Chapter 10

UTILIZATION OF IMMOBILIZED HUMIC ORGANIC MATTER FOR *IN-SITU* SUBSURFACE REMEDIATION

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Abstract

HOM enriched areas within aquifers retain or bind organic pollutants by sorptive or specific interactions. This contribution briefly reviews some established concepts on *in situ* remediation for removal of dissolved organic contaminants from groundwater using reactive and sorptive barriers. In particular, we present a new concept for use of HOM (humic organic matter) as sorptive barrier. According to this concept HOM is sorbed to metal salt surface precipitates on aquifer minerals. Induced by sorptive interactions HOC (hydrophobic organic carbon) groundwater pollutants are retarded while passing the HOM barrier. An extended residence time within the aquifer subjects the pollutant plume to extensive microbial degradation and diminished spreading. We give information on pertinent laboratory experiments and field considerations describing design and possible ways to construct HOM barriers *in situ* in the subsurface by infiltration techniques. With regard to sorptive pollutant removal we discuss the mechanisms that drive the binding of HOM to mineral surfaces and those that govern the interactions between HOC and HOM. Operational approaches to determine sorption coefficients of HOC on HOM are conferred. The sorption of HOC on HOM in flocculated, surface-bound, and the freely dissolved state is compared.

1. Introduction

1.1. ESTABLISHED CONCEPTS FOR *IN SITU* SUBSURFACE REMEDIATION WITH SORPTIVE AND REACTIVE BARRIERS

Contamination of groundwater by chlorinated solvents, gasoline components, diesel fuel residues, and gas plant wastes is a worldwide problem. Contaminant plumes up to several kilometres in length downstream of contamination sources have been reported [1-3]. Although many contaminants of such plumes are known to be biodegradable, they sometimes appear to be refractory under natural groundwater conditions [1, 4, 5]. These

I. V. Perminova et al. (eds.),
Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice, 203–232.

findings are frequently attributed to the lack of electron acceptors, nutrients, or suitable microorganisms to support the subsurface bioremediation process [6-9].

Available technologies for groundwater remediation can be classified as above-ground and below-ground (or "*ex situ*" and "*in situ*").

Traditional technologies to clean up groundwater involve pumping the contaminated water to the surface and then treating it. However, in many cases *ex situ* field scale remediation applications result in unsatisfactorily high costs and indefinite operation time assessments [10-12]. An approach to increase the viability of pump and treat technologies at contaminated sites has been to solubilize and mobilize HOC by various agents including surfactants and dissolved and colloidal [aqueous] HOM. This approach is described in Chapter 11 of this book.

A potentially more cost-efficient alternative to pump & treat systems is the implementation of permeable reactive barriers (PRB) into the subsurface. They are often designed as a "funnel and gate" configuration in order to focus the plume towards the permeable sorption or reaction barrier by means of impermeable walls [13, 14]. During the passage through the barrier, the contaminants are bound, precipitated or chemically degraded, often merely resulting in less hazardous products rather than in complete mineralization.

PRB can be classified into three types:

– oxidation barriers,
– reduction barriers, and
– sorption barriers.

Oxidation barriers are based on the introduction of an electron acceptor into the groundwater flow (usually NO_3^-, O_2, peroxides) in order to provide either biodegrading microorganisms with conditions suitable for their reproduction, or to facilitate direct chemical oxidation (e.g., by permanganate) [12, 15, 16]. If oxygen is introduced as a gas, i.e., by air sparging, the dominant pollutant removal mechanism is often volatilisation rather than on the establishment of a biobarrier [17].

Oxygen-based oxidation barriers are most amenable for contaminants having chemical structures that are susceptible for initial oxygenase enzyme attacks. These include BTEX, phenols, PAHs, halogenated aromatics with up to three ring-bound halogens, or halogenated olefines and alkanes possessing up to 2 or 3 halogen atoms. Nitrate amendments may assist in anaerobic biodegradation of oxygenated metabolites of aromatic structures [18].

Higher oxidized organic compounds such as polyhalogenated hydrocarbons can act as oxidants (that is, electron acceptors) at high dissolved hydrogen levels and conditions lacking natural electron acceptors provided that bacteria capable of an initial reductive biotransformation are present. Hydrogen or enzymatic bound forms of hydrogen can be produced *in situ* by fermentative processes [19] or by **reduction barriers** based on zero valent iron (ZVI) while carbon dioxide serves as the carbon source for bacterial growth [20-22].

Sorption barriers are designed to retard dissolved pollutants in relation to the groundwater flux. The sorption approach can be regarded as the opposite strategy to the above-mentioned "mobilization/solubilization" strategy. The pollutant mass flux throughout the passage of the barrier does not necessarily have to be reduced to zero (complete sorption). In some cases it may also be desirable to achieve longer residence times in order to achieve better biodegradation within a segment of an aquifer.

In several pilot plant and full scale cases permeable walls were constructed using particulate sorbent materials such as peat, coal-derived HOM, or activated carbon [23].

Another promising strategy to establish permeable sorption walls has been demonstrated by means of subsurface injections of surfactants. After injection, attempts were made to immobilize the surfactants onto the aquifer matrix, thus serving as a hydrophobic mineral coating capable of HOC retardation [24-26].

1.2. THE NEW CONCEPT

Several features of humic organic matter (HOM) cause it to have a high potential in subsurface remediation.

The utilization of HOM as a means to increase the organic carbon (OC) content of the aquifer matrix results in higher retardation of HOC within the aquifer. In contrast to solid OC-rich materials placed in the aquifer, such as activated carbon, HOM liquid injections are not in need of soil excavations which potentially makes the approach less cost-intensive, especially at deep aquifer contamination. In contrast to surfactants, HOM does not only sorb HOC, it can also undergoes specific interactions with functionalised organic pollutants [27-29], it promotes biodegradation processes [30-32] (see also Chapter 17 of this book for details), and it may result in irreversible binding in the long term [33]. The ultimate goal should be therefore the formation of so called bound residues, humification by formation of covalent bonds or other very strong interactions between pollutant and the humic matrix.

In succeeding to establish a stable but permeable HOM barrier by injection of dissolved humates and their precipitation onto the surfaces of aquifer materials the sorption potential of coarse sand poor in organic carbon (OC) and gravel aquifer mineral matrices is improved. However, since several parameters limit the increase in the OC content by HOM precipitation (low specific surface area of aquifer sands, limited porosity) we consider extended sorption zones with moderately increased OC content in the subsurface rather than permeable high OC sorption walls.

