹

¹Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, Auf dem Aberg 1, Grafschaft, D-57392 Schmallenberg, Germany

²Department of Chemistry, Section III, University of Athens, 15 Athens, Greece

³Institut für Ökologische Chemie, GSF Forschungszentrum für Umwelt und Gesundheit, GmbH, Postfach 1129, 85758 Oberschleissheim, Germany

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The importance of natural organic material for environmental processes in waters and soils (Technical Report)

Abstract: The role and function of natural organic material (NOM) for the terrestrial and aquatic environment is strongly related to nutrient availability for plants, relevant for crop production, as well as to be a source of energy for macro- and microorganisms, to influence physico-chemical conditions of soil and sediments and to buffering and exchange capacity, relevant for the immobilization and mobilization of environmental pollutants. This article will review the available information about the importance of natural organic material for environmental processes in water and soil. After explaining general terms regarding natural organic material and its chemical structure and presenting the actual state of analytical methods, interactions between environmental variables and the natural organic material as regards its formation and behaviour, as well as interactions between natural organic material and the fate of pollutants in the terrestrial and aquatic environment are discussed emphasizing some relevant processes such as sorption, mobility and bioavailability. Finally some aspects on modeling such processes are presented.

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1. INTRODUCTION

Research results show that natural organic material (NOM) occurring in the terrestrial and aquatic environment influences the behaviour of contaminants. Examples range from reduced solvent extraction efficiency in analytical measurements through to changes in adsorption behaviour and organism uptake. Natural organic material occurs in the solid and aqueous phase of the terrestrial and aquatic environment in various kinds of structure, binding and state of solubility:

- | | | |
|--------------------------|--|---|
| terrestrial environment: | <ul style="list-style-type: none">• solid phase of soils• soil water:• groundwater | <ul style="list-style-type: none">• interstitial water• drain and seepage water |
| aquatic environment: | <ul style="list-style-type: none">• surface water:• sediment: | <ul style="list-style-type: none">• freshwater• sea water• solid phase• interstitial water |

As regards the solubility of organic substances in the aqueous phases of the terrestrial environment (soil water) as well as of the aquatic environment, the natural organic material (NOM) can be divided into two categories: dissolved (DOM) and particulate (POM) organic material [1]. The latter embraces material having a diameter greater than 0.5 μm , whereas the former includes true dissolved matter together with colloidal material passed by a 0.5 μm membrane filter. Taking the content of total organic carbon (TOC) as basis for definition of the content of organic material the dissolved fraction (DOC) is measured as units of carbon instead of units of dry residue for DOM.

Comparing the content of total carbon in terrestrial and marine environments, humic substances (soil organic matter) in soils make out 2500×10^{12} kg, while humic substances in marine environments (marine humus) reach about 3000×10^{12} kg [2].

Physico-chemical processes in the environment affect interactions between the aqueous and solid phases as well as between the terrestrial and aquatic environment. Such processes like formation, transformation and transportation of organic material are correlated to sorption effects between organic substances and other compounds. They are mainly responsible for the mobility, transport and availability of various pollutants in the environment. This aspect is preferably discussed for the aquatic environment. As regards the terrestrial environment more attention should be paid to the role of the dissolved fraction of organic material for transport of pollutants. This is also quite important for cropland and grassland soils, which are used for food production, but which are also artificially treated by man as regards the water balance (irrigation, drainage), the fertility (content of minerals and nutrients) and the control by pesticides and herbicides.

2. CHARACTERIZATION OF NATURAL ORGANIC MATERIAL (NOM) AND ITS CHEMICAL STRUCTURE

The content of natural organic material occurring in the terrestrial environment as well as in aquatic systems is defined as all withering material from plants and animals and their degradation products. Those organic compounds are all compounds containing carbon with the exception of carbon dioxide (CO_2), carbonates, carbide and metal cyanides.

Therefore, in various studies the total content of organic material is also expressed as the content of the total organic carbon (TOC), i.e. the total content of organic bonded carbon. Using this definition, TOC is measured as unit of carbon from total substances, in contrary to the content of total organic material (OM), which is measured as unit of volume.

Degradation compounds can be categorized as biopolymers, which are predominantly polysaccharides and polypeptides, and as geopolymers (humic substances), which are random polymers of a variety of biological monomers [3].

Humic substances are dark-coloured high-molecular substances. They form small aggregates ($< 2 \mu\text{m}$) on a specific surface. Water and other molecules as well as ions can be taken up reversibly.

According to their behaviour in aqueous solution at different pH-values, the humic substances are mainly divided in three groups:

- | | |
|--------------|---|
| humic acids | • the acid components of humic substances, which are soluble in bases, but precipitate in acids |
| fulvic acids | • the acid components of humic substances that are soluble in both, bases and acids |
| humins | • the components of humic substances that are soluble neither in bases nor in acids |

These fractions differ in colour, C- and N-content. From fulvic acids beyond humic acids to humins the solubility in water as well as acid and reductive properties decrease while their molecular size increases (for detailed information see Scheffer/Schachtschabel [4]).

Under natural conditions humic substances do not occur in real solution. Due to their chemical and physical behaviour, particularly due to their solubility, they are soluble as colloids [5].

From a geochemical point of view, organic matter may be subdivided into different groups according to its behaviour upon treatment by various solvents [6]:

- substances extractable with organic solvents, such as benzene, ether and chloroform, are commonly known as bitumen;
- the bitumen free or insoluble organic matter is frequently referred to as kerogen;
- humic acids extracted when the organic matter is treated with weak alkali solution;
- the component of the original mass that remains after the extraction procedures described above referred as residual organic matter.

The structure of humic substances is strongly related to the biological components from which they are formed. The greatest difference among these biological components is between those of marine and terrestrial environments. Terrestrial humic acids which are generally derived from lignin are more aromatic than marine humic acids, while marine humic substances have more protein and carbohydrate residues, which are the main components of marine algae. The low molecular weight humics are more prevalent in sediments and in river and sea water, while heavier ones predominate in soils [7].

The general molecular structure of aquatic humic acids may consist of (a) single aromatic rings with mainly three to six substituents as alkyl side chain, carboxylic acid, ketone or hydroxyl groups, (b) short aliphatic carbon chains, (c) polycyclic ring structures including polynuclear aromatic-aliphatics and fused rings involving furan and possibly pyridine. These structural features are present in rather generalized forms and are not exclusive. For example the aromatic segments may include a variety of isomers in different substitution patterns, or the polycyclic structures may not be limited to two or three big ring systems [8].

Fulvic acids, the most hydrophilic of several classes of geopolymers, have a wide variety of aromatic and aliphatic structures bearing many oxygen-containing functional groups, particularly $-\text{COOH}$ and $-\text{OH}$. These functional groups, which can be protonated and deprotonated, enable fulvic acids to behave as a polyelectrolyte [3].

Intermolecular interactions between humic molecules and intramolecular interactions between a molecule's functional groups change the chemical and physical properties of humic material in different aqueous environments. These interactions control the self association and ultimately the size, shape and polarity of humic substances. Both, non polar and polar interactions are thought to be responsible for the self aggregation of humic material although non polar interactions are thought to be insignificant for the humic and fulvic acids. Molecular interactions of DOM are dependent on temperature, pH, ionic strength and type of ions in solution as well as other chemical parameters. For intermolecular interactions the concentration of DOM is also important [9].

3. ENVIRONMENTAL VARIABLES INFLUENCING THE FORMATION AND BEHAVIOUR OF NATURAL ORGANIC MATERIAL

3.1 Formation and origin of natural organic material

3.1.1—in soils

All withering material from plants and animals and their degradation products which are in and upon the mineral soil belongs to the organic matter in soils.

Primary materials are

- biomass from green plants produced by photosynthesis, which falls down onto the surface (litter);
- withered roots;
- organic secretions from plant roots and micro-organisms;
- corpse of soil animals and micro-organisms;
- in agricultural soils e.g. also residues from harvest and through manuring.

The most important substance groups for humification are pectins, celluloses, hemicelluloses and lignins as elements of cell walls, proteins and related N-substances, sugars and polysaccharides as substances of cells as well as minerals. In smaller amounts fats, waxes, tanning agents and dyes are found.

In the soil profile the extent of degradation and humification decreases from top to bottom. Mineralization and humification proceed in three phases. The first phase starts just before or directly after withering of the organism by enzymatic reactions. In the cells highly polymer substances are decomposed into separate elements by hydrolysatation and oxidation in enzymatic reactions (e.g. starch into sugars, amino acids are split off from proteins). A part of the mineral nutrients like Fe, K, Mg are released and can be washed out with the rain water.

In the second phase the biomass is reduced to small pieces by organisms of the macro- and mesofauna. During this process the ground plant residues on the soil surface are worked into deeper soil layers. Passing through the intestine especially of earthworms the residues are digested and mixed intensively with the soil particles ('bioturbation').

The reduced pieces of plant and animal material as well as the excrements from soil animals are converted by micro-organisms in the third phase. Low molecular weight substances like carbohydrates, pectins and proteins are degraded first. During this degradation process the original molecular structure of the biomass is lost.

The degradation products of the litter are inorganic substances (CO_2 , H_2O , etc.) as well as low molecular weight organic acids. In anaerobic areas degradation to these organic acids increases, and hydrocarbons and hydrogen are produced. The degradation time depends on the living conditions of the soil organisms (temperature, water and oxygen content, nutrient content) [4, 10–12].

The formation of chaff throughout the year depends on climate (temperature, precipitation, altitude, etc.), the conditions in the soil and the type of vegetation [13] and cultivation. The production of biomass is highest in forest. In agricultural soils biomass production depends on the harvest. One part of the organic material attaining to the soil is mineralized quickly while another part is humified and degrades over decades. The rate of both reactions depends on the living conditions of the soil organisms. The mineralization is stimulated by frequent changes of soil humidity. During these processes aggregates decompose and on the other hand organic substances are desorbed [4].

In long-term experiments under different management conditions it was found that intensive soil management leads to less active humus [14].

3.1.2—in freshwater systems

Rivers integrate biogeochemical processes occurring in their entire drainage basins and thus contain organic matter synthesized and degraded in both, the terrestrial and aquatic environments.