Further advantages of the HOM based approach are that HOM is not known to be toxic as, for instance, described for cationic surfactants [34] and is hardly biodegradable in the absence of oxygen and light. At last, HOM is commercially available at technical scale by alkaline extraction of lignites and weathered lignites, so called oxygen-coals.
Sorption by hydrophobic partitioning of HOC between the humic and the water phase is only little effected by the present environmental conditions (e.g., pH, ionic strength, redox potential). These features make HOM a powerful and robust tool to remove HOC from a polluted groundwater. Besides its hydrophobic moieties HOM carries a variety of functional groups that can specifically interact with pollutants. However, sorption governed by specific interactions can be constricted by the amount of active functional groups or units (e.g., carboxylic groups for heavy metal sorption [29].

Disadvantageous can be that by the suggested method only a relatively small OC enrichment of the aquifer material can be achieved, the risk of aquifer clogging by precipitated HOM is given, and the contaminants are not removed from groundwater flow by degradation.

Figure 1 elucidates the general idea of the suggested procedure. Subsequent to an extended hydrogeological survey on site, dissolved (coal-derived) HOM is infiltrated

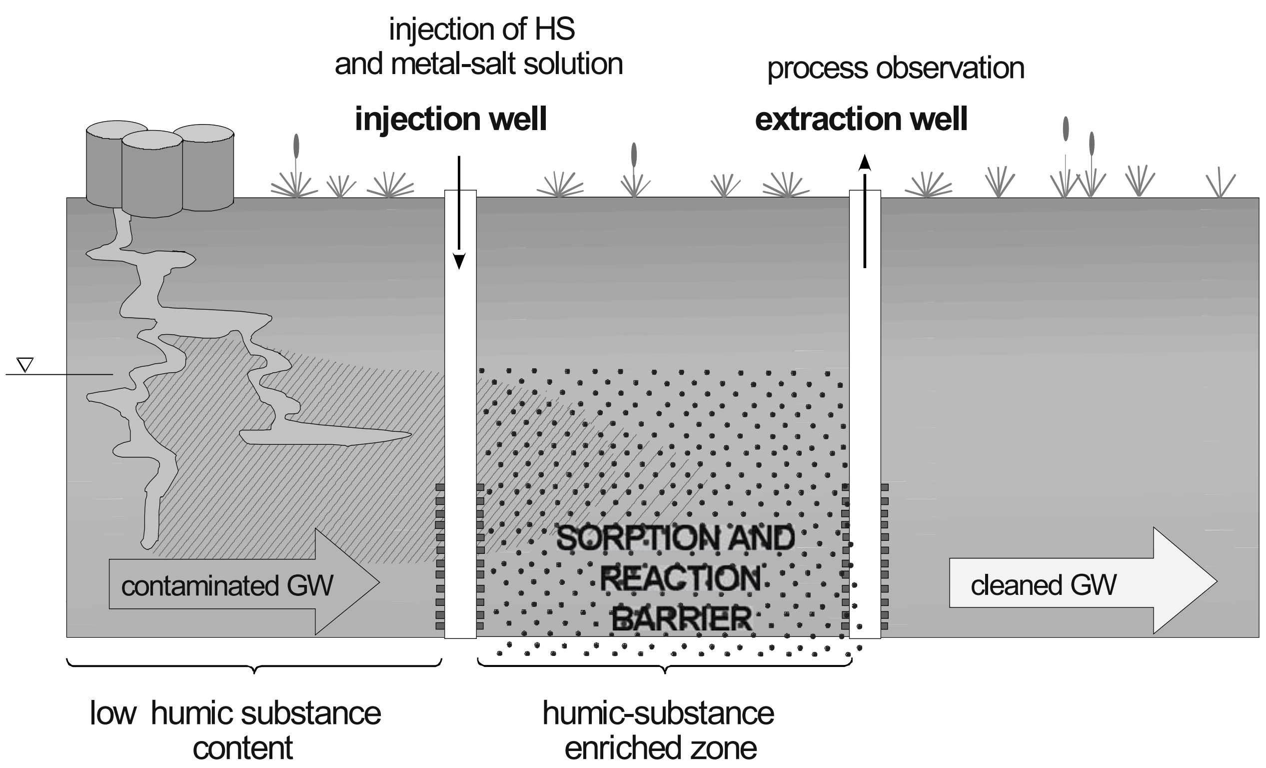


Figure 1. Conceptualisation of the procedure how to build up a permeable HOM barrier.

via injection wells to the subsurface. To promote the infiltration velocity the groundwater table is lowered by a net of pump wells. These wells serve to set the position of the HOM-barrier and can be used later as observation wells. Immobilization of the injected HOM is achieved by direct surface precipitation on clay coatings of aquifer sand grains, or calcium- or iron-mediated HOM precipitation facilitates the binding to the aquifer matrix (see section 5 of this chapter). The humic enriched zone serves as a sorptive/reactive barrier. While sorptive processes prolong the time during which HOC are exposed to natural attenuation processes, reactive binding to the HOM barrier removes HOC from the groundwater.

2. Humic Binding to Mineral Surfaces

The sorption of HOM onto oxide surfaces has been explained in the literature by mechanisms of ligand exchange of surface hydroxyl for humic carboxyl and phenolic groups [35-40]. The strength of sorption is determined mainly by the degree of dissociation of carboxyl and phenolic groups of the HOM and by the position of these groups relative to each other. Particularly ortho-positioned phenolic groups in neighbourhood to carboxylic groups promote sorption of HOM onto metal oxide surfaces [38]. Also hydrophobic moieties of HOM support sorption to mineral surfaces [39-44].

At pH values common for groundwater conditions (pH about 6.0 to 7.5) both, the dissolved HOM and most mineral surfaces, carry negative net surface charges [37, 45]. While a negative net surface charge for HOM is caused by dissociation of carboxylic moieties [46], negative surface charges of mineral surfaces may be of various origins.

The charge on mineral surfaces is attributed to

- isomorphic substitution in tetrahedrons of silicates [47] (e.g., Al^{3+} for Si^{4+}, i.e., the replacement of cations of lower total positive charge results in a permanent “charge deficiency” that needs to be balanced by monovalent cations, which can be replaced easily),
- the protonation/deprotonation equilibrium of hydrolysed surface hydroxyl groups: SS≡Si (Fe, Al)-OH2+ ↔ SS≡Si (Fe, Al)-OH ↔ SS≡Si (Fe, Al)-O-, (SS-sorbent surface, ≡ refers to inner crystal bonds),
- the adsorption of charged species on the mineral-water interface, e.g., humic substances or biofilms or competition with other surface complex forming anions [45]. The state of the surface protonation equilibrium at a given pH is mainly determined by the electron deficiency of the central ion in the surface complex. Whilst aluminium or ferric ion surface complexes exhibit typical Lewis acid character, silicate surfaces are described rather by weak Broenstedt acid behaviour. Accordingly, the first are good and the latter poor sorbents for HOM [37].

Moreover, typical coarse materials of unconsolidated aquifers exhibit small specific surface areas ($<2\ m^2g^{-1}$) [3]. As a result dissolved HOM is only poorly retarded on materials like quartz sand or gravel [48].

To avoid repulsion forces between negatively charged HOM and mineral surfaces with negative charges these surfaces need to be modified.

Looking at the nature we observe that podzolization of soils results in ferric iron coatings of silica surfaces. In principle, this also might be accomplished by means of precipitation of iron or aluminium salts as a “mediator” between HOM and mineral surface.

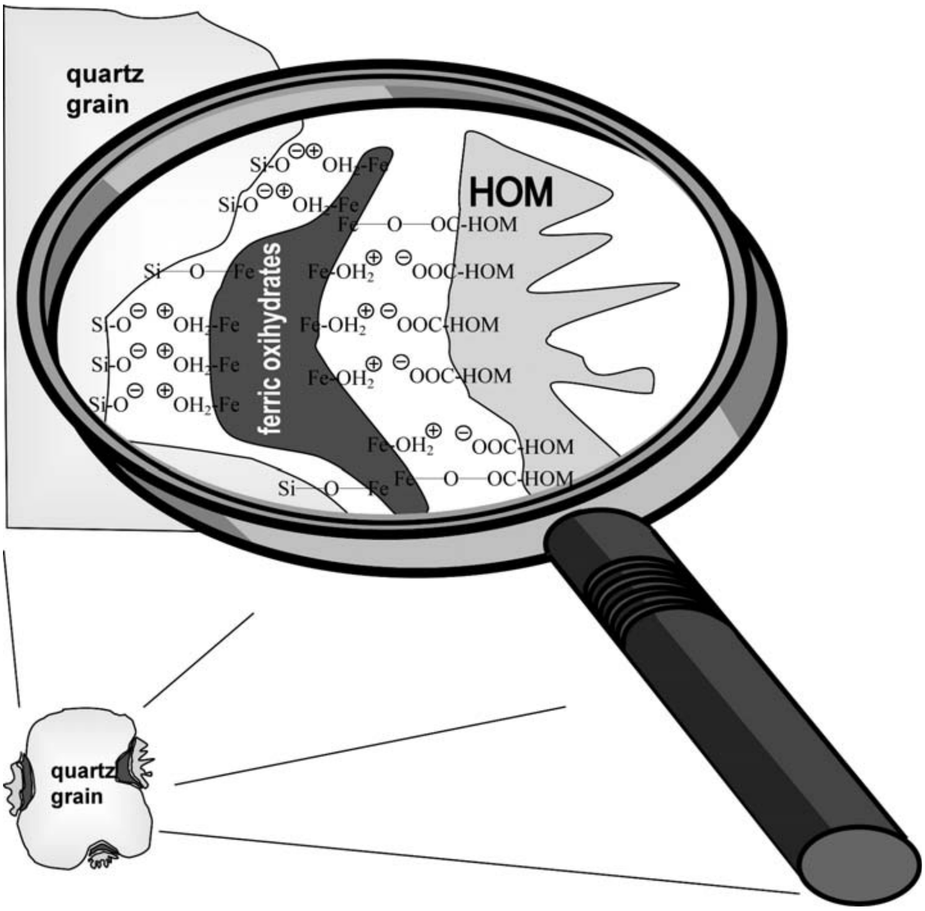


Figure 2. HOM coatings on ferric iron precipitates in niches of a quartz sand surface.

Figure 2 schematically illustrates HOM sandwich coatings on iron surface precipitates on silicate materials. Microscopic magnifications reveal that iron and HOM enrichments on quartz surfaces occur predominantly in glyphs and cavities [3].

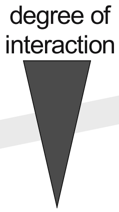
Despite their high binding affinity to mineral surfaces, hydroxides of Fe(III) and Al(III) have drawbacks. Aluminium salts are known to display a potential toxicity under acidic conditions [49, 50]. Even though at neutral pH values aluminium is almost completely insoluble and non-toxic, Al(III)-salt solution injections may not be tolerated by regulatory authorities.

Table 1. Adsorption of different metal salt precipitates on quartz sand after precipitation of the metal salt at neutral pH ($c_{Me} = 0.25$ mol L^{-1}) in the presence of the sand (specific surface = 0.4 m^2 g^{-1}, 500 g L^{-1}).

Table 2. Adsorption of HA (Roth humic acid, Germany) by different metal salt precipitates ($c_{Me} = 0.5$ mmol L^{-1}) from a 200 mg L^{-1} HA-solution (pH 7) and degree of HA desorption from HA-coated minerals after a single replacement of the supernatant by 0.1 M NaCl.

The triangle symbolically depicts the degree of interaction between either quartz mineral surface and metal ion precipitate or metal ion precipitate and HOM.

sand / metal salt	
metal salt	$x_{adsorbed}$ [mg/g]
$Fe(OH)_3$	4
$FeCO_3$	2.6
$Fe_3(PO_4)_2$	1.6
FeS	1.2
$Ca_3(PO_4)_2$	0.1



HA / metal salt			stability under anaerobic conditions
metal salt	% HA adsorbed	% HA desorbed	
$Fe(OH)_3$	99.8	0.6	-
$Fe_3(PO_4)_2$	96.9	3.0	+
$Ca_3(PO_4)_2$	87.8	n.d.	+
$FeCO_3$	24.2	81.7	+
FeS	4.5	n.d.	+

Although the placement of $Fe(OH)_3$ as a precipitate on silicate surfaces that can also bind HOM is relatively straightforward, attention should be paid to anoxic groundwater conditions. Ferric hydroxide shows poor redox stability under reducing conditions [51]. Moreover, it was shown that dissolved HOM facilitates the biodegradation of organic pollutants with ferric iron as terminal electron acceptor [31]. A remobilisation of dissolved ferrous iron could lead to non-stable HOM- Fe(III) oxide barriers. Therefore, we tested the sorption behaviour of several environmentally important precipitates, including poorly soluble Fe(II) salts, with respect to their binding abilities towards a quartz surface (Table 1), and towards dissolved HOM (Table 2). Details of these tests were reported earlier [3]. Next we investigated the stability of a HOM barrier under simulated ferric iron reducing conditions (Figure 3A and 3B) [3].