Three major components of organic matter can be identified: The refractory allochthonous material, the relatively labile autochthonous contribution and the anthropogenic input to the river. Relatively few characterizations of major biochemical compounds like carbohydrates, proteins or lignins have been made [15, 16].

During the humification process of organic matter increases are observed in the aromatic character of the material and in carbon content, furthermore, condensation of unsaturated aliphatic chains with each other, decreases in hydrogen content, and increases in carboxyl and methoxyl contents. For aquatic humic matter carbon, hydrogen and nitrogen contents normally diminished with increasing molecular weight of the material; for oxygen the reverse was usually true. Aquatic fulvic acids are richer in oxygenated groups than soil ones. Fulvic and humic acids of aquatic origin resemble each other more closely than their terrestrial counterparts. Low molecular weight fractions of aquatic fulvic and humic acids would appear to have a very similar basic carbon structure. Whereas higher molecular weight humic matter fractions normally have a more aromatic structure than low-molecular weight fractions in fulvic acids of microbial origin, an increase in aromaticity was noticed towards the lower molecular weight range. The degree of humification of humic matter present in natural waters was found to increase in the course of the summer season [17].

3.1.3—in the marine environment

There are four main sources of organic carbon in the marine environment [18]:

1. From the land: organic materials from the land are transported to the sea by both wind and rivers, the latter being quantitatively the more important.
2. Production of organic matter by the decay of dead organisms: the decay of dead organisms occurs by two mechanisms: autolysis and bacterial action. In nature both mechanisms will act together, the extent of each varying according to the conditions of death and to the availability of the necessary enzymes and bacteria.
3. Excretion of extra cellular products by algae: algae liberate appreciable proportions of the compounds produced by photosynthesis into the surrounding water.
4. Excretion by marine animals: excretions of zooplankton and marine animals may be an important source of dissolved organic matter.

Aquatic humic substances contribute about 40–60 % of DOC and are the largest fraction of natural organic matter in waters [19]. They are formed by random condensation of degradation products of plants and algae. According to their composition they can be classified as of allochthonous (terrestrial) and autochthonous (aquatic) origin [20].

Much of the colloidal organic matter in sea water is largely uncharacterized with a complex and probably variable structure. The amounts of both POM and DOM are usually smaller than the corresponding amounts of inorganic material. The amount of the DOM in sea water usually exceeds the POM fraction by a factor of 10–20.

The POM in the sea comprises both living organisms (mainly phytoplankton) and detritus [21]. The relative proportions of these two classes vary with depth and location. POM is an extremely important part of the marine food chain as it provides food for organisms at several trophic levels, but also is the first step for bioaccumulation of pollutants.

The composition of the organic matter depends on the sedimentary environment. As described by Leenheer [22] it might be influenced by salinity changes, dissolved oxygen changes, seasonal changes that affect primary and secondary productivity, temperature, allochthonous inputs, hydrologic variables, and anthropogenic inputs.

Marine productivity might also be controlled by the presence of biologically active substances which are excreted by the lower forms of marine life and either promote (Thiamine, biotin, vitamin B₁₂) or inhibit (antibiotics, toxins) growth. Lipid molecules exhibit great specificity as indicators of contribution from marine algae, terrestrial vegetation and bacterial sources as they are remarkably stable in sediments and permit the investigation of historical records through the study of sediment cores. Steroids are another class of biogenic compounds which may serve as an indicator of processes transforming organic matter in sea water and sediments.

3.2 Behaviour of natural organic material in the environment

Natural organic material, particularly humic substances as their degradation products, are of special relevance for the terrestrial and aquatic environment because of their physio-chemical attributes and their interactions with other natural compounds and with contaminants. Due to reciprocal effects with various kinds of substances humic substances are considerably reactive. Sorption processes and solubility, mobility and accumulation effects are important for the equilibrium of the terrestrial and aquatic environment.

3.2.1 – in soils

Organic material, particularly humic substances, are characteristic substances of soils where they are mainly produced and where they mainly effect. They are strongly influencing the soil quality. Influences on increase of soil temperature, on water capacity, on the maintenance of soil structure and stability as well as effects such as buffering are responsible for the mobility and availability of trace elements [23].

The behaviour and importance of humic substances are mainly discussed for forest soils. But also for those terrestrial ecosystems, which are of agricultural relevance, humic substances should not be disregarded. Particularly in these ecosystems humic substances are important as regards the sorption and solubility of toxic compounds due to their input by pesticides and by fertilizer.

Table 1. Content of organic material in soils with various cultivation:

cultivation	organic material in the upper floor (%) (a)	organic material in 1 m depth (dt/ha) (a)	organic material (kg/m ²) (b)
deciduous forest	4	2000	17
coniferous forest	6	2400	21
grassland	7	3500	30
cropland	2	1600	15

(a) Schröder [24]

(b) Scheffer/Schachtschabel [4]

The content of organic carbon of grassland soils is substantially higher than that of forest soils. Some reasons for this are given by Stevenson [2]:

1. larger quantities of raw material for humus synthesis are given under grass,
2. nitrification is inhibited in grassland soils, thereby leading to the preservation of nitrogen and carbon,
3. humus synthesis occurs in the rhizosphere, which is more extensive under grass than under forest vegetation,
4. inadequate aeration occurs under grass, thereby contributing to organic matter preservation,
5. the high base status of grassland soil promotes the fixation of NH₃ by lignin and thereby conservation of nitrogen and carbon.

A combination of several factors is probably involved, with item (3) being of major importance. Reid and Goss [25] found that decomposition rates for organic matter were reduced in the rhizosphere of corn and perennial rye.

In the case of forest soils, differences in the profile distribution of carbon and nitrogen occur by virtue of the manner in which the leaf litter becomes mixed with mineral matter. In soils formed under deciduous forests on sites that are well drained and well supplied with Ca, the litter becomes well mixed with the mineral layer through the activities of earthworms and other faunal organisms. In this case, the top 10–15 cm of soil become coated with humus. On the other hand, on sites low in available Ca, the leaf litter does not become mixed with the mineral layer but forms a mat on the soil surface. An organic-rich layer of acid humus accumulates at the soil surface and humus accumulates only in the top few cm of soil.

Marked changes are brought about the C and N content of the soil through the activities of man. Usually, but not always, organic C levels decline when soils are first placed under cultivation. A new equilibrium is reached which is characteristic of cultural practices and soil type. Increases in plant yield brought about by improved varieties, more widespread use of fertilizers, or adoption of better management practices would be expected to have a positive effect on equilibrium levels of organic matter in soil through return of larger

quantities of plant residues. However, the increase will generally be slight. For most soils, organic matter can only be maintained at high levels by inclusion of a sod crop in the rotation or by frequent additions of large quantities of organic residues.

In undisturbed (uncultivated) soils, considerable migration of organic matter occurs into the lower soil horizon during the soil development, often in association with clay and polyvalent metal cations. The transport of organic material is mainly a result of leaching by downward seepage. The mobility of the transported organic material and therefore its distribution in soil profile depends on the solubility and on sorption and desorption effects (see below). Transfer of organic matter into the lower soil horizons can continue for some time after equilibrium levels are reached in the surface layer. Eventually, the total quantity in the profile stabilizes and remains essentially constant over time. In addition to leaching, organic matter can be transported downward in soil through the action of animals. Earthworms, for example, can completely mix soil to depth of a meter, transferring organic matter downward in the process. Burrowing animals move soil material low in organic matter from the deeper horizons to the surface and vice versa [2].

Specific binding effects occurring in soils produce compounds of humic substances with clay minerals. One part of the mineral components in soil is associated to the organic substance to form stable organo-mineral compounds by the following interactions: van-der-Waals, hydrophobic bonding, charge transfer, hydrogen bonding, ligand exchange, ion exchange, ion-dipole and dipole-dipole forces, and chemisorption. For further details about the binding mechanisms and properties see e.g. Stevenson [26], Hamaker and Thompson [27], Theng [28], Baker [29].

60–90 % of the total organic carbon in soils occurs as organo-clay complexes [5]. The organo-mineral compounds are important for chemical reactions in soils because humic substances associated with the clay minerals are fine spreaded, and therefore they are more reactive than other systems [23].

The interactions between the solid phase of soil (soil matrix) and the soil solution are important for the transport of humic substances and complexed compounds (see chapter 5.) within the soil profile and to the groundwater level as well as for the availability of nutrients. Microorganisms and the roots of plants mainly absorb nutrients from soil solution. The sorption of humic substances to the solid phase of soils or their desorption and their solubility in soil solution is strongly related to acidity conditions. More acid conditions are entailing desorption effects. This concerns humic substances as well as compounds sorbed by humic substances. The effects of acid precipitation on the displacement of humic substances and the availability of desorbed compounds are obvious.

Due to their large surface humic substances are important for the water storage capacity in soils as well as for the exchange capacity, buffering and sorption of nutrients. These effects are strongly related to sorption mechanisms. The buffer capacity of soil material enriched with humic substances is based on the adsorption of organic and inorganic cations, anions and of neutral molecules available in soil solution by humic substances. These compounds are precipitated after reaction, and acids are neutralized [30].

The content of organic matter is important for crop production. Humus contributes to the fertility, or productivity, of the soil through the positive effects on the chemical, physical, and biological properties of the soil. It has a nutritional function in that it serves as reservoir of N, P, and S for plant growth, a physical function in that it promotes good soil structure, and a biological function in that it serves as a source of energy for microorganisms [2].

3.2.2—in the marine environment

The production and destruction of organic matter are primarily biologically mediated. The range of organic compounds may therefore embrace the whole range of cellular, metabolic and decay products. These

Table 2. Indicative concentrations of organic carbon (OC) in the various parts of the marine environment [31]

Organic carbon (mg/l)	River	Estuary	Coastal sea	Open sea		Sewage
				surface	deep	
dissolved	10–20 (50)	1–5 (20)	1–5 (20)	1–1.5	0.5–0.8	100
particulate	5–10	0.5–5	0.01–1.0	0.01–1.0	0.003–0.01	200
total	15–30 (60)	1–10 (25)	1–2.5	1–2.5	0.5–0.8	300

materials play a vital role in marine ecology since they provide part of the energy, food, vitamin and other requirements for bacteria, plants and animals. In sea water hydrophobic organic compounds commonly exist in a micellar or colloid-accommodated state rather than as true molecular solutes.