A set of metal ion precipitates representative of mineral surfaces in a polluted aquifer were formed (partially under exclusion of oxygen) in presence of quartz sand (200 – 630 μm) at pH 7. As can be seen from table 1, surface coatings of silicates can be achieved by several metal ion surface precipitates. Besides $Fe(OH)_3$, several Fe(II)-coated mineral surfaces show a strong tendency to sorb to quartz (e.g., $Fe_3(PO_4)_2$). Ferrous iron sulphide, on the other hand, shows neither a high degree of interaction towards the quartz surface nor towards HOM. For some salts like $Ca_3(PO_4)_2$ and $FeCO_3$ complexes with HOM are only weak.

In combining the results of tables 1 and 2 it becomes clear that not all ferrous iron species may work as mediators for sorption of HOM onto silicate surfaces. Some precipitates, like $Ca_3(PO_4)_2$, do not form stable surface complexes with the quartz surface. Others, like $FeCO_3$, redissolve when the supernatant is exchanged against a 0.1 M NaCl solution (maintaining the same ionic strength and pH conditions). Under reducing conditions, the ferrous compound $Fe_3(PO_4)_2$ may serve as an alternative to ferric species such as $Fe(OH)_3$/FeOOH for it forms stable complexes with HOM and silicate surfaces.

In another experiment [3] we subjected a ferric iron hydroxide/HOM-coated quartz sand, that has been produced by batch $Fe(OH)_3$-precipitation prior to the experiment (Fe: 1.5 g/kg, OC: 0.1 g/kg), to anaerobic respiration under flow through conditions in order to investigate the stability of ferric humate coatings against reductive dissolution. As carbon source we used a lactate solution (500 mg/L). A groundwater bacteria consortium from the Rositz site, a former tar factory site south of Leipzig, Germany, was inoculated to grow on lactate in the absence of oxygen. 0.33 L of a slightly modified Brunner nutrient solution containing the bacteria have been recycled through the coated quartz sand column for several days maintaining a flow rate of 10 mL/min (equivalent Darcy velocity: 35 m/d). System parameters such as redox potential, pH, dissolved ferrous iron, and the disappearance of lactate were measured.

Figures 3A and 3B represent the reductive dissolution of ferric iron humates in the presence and in the absence of phosphate.

In both experiments lactate was consumed rapidly. Further, sulphate was rapidly consumed by the microbial community, and the redox potential dropped slowly. The marked difference between Figures 3A and 3B is the appearance of ferrous iron in the effluent only in the absence of phosphate.

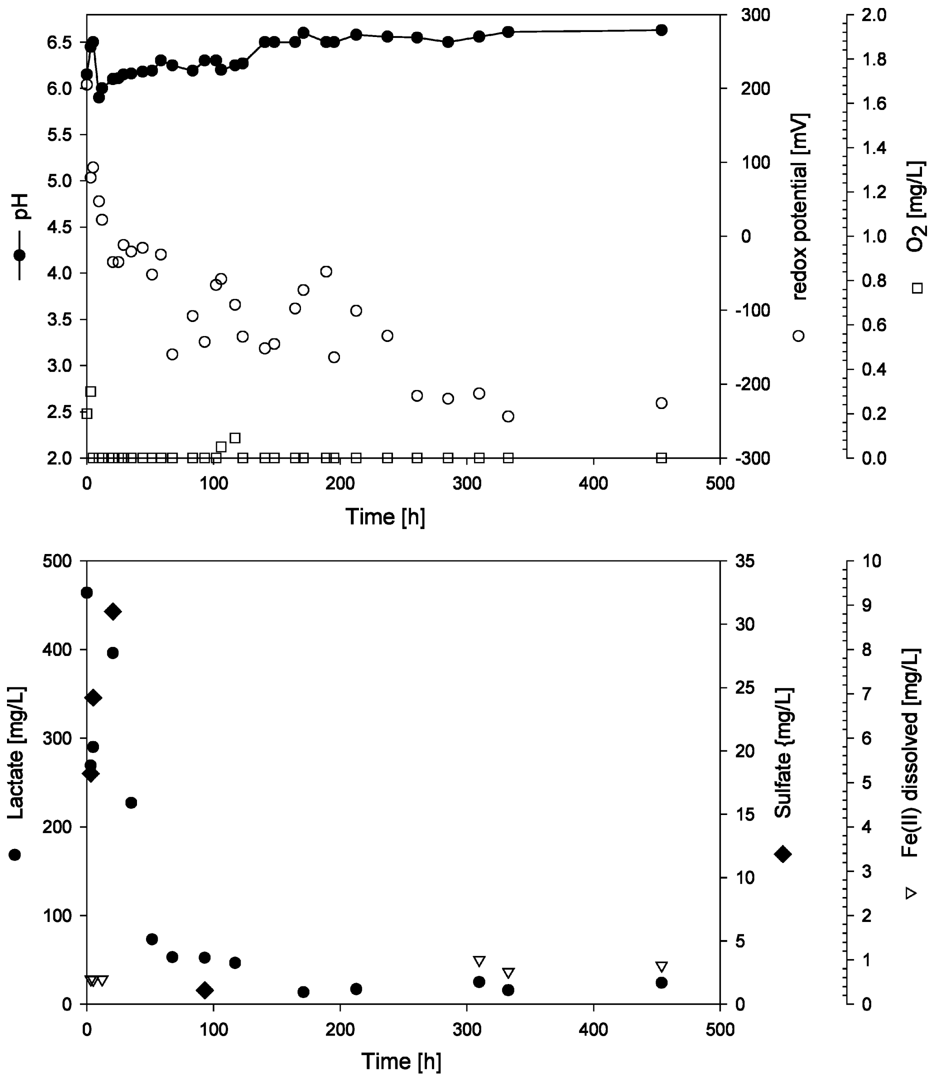


Figure 3A. Anaerobic respiration of lactate in presence of a Fe(III)-HOM coated sand and of a phosphate buffer. Even though ferric iron is reduced to ferrous iron no resolubilization of Fe(II) and of the sorbed HOM is observed.