The carbon cycle in coastal zones has characteristic features such as high biomass, high turn-over rates and larger transfer of organic matter to sediments as compared with the majority of open waters. The organic matter produced in the euphotic zone falls into deeper waters and gradually decomposes. Two primary processes are recognized: biological production as the major source and heterotrophic consumption as the major sink. Particle-solution interactions in the water column are important processes in the cycling of organic matter. A variety of chemical reactions such as oxidation-reduction, carbon-carbon bond formation or cleavage and organic-inorganic interactions are also involved. These mechanisms are related to the reactivity of organic matter and to its solubility.

The extent of recycling and the subsequent accumulation of refractory carbon to the benthic pools depend, however, upon a variety of physico-chemical parameters, primarily the oxic/anoxic environmental conditions. On the other hand the coastal areas are the recipient of many different types of anthropogenic compounds producing interferences or threatening the natural cycles.

DOM is removed from the sea by several processes. The most important of these processes are those in which the breakdown and respiration of this material provides energy and cellular carbon for living organisms and brings about regeneration of CO₂ and nutrients. The heterotrophic bacteria are the principal users of dissolved carbon compounds, although the amount of available organic carbon in the sea is rather limited since most of the DOC present is resistant to bacterial decay.

It is generally observed that sediments below anoxic water contain a higher concentration of organic matter than do those below aerated water. The elevated content of organic matter in anoxic sediments is not a consequence of the anoxic conditions but rather of the higher productivity which produced the anoxic conditions in the first place [32].

In the euphotic zone phytoplankton constitute more than 1/4 of the total particulate matter. The concentration of the POC in this zone is usually considerably higher than in the water lying beneath it. It shows geographical and seasonal variations similar to that of primary productivity because less than 10 % of the primary production enters the grazing food chain. The remainder becomes POM derived from the action of the decomposer network on dead plants. The total POC in oceanic water is always at least an order of magnitude greater than the yearly primary productivity. Beneath the euphotic zone the concentration of POC decreases rapidly and below a depth of approx. 200 m remains more or less constant to the bottom. Bacterial decomposition is thought to be the principal mechanism by which detritus is removed from the water column.

DOM may be incorporated into the food chain by direct uptake or after conversion to POM. It is probable that part of the POM occurring in sea water has been formed by the aggregation of DOM. The aggregates form especially in shallow inshore waters, where the levels of DOM are high. The non-living POM in waters have usually been assumed to be faecal pellets and remains in various stages of disintegration. Many of these particles are delicate plate-like aggregates a few μm to several mm in diameter. They are amorphous and contain both organic and inorganic non living material. The nuclei of such particles can be formed by adsorption of DOC on air bubbles and other surfaces. The initial aggregates tend to increase in size with further aggregation and adsorption [33].

The highest concentrations of OC are found in the surface layers especially of waters on the continental shelf and of regions where nutrients are returned to the surface by up welling. Only in these layers significant seasonal variations occur. Around the base of the euphotic zone the concentrations begin to decrease with increasing depth, at rates which differ from place to place, in accordance with the productivity, and availability of heterotrophic and hydrographic conditions. At depths greater than a few hundred meters the concentrations are relatively constant. This suggest that material present in deep waters are resistant to further metabolic decomposition [18].

POM is not only distributed throughout the water column but also occurs as surface-active films over extensive areas of the sea. These films often considerably modify the physical properties of the sea surface, including the surface tension and viscosity, and lead to the production of slicks which are areas of wave-

damping. They have been shown to be monolayers composed of fatty acids (C_8 - C_{18}), methyl esters of fatty acids (C_{11} - C_{22}), higher aliphatic alcohols ($C_{12,16,18}$) and hydrocarbons [33].

Different surfaces freshly exposed to sea water become covered by a tenacious film of natural surface-active organic material which dominates their subsequent surface chemistry. The macromolecular species and hydrophobic humic material are important contributors to the ambient organic films. Most particles are negatively charged due to adsorbed NOM which can mask the physicochemical properties of the underlying solid [34].

The adsorbed NOM coatings may also render hydrophilic surfaces to hydrophobic, ones, which make them more capable of sorbing organic contaminants. The major mechanisms by which NOM adsorbs onto mineral surfaces have been proposed to involve: anion exchange (electrostatic interaction), ligand exchange-surface complexation, hydrophobic interaction, entropy effect, hydrogen bonding, cation bridging [35]. Organic coatings on clay minerals may greatly affect size distribution and settling rates of inorganic sediments, flocculation at the river/sea intermixing zone and contribute to the ubiquitous increase of organic matter in coastal marine sediments.

The adsorption of NOM onto minerals mainly depends on NOM source and mineralogy, with soil-derived humic materials exhibiting a stronger adsorption to mineral surfaces than aquatic NOM. Hydrophobic attraction seems to be the most important mechanism of NOM interaction at marine interfaces. Unsaturated lipid molecule micelles and aggregates represent the most reactive surface-active materials. They also seem to mediate interaction of other NOM constituents with particles once a monolayer, or its fraction, has been formed [36-38].

The major fraction of the DOC in the sea consists of a complex material which is very resistant to bacterial attack. The minor fraction composed of more labile compounds contains substances representative of the main biochemical classes [38]. Carbohydrates appear to occur in sea water as free saccharides and to only a negligible extent as their derivatives e.g. amino sugars. Dissolved amino acids occur in the sea mainly combined as peptides but also in the free form. Several carboxylic acids have been detected in sea water, including acetic and glycolic and the Krebs-cycle acids.

3.2.3 Interactions between the terrestrial and aquatic environment ⇒ transport and mobility of NOM

Many organic substances are formed in soils and eventually find their way to lacustrine, riverine and estuarine waters (see table 2).

The riverine transport of organic material appears to be related to the annual production in the drainage basin. It arises mainly from the leaching of humic materials and other decomposition products of vegetable matter from the soil. The total export to the oceans has been estimated to ca 4.5×10^{14} g C/y.

Riverine DOC has been suggested to behave conservatively in estuaries and thus has the potential to contribute to offshore marine environments. The total global POC discharge (approx. 2.3×10^{14} g C/y) is thought to comprise an average 35 % labile components with the majority comprising non hydrolyzable refractory material (i.e. 1.5×10^{14} g C/y). It has the potential to accumulate in marine sediments most probably in delta and shelf systems where more than 80 % of present day ocean carbon is thought to be buried.

The transport behaviour of sub components of NOM is influenced by their physical and chemical properties. It is evident that the surface electrical properties of suspended material and the presence of surface oxide or organic films are matters of central importance in the estuarine transport (see table 2) [39-41].

During the transport of dissolved and suspended organic substances from surface to ground water seepage water acts as a solvent and a transport medium. The physical transportation processes are diffusion and dispersion. The mobility of these substances is influenced by dissolution and precipitation, sorption and ion exchange; the chemical processes are accelerated by microbial processes.

Humic and fulvic acids make up 80 % of the DOC. Humic acids show a higher affinity towards particulate adsorption and removal mechanisms than the more degraded fulvic acid fraction. Whereas the humic acid fractions are adsorbed onto particles and undergo removal in estuaries.

The humic substances isolated from water samples of different origins show lower molecular weights and aromaticities than in soils (e.g. [42–46]). When associated with aquatic sediments many types of organic matter are not stable. Simple molecular structures are readily biodegraded while branched and cyclic structures are more resistant. Abiotic processes that transform organic substances and associated contaminants in aquatic sediments include photolysis, hydrolysis, pH change, and various salt effects; also photo-reduction and organic acid oxidation of metals are found [22].

4. ANALYTICAL ASPECTS

Since the recognition of the importance of dissolved organic material (DOM) for most processes in the environment, great efforts have been made to classify, characterize and elucidate chemical structures of this complex class of compounds.

As mentioned above DOM is the term for the dissolved fraction of a broad, complex mixture of natural substances. The constitution of DOM is dependent on the environmental compartment and location. Usually, only a minor part of DOM consists of simple compounds like carbohydrates, carboxylic acids, amino acids and hydrocarbons. The main part is formed by humic substances - coloured, polyelectrolytic acids [47].

Classifications and terms used for DOM and its various compounds or classes of compounds are mainly based upon procedures applied for fractionating this complex mixture of natural substances. As already mentioned above, DOM itself is called the amount of organic carbon in aqueous solutions that passes through a 0.45 μm silver or glass fiber filter, whereas the part of organic compound retained on the filter is called particulate organic matter (POM) [47].

During the years after their classification a number of important analytical methods of studying DOM from soils as well as from water have been established. The mostly used of these strategies shall be outlined here. For a deeper insight a lot of books occupied in the field of humic substance research are meanwhile available [12, 26, 48–57].

For a suitable application of sensitive analytical methods sample pretreatment for fractionating and clean-up are normally a prerequisite. The most difficult part from the analytical point of view are the humic substances on which the scientific interest is mainly focused (Chap. 4.3). The simple small substances can of course more easily be investigated by the methods presented (Chap. 4.1. and 4.2).

4.1 Characterization of the dissolved fraction of natural organic material

Conventional elemental analysis allows the determination of carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur, halogens, ash and elemental ratios. Thus, elemental compositions and differences between DOM of various sources or alterations after chemical treatment can be examined. Parameters like acidity and cation exchange capacity of separated fractions or single compounds can be determined using titration or chemical derivatization.

A further important strategy is the determination of the molecular weight of DOM-fractions. This can be done by gel permeation chromatography, ultrafiltration, small-angle x-ray scattering or by investigating the colligative properties of DOM [58–62]. Normally different methods should be used, and the results which often differ strongly have to be considered critically. The problem is that for most of the methods, e.g. gel permeation chromatography, standards like proteins or polymers with known molecular weight are used. But the different behaviour of these well defined compounds compared to the unknown humic substances can lead to misleading results, as investigations could show [12, 63–66].

NMR-spectroscopy turned out to be one of the most important analytical methods for structure elucidation of DOM. Applying ^1H -, ^{13}C -, ^{15}N - and ^{31}P -NMR-spectroscopy, detailed information about binding characteristics of these elements can be obtained [33, 50–53]. Especially ^{13}C NMR spectroscopy appears to be well suited for obtaining an inventory of the chemical composition of humic materials. Spectra can be obtained in solution-state and solid-state NMR-spectroscopy. Information about the presence of functional groups, aromatic systems or branched alkyl groups can be obtained.

Although the ultraviolet and visible spectra of DOM are not a useful characteristic for structural understanding because less significant bands are detected, they may be of some value in comparing

samples from various sources. An often used relationship is the ratio of absorbances at two wavelengths, 460 and 660 nanometers, the so-called E4/E6 ratio, that has been correlated to molecular weight and to aging or humification. Although these correlations are controversial because different results have been found [58, 67].

'While infrared spectra of humic materials provide worthwhile information on the distribution of functional groups, they tell little about the structure of aquatic humic substances'. This conclusion drawn by Schnitzer and Khan 1978 [12] expresses that one learns the presence of hydroxyl, carboxyl, carbonyl and methyl groups present in humic substances which exhibit characteristic absorption frequencies, but that IR-spectra cannot provide detailed information about chemical structures of humic substances [68].

One promising method that has been pioneered by Schulten [69] and applied to a variety of high-molecular weight natural materials is pyrolysis-soft ionization mass spectrometry. The sample is pyrolyzed directly in the high vacuum of the mass spectrometer and the components derived during this process are investigated by field ionization (FI) mass spectrometry (MS). The method is used for the characterization and identification of major components of biomaterials. The Py-FI mass spectra give an insight into the molecular complexity of humic acids and indicate that these materials contain polysaccharides, proteinaceous materials, n-fatty acids, n-alkanes, n-alkyl esters, phenols and lignin monomers and dimers [69–71].

Chromatographic methods like high performance liquid chromatography (HPLC), gel permeation chromatography (GPC) and gas chromatography (GC) are mainly used for a separation of fractions of DOM. They are sometimes helpful for comparing DOM fractions deriving from different sources. In combination with further analytical methods (e.g. GC-MS) chromatographic separations can provide important structural informations [72].

What is said for chromatographic methods is also true for electrophoretic methods, they are helpful for comparing DOM of different sources but provide little or no structural information. Applied are conventional polyacrylamide-gel electrophoresis or isofocussing (informations about molecular weight and isoelectric points) [73–75]. In recent years capillary zone electrophoresis has grown up allowing high resolution separations in short times and rendering the different kinds of electrophoretic methods better available [76–78].

Chemical degradation methods like permanganate and copper oxidation, chlorine oxidation, periodic-acid oxidation, alkaline hydrolysis, hydrogenation and sodium-amalgam reduction are applied to DOM to obtain structural information on the humic carbon skeleton by simplifying the molecule to specific compounds. The different methods cleave various chemical bonds and yield different products which can be further investigated by the analytical methods outlined above [79–85]. GC/MS seems to be the most powerful analytical tool for identification of simple organic compounds generated in chemical degradation [72].

All the analytical methods described here are of course also useful tools for the investigation of interactions between xenobiotic substances and humic substances.

4.2 Analytical problems arising from DOM (dissolved organic matter)

During the last few years it has been learnt that DOM in environmental samples can cause serious analytical problems. Analysis of trace organic and inorganic compounds requires sample pretreatment prior to analysis which normally includes extraction of the analytes of interest from the matrix and their enrichment.

In the ideal case the analytes are quantitatively separated from the residual matrix including DOM, concentrated in the extract and analyzed by various methods. This ideal case is - especially for organic analytes and metals - never fulfilled. The presence of DOM - especially of high molecular fulvic and humic acids - can evoke two effects: Due to interactions (e.g. ionic, hydrophobic, van der Waals, cf. chapter 5) between DOM and the analytes which are not destroyed during sample processing a quantitative extraction is not possible. The concentration of the substance extracted and analyzed is too low because the part associated with or bound to DOM is lost with the residual matrix. This is especially the case for hydrophobic substances like polycyclic aromatic hydrocarbons (PAH) or chlorinated hydrocarbons [85, 86].

On the other hand some fractions of DOM are co-extracted during sample processing leading to interferences, which can effect seriously the analytical determination. This observation was often made for more polar chemicals like pesticides but can also be found for lipophilic compounds [87–89].

Amount and extent of the problems shortly described depend on the analytes, composition of the sample (e.g. content of DOM) and last but not least on the kind of sample processing and analytical determination chosen. Since the recognition of these effects some efforts have been made to understand principal mechanisms as well as to avoid the problems by various techniques like on-line dialysis for quantitative removal of DOM prior to analysis [87] or using selective extraction procedures for destroying non-covalent interactions between DOM and the analytes [85].

The problems that can arise from the presence of DOM must be kept in mind interpreting analytical results found for environmental samples.

4.3 Analysis of humic substances

The first step of analysis of humic substances in soil is their extraction from the matrix. According to Stevenson an ideal extraction method should fulfill the following criterions [26]:

It should allow the isolation of unaltered material.

- The extract should be free of inorganic contaminants such as clay and polyvalent cations.
- The extraction should be quantitative, ensuring representation of fractions from the entire molecular-weight range.
- The method should be applicable to all types of soil.

To reach this objective various extraction methods have been examined and published since 1986 when Archard first proposed the use of dilute aqueous NaOH solution [90]. The extraction with alkali has been criticized from time to time because, dependent on the soil, it can influence and alter the humic substances e.g. via oxidation. Nevertheless it is the most employed method still today because it is very efficient.

Younger techniques like extraction with $\text{Na}_4\text{P}_2\text{O}_7$, organic solvents or supercritical fluids were established to overcome the disadvantages of dilute alkali and to increase selectivity [91–93].

The crude extracts obtained after extraction of humic substances from soils or water can be further subdivided into various fractions applying mainly chromatographic separation techniques. The most powerful tools for this purpose seem to be adsorption chromatography with XAD-resins, ion-exchange chromatography with weak-base ion-exchange resins, gel permeation chromatography, cation-exchange chromatography.

The theory of resin adsorption is that the hydrophobic part of the humic molecule sorbs into the resin matrix, the functional groups on the molecules are oriented to the water phase. The adsorption interaction is a relatively weak force, thus it is easily reversible. Desorption and elution of groups of components is accomplished by changing the pH of the solution.

Weak-base ion exchange chromatography is a helpful method because it is based upon the types and amounts of functional groups of humic substances. The weak-base resin works as an ion exchange material at pH 6 or below. At this pH, the resin contains a positive charge and is an anion exchange resin. At a pH greater than 7, the resin losses the positive charge and is neutral. This kind of material is highly selective for phenolic functional groups.

Cation exchange chromatography is important because it removes sodium and calcium from the humic extracts and saturates the humic substances with hydrogen atoms. During this chromatographic procedure also trace metals and other cations associated with the humic material are removed.

Gel permeation chromatography is mainly used for a characterization by molecular weight, but of course can also be used for collecting the fractions which differentiate because of their molecular weights [94, 95]. DOM can be quantified, as a whole or in single fractions after chromatographic separations, by oxidation to CO_2 which is measured by infrared spectrometry [96, 97]. Other techniques like fluorescence or ultraviolet absorption are used for selective detection of functional groups of DOM [94].

5. BEHAVIOUR OF ENVIRONMENTAL POLLUTANTS INFLUENCED BY NATURAL ORGANIC MATERIAL

5.1 Interactions between NOM and environmental pollutants

As it was previously described, NOM is a complex mixture of organic solutes and macromolecules, and possibly aggregates of those components that result from degradation and subsequent repolymerization of plant material. It is not surprising that different components of such a complex mixture display different behaviour with respect to binding of contaminants.

For example, hydrophobic organic contaminants have a much greater affinity to bind to hydrophobic components of NOM than to hydrophilic fractions of the same NOM. Likewise affinity for complexation of metals and radionuclides has been associated with more polar NOM that is rich in acidic functional groups. [98, 99]

The sorption of heavy metals by humic substances is mainly based on complexation and for organic pollutants on adsorption effects. Interactions between solid and liquid phases in soils and aquatic systems result in sorption and desorption, accumulation and mobility (transport) of pollutants. Sorption and mobility of heavy metals, for instance (see Chap. 5.2), are also strongly influenced by both, the soil organic matter and the concentration of DOM in soil solution. Using electro-ultrafiltration of aquatic soil extracts, the major part of the heavy metals was found to be bound to DOC moving to the anode.

Mobility of adsorbed contaminants like organic pollutants or organo-metallic complexes like heavy metals by NOM results in their transport within the soil system as well as in transport between terrestrial and aquatic systems and the transport within the natural aquatic system.

After describing the principle chemical and physical mechanisms of the interactions between NOM and environmental pollutants causing the sorption and mobility of heavy metals (chapt. 5.2.1) and organic contaminants (chapt. 5.3.1.) in soil systems as well as in aquatic systems, for both groups of pollutants some relevant effects of these interactions for the terrestrial and the aquatic environment are discussed.

Binding of environmental contaminants to dissolved humic materials not only affects transport and aqueous concentration of pollutants, but it can also influence chemical degradation, photolysis, volatilization, toxicity, and bioavailability (see chapt. 5.4.).

5.2 Sorption and mobility of heavy metals

Contrary to organic contaminants heavy metals in the terrestrial environment occur as natural components of minerals of parent rocks. The anthropogenic input of heavy metals to the terrestrial and aquatic environment mainly results from wet and dry deposition. Cropland soils are additionally contaminated by fertilizers and sewage sludge. Heavy metals are transported into groundwater as well as into freshwater systems and the marine environment due to the mobility of the ionic form and of metal-organo complexes. Aquatic systems are additionally contaminated by waste water release.

5.2.1 principles

Metal ions react with organic dissolved components and particles in various ways. Many books and review articles have dealt with the different aspects of the interactions. The main publications are those by Buffle, Tessier, Lund, Florence, Frimmel, Campbell and Driscoll (e.g. in Broekaert *et al.* [100]).