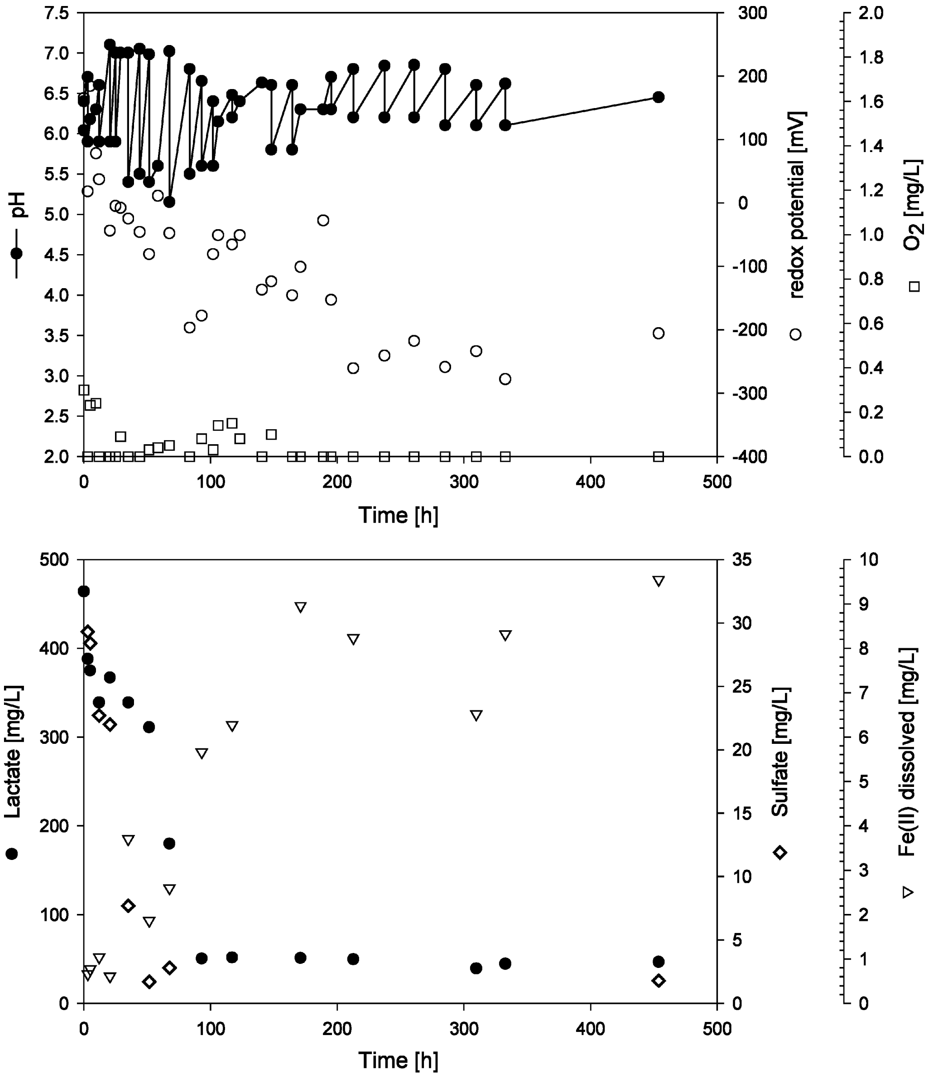


Figure 3B. Anaerobic respiration of lactate in presence of Fe(III)-HOM coated sand but in absence of phosphate (only Redfield formula conserving amounts). Iron is partially dissolved by reduction. Despite this no mobilization of sorbed HOM could be observed. The pH value was artificially forced to a range between 6.0 and 6.5 by successive amendments of 0.1 M NaOH solution.

In the presence of phosphate, ferric iron was completely reduced to ferrous iron. After the experiment was finished the washed sand surface contained high amounts of phosphate and iron, most likely indicating the formation of $Fe_3(PO_4)_2$. No ferrous iron formation could be detected in the effluent. A high phosphate background obviously facilitates ferric iron reduction. In the absence of phosphate only about one quarter of the initial surface-bound iron was reduced. During the course of the experiment (450 hours) it was only partly mobilized. The level of dissolved Fe did not decline or approach zero at the apparent end of the experiment, about 450 h. This suggests that ongoing ferrous iron mobilization would occur at a longer time scale. Further studies are required to examine long term stability/instability of the iron precipitates. A quantitative evaluation of the HOM in solution in the presence of bacteria, lactate and extracellular polymeric substances (EPS) is difficult. We solved this problem by sterile filtration over 0.2 µm cellulose acetate and subsequent UV spectroscopy. While bacterial cells are retained, HOM is small enough in size to pass the filter. Preliminary investigations showed that bacterial EPS suspensions possess much lower extinction coefficients at 270 nm than the HOM. By introduction of one dilution step before UV-absorption analysis the contribution of EPS to the total absorption signal could be neglected. By this method the HOM concentration in the column effluent at the last day of the recirculation was below the detection limit (ca. 2 mg/L DOC), the effluent was turbid from washed-off cells but not brown coloured. With progressing iron reduction the colour of all coated sand columns turned from ochre to deeply brown, which is typical for humic substances.

Moreover, all HOM-OC precipitated as an HOM coating was recovered at the end of the experiment by elution of the columns with 0.1 N NaOH, readjustment of the pH to 6.5, and UV measurement as described above. From these indications we derive that HOM is not significantly redissolved despite the reduction of ferric iron. Mobilization following a reductive dissolution of ferric iron at pH 6.5 is prevented by the presence of phosphate that forms slightly soluble ferrous iron species under these conditions. As shown in the above mentioned batch experiments, ferrous phosphate also strongly binds HOM hence not releasing any HOM to the effluent. In the absence of high concentrations of phosphate not all of the ferric iron was reduced. We may conclude that HOM is not redissolved as long as still enough ferric iron is available to retain the HOM on the sand grain surfaces. Future experiments will show whether anions that are more prevalent under natural conditions, such as sulphide or carbonate, also function as scavengers for ferrous iron, and whether these precipitates also inhibit a redissolution of the surface-HOM complexes.