Metal association with organic materials can affect their chemical state and availability in natural waters. Among other characteristics, organic materials mask metal toxicity to phytoplankton, increase metal solubility and act as metal buffers via their so-called 'complexation capacity' [101].

The order of bonding strength for a number of metal ions onto humic or fulvic acids is $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$, whereas the sequence of complexing capacity is: $\text{Pb} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$ [102].

Organic surfaces for metal sorption may arise from organisms such as bacteria and algae by the breakdown of plant and animal material, by the condensation of lower molecular weight organics and by lower molecular weight organic matter sorbed onto clay minerals or metal oxide substrates. Although the

differences between these surface types are not well understood with respect to trace metal uptake, at least one major binding mechanism involves salicylic entities; other stronger binding entities (such as peptides) may also be present in some systems, since part of the organics adsorbed onto the particulate matter has carboxylic and phenolic functional groups available for binding with trace metals. The trace metal adsorption capacity of organic matter generally ranges between the sorption capacity for metal oxides and clays [103–105].

Dissolved organic substances are capable of: (1) complexing metals and increasing metal solubility, (2) altering the distribution between oxidized and reduced forms of metals, (3) reducing metal toxicity and altering metal availability to aquatic life, (4) influencing the extent to which metals are adsorbed on suspended matter, (5) affecting the stability of metal-containing colloids [106].

The attractive forces between metal ions and soluble, colloidal or particulate organic material range from weak physical adsorption (ions are easily replaceable) to strong metal chelation by organic material (indistinguishable from chemical bonds). Increased use of natural and synthetic complexing agents can form soluble metal complexes, sometimes of high stability, with heavy metals that otherwise would be adsorbed to solid particles [107].

Factors that affect NOM complexing of metals are pH, ionic strength, NOM source characteristics and competing ligands. Humic substances can be important metal complexing agents and may also significantly coat the solid mineral controlling the electrochemistry of the solid phase. Suspended solid surfaces are generally coated by adsorbed organic matter. Mechanisms involved are physical adsorption, electrostatic attraction, hydrogen bonding and co-ordination complexes. In case clays and humic substances are similarly charged, NOM adsorption may be facilitated by bridging associated with polyvalent cations. Ca^{2+} , Fe^{3+} and Al^{3+} are important in binding organic matter to clays. Ca-facilitated adsorption is reversible, whereas Fe^{3+} and Al^{3+} which can form strong complexes with organic matter are not readily desorbed. The presence of Cu^{2+} can increase the adsorption of dissolved humics to clays. Organically bound Cu^{2+} is the predominant Cu^{2+} species when the Cu^{2+} concentration is less than organic ligand concentration [105, 108–110].

The transformation of Fe^{2+} and Fe^{3+} has significant effects on many natural processes. Ferric oxide/hydroxide formation caused by changes of redox potentials has an impact on the distribution of trace metals and organic compounds through adsorption and coprecipitation. Although some organic compounds accelerate Fe^{2+} oxidation (e.g. citric acid), most organic compounds inhibit the reaction, varying in effect from mild (e.g. glutamic acid) to strong (e.g. tannic acid). Humic materials have little effect on the initial stage of oxidation, but thereafter the rate is greatly reduced. Fe^{2+} -organic complexing has been hypothesized to be the mechanism underlying the reduced rate of oxidation [109, 111–113].

It is clear that pH, ionic composition and the presence and apparent molecular size distributions of dissolved humic substances are fundamental variables determining the nature and extent of abiotic transformations of Fe and PO_4^{3-} . The presence of dissolved humic substances and iron can foster abiotic transformations of phosphate to material of greater apparent molecular size, thereby maintaining a pool of dissolved organic phosphorus. Ambient pH influences the nature and magnitude of transformations of iron and phosphate in the presence of dissolved humic substances. The precise role of them is not clear but is known as the response to pH of the acid-base properties of dissolved humic substances and the stability of peptized Fe-PO_4 colloids. Ambient ionic composition also influences the nature and magnitude of phosphate and iron transformations. This may be due, in part, to a direct effect via the inhibition of metal binding processes arising from competition for binding sites between iron and divalent cations, especially calcium [114].

5.2.2—in the terrestrial environment

Due to the high sorption capacity of humic substances the distribution of heavy metals in the soil profile is strongly related to the presence of organic material. Therefore an accumulation of heavy metals is often observed in the humic-rich top layer of soil profiles [30, 115]. This effect is described in detail, for instance, for the behaviour of mercury in forest and grassland soils [116].

The concentrations found in litter horizons mainly reflect the different deposition rates into the terrestrial environment. Due to decomposition of organic material heavy metals enter the soil complex, where accumulation and transport processes are connected with sorption and desorption effects [116]. The same

effect was observed for other heavy metals, for instance, by Schäfer [117] and Mayer and Heinrichs [118]. Additionally they described a reduced decomposition of organic material (litter) due to toxicity effects of high heavy metal concentrations on the activity of soil microorganisms.

Table 3. Distribution of mercury in soil profile - comparison of forest and grassland soil [116]

profile layer	forest soil	grassland soil
	concentration of mercury (ng/g)	
litter	668.16	281.10
Ah (rich of humus substances)	563.04	807.40
Bv1	144.11	125.56
Bv2	103.20–70.27	80.39–63.48
Cv	57.06	47.02–38.50

Heavy metals sorbed by organic material in soil matrix may be considered to be immobile and to present little danger to groundwater supplies. Transport and transformation processes in soils depend on the availability of soil water and on soil chemistry conditions influencing the behaviour of heavy metals and organo-metal compounds as regards their immobilization and remobilization [30].

Organic substances occurring as collides in the solid phase sorbing metal contaminants, however, may be mobile in subsurface environment and stabilize these compounds in the mobile phase. Whether particles like organo-metallic complexes will be stable, aggregated, filtered, or will settle in groundwater depends on a complex of density, size, surface chemistry, chemistry of soil water, and the seepage water rate [119]. Influences changing the soil and soil water chemistry like atmospheric acid deposition are responsible for desorption effects and the mobility of heavy metals as well as for the mobility of organo-metallic complexes. Therefore, the content of dissolved heavy metals compounds in seepage water from soils influenced by such acidification effects is often high [30].

In neutral or alkaline reactions of soil solutions only slight displacement of strong bonding organo-metallic compounds are observed. After a decrease of the pH of the soil solution the bonding capacity of humic substances is still high and the heavy metals are not desorbed, but the organo-metallic complexes start to be mobile.

Table 4. pH for mobility of heavy metals [30]:

	Cd	Zn	Ni	Co	Cu	As	Cr III	Pb	Hg
pH	6.5	6–5.5	5.5	5.5	4.5	4.5–4	4.5–4	4	4
bonding capacity of humic substances	4	2	3.5	3	5		5	5	5

relative bonding capacity: 1 - very low, 2 - low, 3 - medium, 4 - high, 5 - very high

The bonding interactions between contaminants and humic substances, which are responsible for the mobility and transport of heavy metals within the soil profile, may be described by adsorption-isotherms [23]. Such isotherms present the relation between the content of adsorbed substances and their concentration in solution.

5.2.3—in the aquatic environment

Perhaps the most perplexing chemical equilibrium problem that is yet to be resolved for aquatic systems is the thermodynamic description of the binding metal ions to the complex mixture of organic substances.

Metal binding by aquatic humus is well described by the Gaussian distribution model. Even data generated from the two-component Scatchard equation (with four fitting parameters) were successfully modeled by a Gaussian distribution with two fitting parameters [120, 121]. With the aim of predicting the extent of interactions between trace metals and humic substances an equilibrium discrete size-electrostatic model (model V) has recently been developed, and parameters for a number of metal species have been estimated. Model V allows the prediction of metal binding at different pH and ionic strength values and includes potential competition among different metal species. The most important competition effects in natural systems are likely to be due to the alkaline earth cations (Mg^{2+} , Ca^{2+}) the high concentrations of which will compensate for their relatively weak humic-binding affinities [122–124].

The behaviour of the elements in sea water is closely linked to the extent to which they are involved in particle water interactions, either via biological utilization or by adsorption/desorption reactions at active surfaces. A major fraction of the particulate matter in sea water consists of organic aggregates or flocculent organic matter. Their genesis is diverse, involving both, biological processes and physical processes such as adsorption, agglutination, bubble transport and turbulence. They serve as nutrient-rich particles and can be a major component of the particle flux in nearshore waters. In the coastal zone particulate organic flocs can incorporate trace metals, which can be removed from the water by deposition of the flocs.

The rapid incorporation of Mn, Pb, and Cu into particulate organic flocs suggests that these particles can be important transfer mechanisms in both the coastal zone and the open ocean. A number of models have been developed to simulate the adsorption process. The most effective appears to be potential adsorption resulting from complexation at specific sites on the particle surface. Surface-active molecules in estuarine and coastal sea water determine the surface properties of suspended particles [38, 125, 126].

Three major processes lead to the incorporation of particular metal-organic species in a sediment: (1) Reaction between a metal ion and an organic ligand in solution forming a species which can either precipitate directly or be adsorbed on sedimentary material, (2) Incorporation in a sedimentary pile of the total or of a part of an organism containing biogenic co-ordination compounds, (3) Adsorption on sediment of molecules resulting from the solubilization of minerals (sulfides, carbonates, etc.) by natural waters containing organic ligands [127].

A good positive correlation has often been observed between the contents of organic materials and metal concentrations in aquatic sediments. This, however, does not necessarily involve preferential metal bonding by organic substances, since a number of mechanisms (for instance, sorption by clay minerals and precipitation of Mn/Fe oxides) produce simultaneous accumulation of organic material as well as typical metals, particularly in the fine-grained sediment fractions. Moreover, in highly polluted areas, contamination by heavy metals coincides with the accumulation of organic substances originating from both domestic and industrial or rural sludge.

The interaction between hydrous metal oxides and organic substances is particularly complex. These oxides are unstable in certain organic-rich sediments, especially under anaerobic conditions, whereas a close correlation between iron, manganese, and phosphorus has been reported for both river water (dissolved state) and sea water (partly flocculated) organic substances [37, 128].

Aquatic fulvic acid as well as other fractions of dissolved and adsorbed organic matter can alter the geochemical mobility of metal ions. Dissolved organic matter can support the release of metal ions adsorbed to sediments; on the other hand, organic matter adsorbed to sediments can sequester metal ions that are in solution. The stability constants for complexes between fulvic acids and metal ions such as Cu^{2+} and Pb^{2+} are high, which may result in alteration of the metal ion equilibria. Fulvic acid in natural waters buffers metal ions.

Many of the oxygen-containing functional groups associate with metal ions, notably alkaline earth (commonly Ca and Mg) and transition metals (e.g. Cu, Fe, Cd, Zn, V and Ni). Monovalent cations like Na^+ and K^+ can form weak electrostatic bonds with single anionic groups of fulvic acids, whereas divalent metal ions may be complexed at two adjacent anionic sites, forming a chelate ring, an association that generally is much stronger than that formed by complexation through a single site. While H^+ competes with metal ions for anionic binding sites on fulvic acids, OH^- competes with fulvic acids for the cationic metal ions. With increasing pH the availability of fulvic acid for complexing therefore increases whereas the availability of the metal ion decreases. Consequently, an intermediate pH most favours complexation between fulvic acids and metal ions [3].

5.3 Sorption and mobility of organic substances

Organic pollutants from most different sources as chemical industry, traffic, combustion of fossil fuels and other organics, water treatment by chlorination, and application of pesticides in agricultural areas are released into the environment entering all environmental compartments by direct input, transport or precipitation processes.

Many studies have demonstrated that NOM enhances the apparent solubility or mobility of highly hydrophobic contaminants (PCBs, PAHs, hexachlorobenzene, some pesticides). On the other hand the transport of less hydrophobic contaminants (some pesticides) was found not to be influenced by NOM.

5.3.1—principles

As regards the sorption of NOM and organic contaminants there are two general types of adsorption: physical adsorption and chemical adsorption. Physical adsorption or van der Waals adsorption, as it is often called, is due to: orientation or dipole–dipole interactions; polarization or induced dipole interactions; dispersion interactions; ion–dipole interactions in addition to Born repulsion interactions. Chemical adsorption is due to Coulombic forces and results from bond formation between the adsorbent and the adsorbate. A hydrogen bond may be classified under either physical or chemical adsorption, depending on whether the heat of adsorption or bond formation is taken as the major criterion for classification.

The energy of adsorption may be regarded as the sum of the effects of the different forces acting between the adsorbent and the adsorbate. Generally speaking, physical adsorption results in low binding strength, while chemical adsorption results in high binding strength. In physical adsorption, several monolayers may be present; in chemical adsorption several monolayers may be present, but only the first monolayer is chemically bonded to the surface, while the other monolayers are held by dipolar attraction.

The main sorption type to be considered in soil systems is the adsorption from solution rather than adsorption from the vapour phase. By the very nature of the system present, the adsorption of both, the solute and the solvent by the soil colloid is possible [129].

The colloids themselves are particles with diameters less than 10 μm . A variety of organic and inorganic materials also occurs as colloids in groundwater, including macromolecular components of ‘dissolved’ organic carbon (DOC), such as humic substances and ‘biocolloids’, such as micro-organisms [119].

Factors controlling the uptake of the slowly moving organic chemicals include adsorption and partitioning. ‘Partition coefficients are commonly used to quantify the distribution of organic pollutants between the aqueous and particulate phases. The magnitude of the partition coefficient for a specific pollutant in a particular system has been shown to be related to the octanol-water partition coefficient of the pollutant and the organic carbon content of the solid phase onto which sorption occurs.’ [130]

5.3.2—in the terrestrial environment

The influence of organic material on the contamination of soils by pesticides as one main group of organic pollutants and their behaviour should be discussed in more detail considering application to cropland soils and the resulting hazard of plant uptake and of transport to groundwater and other aquatic systems.

Pesticides are synthetic organic compounds including various groups, like triazines for herbicides and chlorinated hydrocarbons (i.e. lindane, DDT) for insecticides.

Regarding their persistence in soil of synthetic organic chemicals can be divided into two general types, those that are biodegradable and those that are recalcitrant, i.e. decompose slowly if at all [2]. Accumulation of such contaminants depends on their persistence as well as on sorption and mobility effects. Comparison of the persistence of various pesticides indicates long-term persistence of organochlorine insecticides, notably DDT. The herbicides Diquat and Paraquat also persist in soils a long time.

A major factor affecting the persistence of synthetic organics in soils is adsorption to clay and organic surfaces. Adsorption of synthetic organic compounds used as pesticides as well as of other organic contaminants originating from other sources, i.e. PAHs, PCBs, mainly by soil organic matter has been shown to be a key factor in the behaviour in soil. ‘It has been well established, for example, that the rate at which an adsorbable pesticide must be applied to the soil in order to achieve adequate pest control can vary as much as 20-fold, depending on the nature of the soil and the amount of organic matter it contains. Soils that are black have higher organic matter contents than those which are light in colour, and pesticide application rates must often be adjusted upward on the darker soils to achieve the desired result’ [2].

Due to the specific binding mechanisms already described as principle sorption effects the adsorption of pesticides increases by increasing the content of organic material in soil and soil profile. The adsorption

capacity of humic substances is expressed as adsorption coefficient K_{OC} (partition coefficient of a substance between organic matter of soil and water).

The K_{OC} -value varies between < 50 for phenoxy butyric acids (2,4-D, 2,4,5-T), i.e. low adsorption, and > 30.000 for DDT, i.e. high adsorption [27]. The nonpolar, hardly water soluble organochlorines are strongly adsorbed, with K_{OC} -values > 10.000 . Investigations on the interactions between humic substances and organochlorine, reported by Ziechmann [23], demonstrate the immobilization of lindane due to sorption by humic substances. But the solubility of various sparingly water soluble organic contaminants in dissolved organic material containing solutes elucidate that these mobile organic fractions act as carrier of contaminants.

Mingelgrin and Gerstel [131] found that the interaction between an organic solute and soil was adsorption, a linear relationship was only observed at significant low bulk concentrations. Contrary to this some investigations by Karickhoff [132], Briggs [133], Chiou [134], and Wershaw [135] indicated that the distribution of non-ionic organic solutes between soils/sediment was partitioning.

With respect to the sediment, Karickhoff showed that the sorption isotherms for all partition coefficients were directly related to the organic carbon content of the studied sediments. In aqueous systems, owing to the strong ability of water to compete against hydrophobic organic solutes for mineral surfaces, the solute partitioning into the soil organic phase is the primary mechanism of soil uptake, as investigated by Chiou *et al.* [136].

Gauthier *et al.* reported that the magnitude of the K_{OC} values correlated strongly with the characteristics of the humic material. Similarly, Kile and Chiou showed that the magnitude of the partition coefficient (K_{dom} or K_{doc} , i.e. partition coefficient of organochlorine pesticides between the dissolved organic material or organic carbon content of soil and water) was a function of the solute and the nature of the dissolved organic matter.

However, recent investigations indicated that significant amounts of free-moving dissolved organic matter (DOM) in the system could enhance the transport of hydrophobic organic contaminants. DOM or DOC including dextran and humic acid could form a third medium for the hydrophobic organic pollutants to associate with and carry them in the moving water [136].

Hutchins *et al.* [137] derived a modification of K_d (distribution coefficient) to consider the possible interactions of a chemical with dissolved organic matter:

$$K_d = \frac{K_d^s}{1 + (K_d^{DOM} * C_{DOM})}$$

where C_{DOM} is the concentration of dissolved organic matter (g/ml), K_d^s the distribution coefficient for a chemical between soil and organic material in free water, and K_d^{DOM} the distribution coefficient between DOM and water.

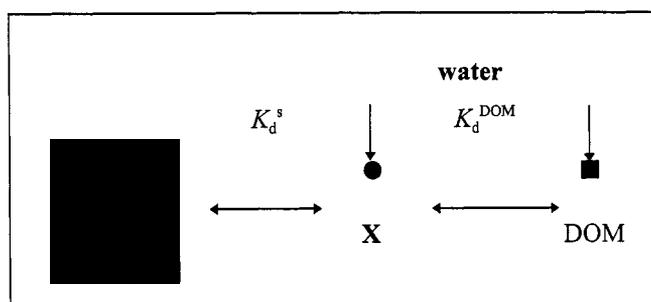


Fig. 1 Conceptual model showing the coefficients quantifying the distribution of a chemical X between soil, water and dissolved organic matter DOM [138].

Three phase distribution models are generally predicated upon three basic assumptions:

1. the total amount of target compound residual in the aqueous phase (i.e. not sorbed by the solid) comprises both free and polymer 'bound' solute;
2. binding of the solute by the organic polymers in question and sorption of both solutes and polymers can be described in terms of partitioning relationships; and

3. equilibrium conditions exist [139].

The DOC content in soil pore water may range from 5 to 40 mg/l [140, 141]. However, not only the concentrations of soil organic matter and of the dissolved and water extractable organic carbon, respectively, are decisive for the partitioning of organic and inorganic compounds between soil matrix and pore water, also, the organic matter composition is of importance for sorption to soils, and for the distribution between sediment and water phase in aquatic environments. Therefore, sorption coefficients can be transformed to K_{OC} values for agricultural soils with an acceptable standard deviation [142]. The normalization of the sorption coefficient to the soil organic matter content will result in much greater standard deviations (up to a factor of 10) when soils of different types and utilization, such as agricultural soils, forest soils and meadows, are compared.

Although the partitioning model with SOM (soil organic matter) has successfully explained a wide variety of data on organic compound sorption by soil from water, and although the normalization of solute sorption coefficients on the basis of SOM (K_{OM}) or soil organic carbon (K_{OC}) has greatly reduced the divergence of results, significant differences in K_{OM} (or K_{OC}) values of various compounds are often observed between soil samples of different origins. These differences can result from various intrinsic properties of the SOM and external factors (including different equilibrium procedures and analytical inaccuracies in determining the amount of sorption).