3. Interactions between HOM and Hydrophobic Organic Compounds

Interactions between HOM and HOC range from reversible sorption equilibrium to the formation of bound residues by chemical reactions. While the latter process has been described to occur with specific functionalised compounds such as aromatic amines and reactive phenols [27, 28, 52, 53] and some very reactive PAHs [54] most of the hydrophobic xenobiotics interact with HOM only by reversible sorption or partitioning unless they are (biologically) transformed into more reactive metabolites. The degree of sorption between HOC and HOM is determined by the specific properties of both partners. The main driving force for sorption of HOC on HOM is the incompatibility of the HOC with the water phase, that is their hydrophobicity. Therefore, K_{OC} values for sorption of HOC on HOM can be roughly predicted by linear correlations with the octanol-water partition coefficients K_{OW} of the HOC [55-57]. However, these empirical K_{OC}-K_{OW} correlations are specific for certain compound classes. The predictive power of K_{OC}-K_{OW} correlations for grouped data including different compound classes is considerably worse [57]. This is due to the fact that the degree of sorption is not only influenced by the hydrophobicity of the HOC but also on the affinity between HOC and HOM, i.e., their ability to form intermolecular interactions. In case of reversible sorption these intermolecular interactions can comprise non-specific intermolecular interactions, hydrogen bonding or charge-transfer interactions. Several more sophisticated models have been developed, based for example on Flory-Huggins theory [58-61] or linear solvation energy relationships (LSERs) [62, 63]. These models that consider at least partly these intermolecular interactions between HOC and HOM and can, therefore, be applied to a broader range of compounds.

With respect to our concept of a HOM-based sorption barrier we were also interested in the question which structural properties of the HOM provide a high sorption potential for HOC. One approach to answer this question is to correlate sorption coefficients of HOM to a variety of structural parameters that can be experimentally determined. In order to consider a broad range of structurally different HOM we chose HOM of various origins. The model sorbate applied was pyrene representing the class of PAHs.

The 11 humic and fulvic acids investigated (table 3) were extracted and isolated according to the methods proposed by the IHSS. They included:

- aquatic humic acid (HA) as well as fulvic acid (FA) from Lake Hohloh, Germany (BW-HA and BW-FA)
- terrestrial HAs from the A_h horizon and the B_v horizon of a forest soil in Bitterfeld, Germany (SoilA-HA and SoilB-HA, respectively) and a moor (Moor-HA, Kleiner Kranichsee, Ore Mountains, Germany)
- humic substance-like polymers isolated from the water body and the sediments of a former lignite wastewater pond (Lake Schwelvollert, Germany) [64], referred to as anthropogenic HOM (Anth-DW-FA, Anth-DW-HA, Anth-Sed-FA, Anth-SW-FA and Anth-SW-HA; where DW, Sed and SW stand for deep water, sediments and surface water respectively as the sources of the HOM), and
- a commercially available, coal-derived HA from Roth Ltd., Germany (Com-HA).

Structural parameters of the HOM investigated were atomic ratios of O/H, O/C, (N+S+O)/C determined by elemental analysis, content of carboxylic groups (f_{COOH}) and total content of acidic groups ($f_{COOH+Ph\text{-}OH}$) determined by acid-base titration (both in mval g^{-1} HOM), UV absorptivity at 280 nm (ε_{280} in cm^2 mg_{DOC}^{-1}) as well as the following properties obtained from ^{1}H-NMR spectra: fraction of aromatic protons (f_{arom}, 6.3-8.1 ppm) and fraction of non-polar aliphatic protons (f_{NPAl}, 0.4-1.7 ppm) of total protons in ^{1}H-NMR spectra as well as the ratio of aromatic and non-polar aliphatic protons f_{arom}/f_{NPAl}.

The sorption experiments were performed using solid phase micro-extraction (SPME) [60, 65, 66].

In SPME a tiny silica fibre coated with a thin polymeric film samples only from the fraction of an analyte that is freely dissolved and not associated with the HOM. If the conditions are adjusted properly, the sampled amount is so little that the sorption equilibrium between HOC and HOM is practically not affected. Since this procedure does not significantly disturb the sorption equilibrium, SPME belongs to the so-called "non-invasive" methods. One must be aware that SPME, like the dialysis or solubility enhancement approaches, supplies activity related K_{OC} values rather than concentration-based partition coefficients [54, 65, 67]. We will later see in our discussion that this point may explain possible differences in K_{OC} values obtained by different methods. The main advantages of the use of SPME include

- the applicability to investigate both dissolved and particulate HOM,
- that the sorption equilibrium on HOM is not disturbed (thus also allowing multiple extractions), and
- that this approach can be applied for multicomponent systems and it is not limited to fluorophores as the fluorescent quenching technique (FQT) is.

A disadvantage of the SPME method is the slow equilibration between solute and fibre (especially in the headspace mode). Furthermore, one has to consider that since SPME is an activity based method it is sensitive to the conditions of the aqueous phase (e.g., ionic strength).

For sorption experiments, pyrene as a highly hydrophobic compound and a representative of the PAH family, was spiked as ethanolic solution into the various aqueous solutions (c_{HOM} = 50 to 1000 mg L^{-1}; pH = 7; 4 mM NaN_3; IS = 10 mM, NaN_3 + NaCl). The final concentration was 15 µg L^{-1} pyrene in reference solutions and 30 µg L^{-1} in solutions containing HOM. The HOM solutions were prepared by dissolving the solid HOM in dilute NaOH. After further dilution with deionised water, the final pH of the solution was adjusted by adding dilute HCl. The sorption and SPME experiments were conducted in 100 mL Erlenmeyer flasks equipped with PTFE-lined septa and glass-coated magnetic stirring bars. Sorption was allowed to come to equilibrium for at least 12 hours. The SPME was performed either in the solution extraction (direct) mode or in the headspace mode according to the procedure described in [65]. For the direct mode, the fibre was equilibrated with the HOM/pyrene solution over 6 h. For the headspace mode, the fibre was placed above the solution for 18 h. The loaded fibre was then transferred into a GC injector (splitless injection at 290°C for 3 min) for pyrene desorption. In order to simplify the quantitative treatment of the SPME data, we used conditions where the depletion of the analytes from the sample and their vapour fractions were insignificant: 7 µm polydimethylsiloxane (PDMS) fibre from Supelco, 80-100 mL sample volume, external calibration.

Tables 3 and 4 contain the sorption coefficients of pyrene as well as the results for the structural parameters of all HOM samples studied, see also [54].

The sorption coefficients of pyrene with the various HOM samples differ by about one order of magnitude. Similar differences between sorption coefficients of one and the same sorbate with HOM of various origins have also been reported by other authors [68-70]. They are in the expected range of variation. Fulvic acids (FAs) generally give lower sorption coefficients than the HAs of the same origin. Within the natural HAs the soil-derived HAs possess the highest sorption potential in accordance with literature data [68, 71]. The highest sorption coefficients within all HOM samples studied were determined for the anthropogenic HA isolated from 15 m depth (anaerobic zone) of a lignite wastewater pond and the commercially available coal-derived HA. Recently, Kulikova and Perminova [72] studied the sorption of atrazine to HOM of various origins and also reported that a coal-derived humic acid showed the highest sorption potential.

Table 3. Sorption coefficients of pyrene (log K_{DOC}) and structural parameters expressing the polarity of the HOM.

Sample	log K_{DOC}	O/H	O/C	(N+S+O)/C	f_{COOH} [1] [mmol g^{-1}]	$f_{COOH+OH}$ [2] [mmol g^{-1}]
Anth-DW	5.02±0.07	0.22	0.21	0.307	2.17	3.67
Com-HA	4.95±0.07	0.36	0.37	0.407	3.41	5.40
Anth-Sed-HA	4.80±0.08	0.36	0.35	0.449	2.27	3.41
Moor-HA	4.77±0.08	0.32	0.38	0.413	2.45	3.07
SoilA-HA	4.70±0.08	0.41	0.50	0.58	2.60	3.16
SoilB-HA	4.47±0.10	0.36	0.50	0.602	n.d.[3]	n.d.
Anth-SW-HA	4.41±0.11	0.41	0.38	0.487	2.49	4.42
Anth-DW-FA	4.35±0.11	0.44	0.49	0.596	2.17	3.67
Anth-SW-FA	4.23±0.13	0.48	0.50	0.603	3.22	5.06
BW-HA	4.21±0.13	0.65	0.52	0.543	3.05	5.27
BW-FA	4.01±0.18	0.68	0.57	0.589	3.83	5.74

[1] mass related carboxyl acidity, calculated from the proton capacity of the HOM in the range of pH 3 to pH 7.5.

[2] mass related phenol and carboxyl acidity, calculated from the proton capacity of the HOM in the range of pH 3 to pH 10.

[3] not determined.

Table 4. Structural parameters expressing the aromaticity or aliphaticity of the HOM.

Sample	ε_{280} [$cm^2 mg_{DOC}^{-1}$]	f_{arom}	f_{NPAl}	f_{arom}/f_{NPAl}
Anth-DW	65.8	0.179	0.453	0.395
Com-HA	83.0	0.287	0.433	0.663
Anth-Sed-HA	71.9	0.174	0.437	0.398
Moor-HA	50.8	0.185	0.288	0.642
SoilA-HA	57.8	0.112	0.371	0.302
SoilB-HA	45.6	0.095	0.515	0.184
Anth-SW-HA	44.2	0.136	0.343	0.396
Anth-DW-FA	46.4	0.128	0.470	0.272
Anth-SW-FA	43.3	0.143	0.395	0.362
BW-HA	46.3	0.133	0.230	0.578
BW-FA	39.2	0.096	0.276	0.35

In general, one can consider two cases for the correlation between structural parameters and sorption affinities. If one regards the sorption affinity of the various building blocks *i* to be more or less independent of their environment in the macromolecule, then the overall sorption coefficient K_{DOC} can be approximated as a linear combination of single $K_{DOC,i}$ values (eq. 1)

$$K_{DOC} = \sum_i x_i \cdot K_{DOC,i} \tag{1}$$

(with x_i being the proportion of e.g. aromatic, aliphatic, polar... units)

In the second scenario, a change in the relative amount, size or arrangement of the structural units may result in a significant change of their sorption affinities. As an example one can consider an increase in aromatic centres which leads to the formation of larger aromatic regions with a higher affinity towards the sorbate than that of all isolated aromatic units combined. In such a case, we have to consider a more complex correlation between structural parameters and the overall sorption coefficient, possibly an exponential correlation (eq. 2) based on the exponential relationship between K_{DOC} and the free enthalpy of interaction $G_{interaction}$.

$$K_{DOC} \sim e^{-\Delta G\ interaction} \rightarrow \log K_{DOC} \sim x_i \tag{2}$$

This relation assumes a linear dependence between $G_{interaction}$ and the proportion x_i of a certain constituent *i* in the sorbent, which is not expected to be completely fulfilled in reality. For the complex and heterogeneous humic substances, a superposition of both effects (symbolized by eqs 1 and 2) is to be expected.

Table 4 shows the results for correlations between the sorption coefficients and the various structural parameters according to both approaches K_{DOC} = f(x) and log K_{DOC} = f(x). For several of the structural parameters studied significant correlations with the sorption coefficient of pyrene of the HOM were obtained. Both approaches, the linear regression according to K_{DOC} = f(x) or log K_{DOC} = f(x) differ only slightly in their r^2 values for each of the parameters. In general, all structural parameters which are a measure of the content of functional groups in the HOM and consequently reflect their polarity, such as the ratios O/H, O/C, (N+S+O)/C as well as the content of acidic groups, show correlation equations with a negative slope. This is in accordance to the results of other authors who also found a negative effect of the polarity of HOM (calculated from atomic ratios) on the sorption potential towards HOC [73,74]. The weak correlation with the content of acidic groups (Table 5) indicates that the polarity of the HOM is not only determined by carboxylic and/or phenolic groups but also to a large extent by the fraction of carbohydrate structures (parameters O/C and (N+O+S)/C).

Furthermore, significant correlations were also found between the sorption potential of the HOM samples and their aromaticity measured as absorptivity at 280 nm or by ^{1}H-NMR spectra. A strong positive relationship between aromaticity of HOM and sorption potential toward PAHs was also found by other authors [69, 70, 72, 75]. Chin et al. [69] reported a negative effect of the content of non-polar aliphatic carbon (determined by ^{13}C-NMR) on the sorption coefficient of pyrene as determined with five aquatic humic substances, which seems to underline the importance of aromatic structures. In contrast, Chefetz et al. [76, 77] found a positive trend between the K_{OC} level of pyrene and the aliphaticity calculated from ^{13}C-NMR spectra for natural organic matter of various origins. In our study no significant correlation between pyrene sorption and the content of highly shielded aliphatic protons in the ^{1}H-NMR spectrum as a measure of the content of non-polar aliphatic structures was observed.