Concerning partitioning interactions of solutes with SOM, certain differences are expected to occur in the partitioning efficiency of a given compound with SOMs of different geographic sources because the compositional differences will affect the solubility of the solute. The effect of organic matter composition on organic solute partition was illustrated by Chiou *et al.* (see below) when studying of the extent of solute interactions with humic and fulvic acids extracted from soils and river waters. He found that the solute partition efficiency decreased with increasing polar group content of the humic and fulvic acids [143].

Chiou *et al.* [134] investigated the influence of dissolved humic and fulvic acids on water solubility enhancement and resulting effects on the partition coefficients of organic chemicals in soils. It was demonstrated that K_{DOM} values of solutes with soil-derived humic acids are approximately 4 times greater than with soil fulvic acids and 5–7 times greater than with aquatic humic and fulvic acids. The effectiveness of DOM in enhancing solute solubility appears to be largely controlled by the DOM molecular size and polarity. On the other hand, the effect of enhanced solubility of organic substances by DOM is correlated with water solubility. Either none or minor effects were observed for easily and medium, soluble substances, respectively, including lindane. The extent of the effects increased with decreasing water solubility of the substances.

5.3.3—in the aquatic environment

NOM-contaminant associations may affect adsorption behaviour and fate of contaminant in aquatic environments. The extent of complexation or association is a function of the hydrophobic character or solubility of the contaminant and of the concentration and reactivity of NOM [144–148].

Hydrophobic pollutants can bind to dissolved humic materials which could significantly affect their environmental behaviour. The rate of chemical degradation, photolysis, volatilization, transfer to sediments, and biological uptake is different from the bound to dissolved humic materials pollutants although there are not enough data on the strength of humic materials-hydrophobic pollutant binding [149, 150].

The distribution or partitioning of non-ionic hydrophobic organic compounds between water and particles or sediments has been shown to depend primarily on the hydrophobicity of the compound and the fraction of organic carbon in the sorbent. The importance of the organic carbon content of sediments suggests that various components of organic material in solution may also bind non-ionic hydrophobic organic compounds. The binding of hydrophobic organic pollutants by NOM depends on the chemical and structural characteristics of the NOM and may depend on the aqueous chemistry of the system which to a large extent controls the polarity and the conformation of aquatic humic substances. Intermolecular interactions between a molecule's functional groups change the chemical and physical properties of humic material. These interactions control the self association and ultimately the size, shape and polarity of humic substances. Both nonpolar and polar interactions are thought to be responsible for the self aggregation of humic material although nonpolar interactions are assumed to be insignificant for the humic and fulvic

acids. However, because both polar intermolecular and intramolecular interactions increase the nonpolar character of humic substances, increased binding of hydrophobic contaminants by humic material may be considered as a result of these interactions [151–153].

Molecular interactions of NOM are dependent on temperature, pH, ionic strength and type of ions in solution, as well as other chemical parameters. As the hydrogen ion and metal ion concentrations increase, the molecular size of the humic polymers will increase. The humic polymers may coil as the pH is reduced and the ionic strength is increased. The charge on the polymer will decrease indicating that the humic polymer becomes less hydrophilic, so it would bind hydrophobic compounds more effectively. The chemical potential of a dissolved non-ionic compound in water will increase with increased ionic strength as salting out of the hydrophobic organic compound is possible. For intermolecular interactions, the concentration of DOM is also important. Since the above parameters are significant for the self association of humic material, they should also be important for organic pollutant binding by humic substances [148, 154, 155].

PCBs, DDT and PAHs can attach to humic substance molecules, especially to the water-soluble portion of such molecules and then be transported in water. The complexation of organic pollutants and humic material was found to vary considerably between different classes of compounds as well as between compounds of the same class. Reaction rates between PAH and humus are high with reached quickly equilibria. Reaction rates between phthalates and humus as well as between chlorinated aromatics and humus are high, but no equilibria are reached [156].

Many organic contaminants have a low water solubility and are strongly adsorbed to colloids as well as to suspended and sediment particles. Many are persistent being only slowly biodegradable with environmental half-lives in the order of years. Small particles in offshore waters and colloidal material in the interstitial waters of coastal marine sediments are found to be dominant carriers of PCB congeners. Hydrophobic contaminants tend to associate with lipid pools which themselves may be less refractory than the contaminants. Organic compounds associated with particles are subject to particle transport mechanisms in the estuarine and marine environments. Desorption of such compounds in estuarine water is not likely to be a quantitatively significant process. The combination of the persistence of these compounds and the long residence time of particles in the estuarine and shelf environments ensures slow transport to offshore waters. Co-deposition of large amounts of high energy, labile organic compounds to sediments such as may occur in estuaries, favours abiotic degradation processes under reducing conditions or degradation as a result of increased microbial activity. For hydrophobic compounds with relatively high solubilities, the dissolved phase assumes a more important transport function even at increased suspended matter concentrations. Examples of organochlorine compounds with high solubilities are γ -HCH (lindane) and its by-product α -HCH. The major river-borne flux of lindane is therefore expected to occur in the dissolved phase and its net export beyond estuaries, shelves and marginal seas is likely to be significant [15, 157, 158].

The affinity of natural organic matter for neutral organic pollutants (e.g. PAH) as well as to mineral surfaces adds complexity to transport phenomena and may play an important role in the geochemical behaviour of PAH, particularly their transport. PAH are hydrophobic organic compounds which are relatively insoluble in water and tend to absorb onto other non aqueous phases either through hydrophobic interaction, when the non aqueous phase is a nonpolar compound, or through conjugate π bonding, when the non aqueous phase is a polar compound. The hydrophobic sites of humic substances represent an important phase for PAH compounds. The interactions between PAH compounds and dissolved humic substances may not only enhance the concentration of hydrophobic organic compounds in the aqueous phase, but may also effectively desorb pollutants. If there is a dissolved NOM phase within the aqueous phase, hydrophobic compounds such as PAH will have a tendency to bind to the dissolved NOM and stay in the solution, potentially facilitating their subsurface transport. In contrast, when an organic matter phase is associated with a soil matrix (mineral bound NOM), PAH may sorb onto the soil phase and its transport will be retarded. Furthermore, if both dissolved NOM and mineral bound NOM are present, the movement of PAH will depend on the partitioning competition of PAH between the aqueous phase NOM and the mineral-phase NOM. The aqueous-phase concentration enhancement of moderately hydrophobic organic compounds (e.g. DDT) in the presence of DOM has been attributed to the interaction of organic compounds with dissolved NOM. Such interactions follow a partitioning process with the partitioning of PAH into the hydrophobic interior of NOM [159–161].

The extent of concentration enhancement of PAH in aqueous phase by NOM depends on NOM characteristics. The degree of NOM effects depends on NOM sources and its transport behaviour. Both aqueous and soil-phase NOM affect the transport of PAH in sea water. The molecular weight and polarity of NOM affects NOM binding both to mineral surfaces and to organic compounds. A higher binding capacity of high molecular weight NOM fractions and NOM humic fractions for PAH was also observed. Aqueous-phase NOM does not enhance the desorption of moderately hydrophobic PAH [162]. Though much research has been conducted on PAH–NOM interactions, a systematic understanding of the effect of NOM on PAH transport is still lacking. Issues that relate to the study of NOM effects on PAH transport mechanisms include the degree to which NOM may facilitate the transport of PAH, the possibility of using NOM to facilitate the cleanup of a PAH-contaminated aquifer, the transport behaviour of NOM in aquifer media and its concomitant effects on PAH transport [163].

5.4 Bioavailability

5.4.1 bioavailability of compounds dissolved in soil solution

For both, a hazard and risk assessment of chemicals in soil and the characterization of the soil quality, information on soil organism exposure has to be evaluated. The analytical determination of the total pollutant content is not sufficient, but the bioavailable fraction of the contaminants has to be determined for the exposure route related soil assessment. Otherwise, the relationship between effect concentrations and observed effects on the soil living organisms cannot be quantified. In this context, bioavailability describes the portion of a present contaminant which can be uptaken by the organism from its environment and food and is subsequently transported, distributed and metabolized by the organism [164]. Such a definition clearly elucidates that only a portion of the compound present in any environmental compartment (preferably soil compartment) is available to organisms, the exact portion depending on the organism's physiology and habitat.

For the scientific development of trigger and cut-off values for soil contaminants an experimental set-up has to be designed for groups of organisms which are exposed via the same uptake-routes (in this case the soil solution). Besides the determination of the total contaminant content this experimental set-up has to aim at the determination of the bioavailable portion. Such a generally applicable extraction method should result in 'soil type independent' concentrations since the specific sorption to the soil is already considered by the extraction method.

For organic anthropogenic chemicals in soil Boesten [166] evaluated the present literature to test the hypothesis saying that bioavailability is a function of the dissolved chemical in the liquid phase of the soil. According to the sorption data he calculated effective concentrations of a chemical in the soil-liquid phase. He showed that the evident differences between the effects in the different soils at least could be explained partially.

5.4.2 binding and bioavailability in aquatic systems

Analogously to the soil, the dissolved organic material (DOM) pool in natural waters consists of a variety of organic molecules, mostly of no readily identifiable structure (referred to as humic substances). DOM is an important factor in water chemistry and aquatic toxicology because a number of studies have demonstrated that it can bind both metals and hydrophobic organic pollutants. The affinity of organic matter for binding a given contaminant appears to vary among waters from different sources. The underlying causes of the observed variability in binding affinity of different waters for organic contaminants is not fully understood and hampers attempts to describe and predict the importance of natural organic matter in the transport and fate of organic pollutants in aquatic systems.

The total concentration of DOM in natural water is also one of the main factors controlling the bioavailability of highly lipophilic xenobiotics ($K_{ow} > 10^4$), but in addition to the quantity, the quality of DOM (i.e. aromaticity and portion of hydrophobic acids) can play an important role. In general, DOM reduces the bioavailability of pollutants, the magnitude of the decrease being related to the binding between the contaminant and the organic matter. Therefore, the capability to predict the role of the organic macromolecules for accumulation and toxicity of hydrophobic organic compounds in aquatic environments is dependent on, and limited by, the poorly understood variability in the binding affinity among natural waters. The qualitative differences in the nature of the organic material from different sources have large

effects on its affinity for binding lipophilic organics. This kind of chemical variability can also explain results indicating that the K_p values for binding xenobiotics differed by orders of magnitude for DOM from natural waters taken from different locations.

One approach to elucidate the source of this variability is to examine relationships between chemical and structural properties of DOM and its capacity to bind organic contaminants. For example, Gauthier *et al.* have reported for pyrene that the binding coefficients in natural waters correlated with the aromaticity of DOM in the water samples.

The results of experiments conducted on invertebrates using 'natural' (i.e. water column) DOC are somewhat mixed. Leversee *et al.* reported that the removal of DOC from two filtered natural waters resulted in about 30 % increase in the BCF of BAP by *Daphnia*. Similarly, Kukkonen and Oikari found that the accumulation of dehydroabietic acid and BAP by *Daphnia* was distinctly reduced in natural humic waters, although no reduction in the accumulation of PCP was observed. Furthermore, Kukkonen *et al.* were unable to reconcile the decrease in the bioavailability of BAP with the fraction of the PAH that was bound to the DOC, suggesting that the BAP was, in fact, still available for uptake by *Daphnia*. Servos and Muir showed that epilimnetic DOC decreased the uptake of dioxin by the amphipod *Crangonyx laurentianus*, but their data suggest that epilimnetic DOC was less effective in reducing uptake than either HA or interstitial DOC. In fact, Servos *et al.* found that water column DOC had little effect on the apparent uptake rate of dioxin by rainbow trout (*S. gairdneri*). Kukkonen *et al.* concluded that the results of their study suggest that water column DOC in lakes may be having a negligible effect on the cycling of PCB 153 and perhaps other hydrophobic organic contaminants. Furthermore, both the size (wet weight) and condition (lipid content) of the *Daphnia* are important factors affecting the magnitude of, and the variability in, the measured BCFs and uptake rate constants. Thus, these variables should be considered in all bioavailability studies. [165].

6. MODELING

6.1 Modeling environmental processes influenced by DOC

In order to describe a chemical's movement through soil, models of different complexity exist: The first attempt is to reduce testing, by finding correlations with other physico-chemical properties of chemicals, including QSAR (Quantitative Structure Activity Relationships). But before modeling sorption of chemicals to soil and their transport through soil systems experimental studies have to be performed at several levels.

Slow movement of chemicals through the unsaturated zone e.g. can be screened by adsorption/desorption data generated by the laboratory bath equilibrium method [142]. For organic compounds the equilibrium state of adsorption to soils or sediments is often reached within several hours [27, 167, 168]. For heavy metals, e.g. cadmium, the time until the equilibrium state is reached may amount to several weeks [169]. For organic pesticides like 2,4-D, 2,4,5-T, the time required to reach an adsorption equilibrium was up to 16 hours. Khan reports sorption of 2,4-D and picloram to humic acids within 1 hour. For PCBs he observed sorption equilibria within 2 hours. In some cases rapid initial sorption is followed by a decreased sorption velocity. Huang and Liao explained this by an initial fast sorption to the outer sites of the particles, followed by slower sorption to the inner particles sites. It is assumed that retardation in reaching the adsorption equilibrium occurs by diffusion through micropores and narrow capillaries.

Based on these experimental data on sorption, the development and application of advanced mathematical modelling has two main objectives: The description of specific processes in soils and the improvement of the respective knowledge (e.g. speciation of a soil solution with the program SOILCHEM). Modelling is therefore a suitable means to improve the understanding of reaction mechanisms in soils and to close fundamental gaps.

In complex transport and fate models the individual processes in soils are combined aiming at a realistic prediction of a chemical's fate in the soil and the dependence of its behaviour on its specific properties, as well as on soil properties climatic conditions, soil cultivation and agricultural practice.

For nonpolar and slightly polar substances the organic matter content of the soil is the predominant soil constituent influencing sorption. On this basis the K_{OC} value is derived by normalisation of the sorption constant to the organic matter content of the soil. Because organic matter may be of considerably variable

composition and properties in different soil systems, the range of K_{oc} -values for apolar substances determined with different soils is usually within a factor of 10.

Obviously the octanol water partition coefficient or water solubility are expected to be the most appropriate PC-data for establishing correlations. For this type of sorption processes several significant correlations have been published between the sorption coefficient and respective compound specific properties describing partitioning between hydrophilic/hydrophobic systems e.g. octanol/water distribution coefficient, water solubility, or capacity factors in reversed-phase chromatography. Different correlations have been developed by Kenaga and Goring [170], Karrickhoff *et al.* [132], Rao and Davidson [171], and Briggs [133].

Furthermore, QSARs are developed [172]. Some authors use the relative simple randic-indices. However, successful estimation of the sorption coefficient could only be achieved for some chemical classes of chemicals where correlations with electronic properties and molecular size are possible. This attempt was further developed by Koch *et al.* [173]. Von Oepen *et al.* [174] tried to develop QSARs for polar substances (e.g. amines, amides and carbonic acids). They showed that significant regression equations for predicting sorption behaviour can only be obtained for hydrophobic compounds, where the sorption to the organic carbon content by van der Waals interactions and hydrophobic bonding are the predominant processes. Then sorption is related to molecular size, self-polarizability or Randic Indices. At the moment polar sorption mechanisms cannot be quantified and used for correlations.

6.2 Modelling fate of chemicals in soil

All presently available models are deterministic and have further common characteristics, as the division of the soil into soil layers, which allows a description of the concentration gradients within one soil horizon. The descriptors used and their resolution in time, however, are not identical. All models start with a separate calculation of the different parallel soil processes (change of water balance, erosion, transport of active ingredient, plant growth) according to a fixed scheme. The fate of the chemical is then calculated considering the results obtained for the single processes. To calculate sorption, in general equilibrium conditions between solid and aqueous phases are assumed; the equilibrium, i.e. the adsorption constant, can be modified for each horizon. The single models describe the different processes with varying complexity. The quality of a model, however, should not be judged upon the complexity of modelling single processes. Since complex simulations finally depend on the general availability of the parameters, it is essential that the available parameters are included most completely into the models. Frequently applied models are: PELMO [175], PRZM [176], SESOIL [177, 178], PESTLA Model [179], STOMOD / WASMOD [180].

7. CONCLUSION

Research results are showing that particulate and dissolved natural organic material in marine and surface waters, interstitial waters in sediments and soil solutions are influencing the behaviour of anorganic and organic contaminants. Examples range from reduced solvent extraction efficiency and problematic clean-up steps in analytical measurements through to changes in adsorption behaviour and mobilisation of sparingly soluble substances. Dissolved and particulate natural organic matter also affects organism uptake, bioavailability and the distribution of contaminants in the environment leading to sinks with high concentrations.

The structure of humic substances is strongly related to the biological components from which they are formed. Therefore the composition and properties of organic matter in marine and terrestrial environments differ considerably. The classical differentiation of organic matter into insoluble humins, humic acids and fulvic acids can only be a first step in a classification and characterisation. Further methods like NMR-spectroscopy, pyrolysis mass-spectrometry and fractionation in classes of different molecular weights have to be included.

Recent publications illustrate the importance of natural organic matter for sorption and mobility of sparingly soluble organic substances and metals. For metals dissolved organic material is capable of:

- complexing metals and increasing metal solubility;
- altering the distribution between oxidized and reduced forms of metals;
- influencing the extend to which metals are adsorbed on suspended matter;

- affecting the stability of metal containing colloids;
- acting as metal buffers via their so-called complexation capacity;
- reducing metal toxicity and altering metal availability to aquatic life.

For organic substances the following effects of dissolved natural organic material have to be considered:

- dissolved humic substances act as significant solubilisers for sparingly soluble substances;
- the transport (mobility) of hydrophobic organic contaminants will be enhanced by a significant amount of free-moving dissolved organic matter;
- the solubilising properties of dissolved humic substances increase rapidly with increasing K_{oc} -values of the pollutants;
- the solubilising properties depend on the origin, the precursors, the molecular mass, the composition and the polarity of the DHS.

For soils and sediments, which contain higher amounts of organic matter a three phase distribution model should be used including DOM. Furthermore, soils and sediment are comprehensively characterised regarding soil type, genesis and chemical composition whereas the organic matter content is just stated as % OM without further characterisation. However, according to the importance of particulate and dissolved natural organic matter for the enrichment, fate and bioavailability of pollutants in soils and aquatic environments much more emphasis should be laid on the classification and characterisation of OM. However, further research is needed for closing the deficiencies on appropriate, well documented and validated routine methods.

Dissolved humic substances are dynamic systems. Their chemical and structural characteristics depend on the aqueous chemistry of the system.

- It controls to a large extent the polarity and conformation of humic substances.
- Intermolecular interactions between the molecule's functional groups change the chemical and physical properties of humic material. These interactions control the self association and ultimately the size, shape and polarity of humic substances.
- As a further consequence the binding and sorption of metals and organic pollutants is affected.

Again these effects are exemplarily shown, however in-depth research is needed to elucidate the consequences for soil and water quality assessment.

Biologically relevant contaminants have to be available for the organisms and lead to undesirable harmful effects. Therefore, the distribution between reversibly and irreversibly bound, sorbed, complexed and dissolved pollutants have to be considered. Humic substances on the one hand enhance the solubility of sparingly soluble substances but on the other hand reduce their bioavailability probably by complexation. These contrary processes are governed by the quality and solubilising properties of the specific organic matter, the properties of the substances under consideration and the vulnerability and feeding behaviour of the test organisms. The combination of these parameters is till now poorly understood leading to a limited predictability of expected results and explaining seemingly false or contradictory findings.

The development and application of mathematical modelling has the following main objectives:

- the description of specific processes in soils and water/sediment systems;
- the use in assessment systems;
- to reduce experimental tests;
- to improve the understanding of reaction mechanisms in soils and to close fundamental gaps.

Since complex simulations finally depend on the general availability of the included variables, it is essential that the available parameters are included completely into the models. This is broadly the case in the set of frequently applied models. However, the paper elucidates that for binding and mobility processes humic substances are important and that most processes are sparingly understood and quantified in reliable correlations. So further research is urgently needed with respect to improve modelling.

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