Table 5. Results of the linear regression according to K_{DOC}=f(x) or log K_{DOC}=f(x) for the correlations between the sorption coefficients of pyrene and different structural parameters (x) of HOM of various origins.

structural parameter (x)	[number of samples]	K_{DOC} = f(x) r^2; F-Test	log K_{DOC} = f(x) r^2; F-Test	slope
O/H	[11]	0.73; s[1]	0.72; s	positive
O/C	[11]	0.74; s	0.69; s	negative
(N+S+O)/C	[11]	0.75; s	0.64; s	negative
f_{COOH}	[9]	0.31; ns[2]	0.,44; s	negative
$f_{COOH+Ph-OH}$	[9]	0.28; ns	0.45; s	negative
ε_{280}	[11]	0.75; s	0.72; s	positive
f_{Ar}	[11]	0.54; s	0.48; s	positive
f_{NPAl}	[11]	0.13; ns	0.18; ns	positive
f_{Ar}/f_{NPAl}	[11]	0.15; ns	0.11; ns	positive

1) significant correlation according to F-test (P = 0.95).
2) correlation is not significant according to F-test (P = 0.95).

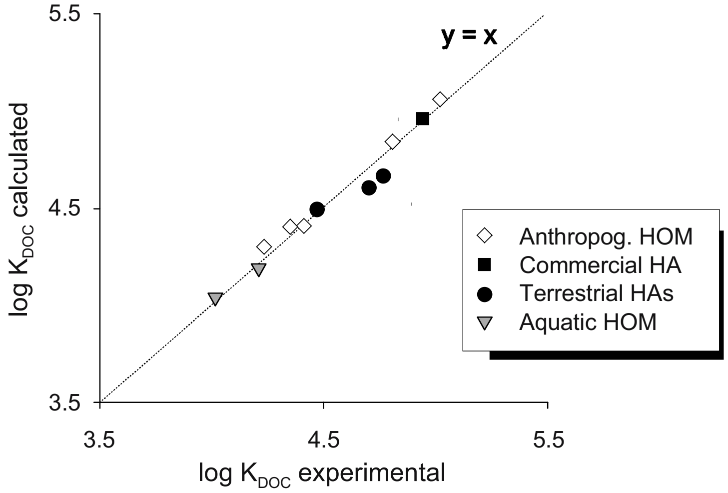


Figure 4. Calculated vs. experimental log K_{DOC} values for pyrene with HOM of various origins (Table 3); calculation according to equation 3.

However, even with the most significant parameters (e.g. O/H, ε_{280}) the predictive power of the correlations is rather poor ($r^2 \leq 0.75$). Obviously, a single parameter alone is not able to sufficiently describe the sorption behaviour of HOM of various origins.

Taking into account *two* characteristic properties of HOM, their polarity *and* aromaticity, we obtained an excellent fit ($r^2 = 0.97$) for our data between log K_{DOC} of pyrene, the O/H atomic ratio and the UV absorptivity at 280 nm [$cm^2\ mg_{DOC}^{-1}$] using eq. 3 (see figure 4):

$$\log K_{DOC} = 1.02 - 1.31 \log [O/H] + 1.75 \log \varepsilon_{280} \qquad (3)$$

Because of possible intercorrelations between several HOM properties (e.g., aromaticity and molecular weight [69], mechanistic interpretations of empirical correlations between sorption potential and specific structural parameters have to be treated with caution. However, the correlation described above might be a guideline for the selection of a HOM that is best suited for establishing a sorption barrier for PAHs. For the various HOM samples studied coal-derived HOM best incorporate both favourable properties: low polarity and high aromaticity.

4. Sorption Potential of Mineral-Associated, Flocculated and Dissolved HOM

The sorption capability of HOM in the dissolved and the mineral-associated state has been a matter of interest both for methodological and practical reasons. In several studies non-invasive methods like the fluorescence quenching technique (FQT) were applied to compare K_{OC} values of HOM in dissolved and solid state. K_{OC} values obtained for the association of phenanthrene to dissolved organic matter (DOM) were found to be about one order of magnitude higher than the corresponding K_{OC} data for mineral-associated HOM [78-80].

With respect to our intention to generate a sorptive/reactive barrier made of mineral-associated HOM coatings, these findings prompted us to scrutinize these phenomena.

The question arises, if the decrease in K_{OC} data measured for mineral-associated HOM is a real phenomenon (e.g., due to steric effects), or if it is an artefact of the analytical method, FQT. There is a lot of debate in the literature about the validity of FQT for determining sorption coefficients [82]. Problems can arise from several effects that must be taken into account: inner filter effects caused by DOM, cross-quenching by other solutes such as oxygen, and degradation of the analyte by UV light. Unlike the references cited above, the determination of K_{OC} data in the present study was conducted using SPME (see paragraph 3).

The sorption behaviour of flocculated HOM was also investigated within this study. The experimental determination of sorption coefficients is depicted schematically in figure 5 and shall be described briefly: Three 250 mL flasks were each filled with a DOM solution (c_{DOM} = 200 mg L^{-1}, DOM: commercial humic acid, purchased from Roth Ltd., Germany), leaving a headspace volume of 75 mL. 200 mg L^{-1} sodium azide was added to suppress microbial activity. Sodium chloride was also added to give a concentration of 0.1 M ensuring constant ionic strength. To investigate mineral-associated HOM (denoted as SOM for sorbed organic matter), the mineral hematite (Fe_2O_3), which was prepared according to [81], was suspended in the DOM solution by rigorous stirring. The pH was set to pH 4.5 for the dissolved and hematite-associated HOM. A flocculated HOM (denoted as FOM) was simulated by preparation of a ferric iron-humate. For this purpose a 0.1 M $FeCl_3$-solution was added to the same humic material and adjusted to pH 5.5. Both the flocculation and the sorption on hematite resulted in an almost complete removal of DOM. A mixture consisting of various PAHs

Table 6. Sorption coefficients of dissolved (K_{DOC}), sorbed (K_{SOC}), and flocculated (K_{FOC}) HOM normalized to the OC contents. $\overline{s}$ standard deviation of 20 replicate measurements (5 different PDMS fibres in fourfold replicate measurement). K_{Min} denotes the sorption to the solid material in absence of HOM.

HOM	Tetrahydro-thiophene		2,4,4-Trimethyl-cyclopentanone		Naphthalene		Acenaphthylene		Phenanthrene	
	$\log \overline{K_{OC}}$	$\overline{s}$	$\log \overline{K_{OC}}$	$\overline{s}$	$\log \overline{K_{OC}}$	$\overline{s}$	$\log \overline{K_{OC}}$	$\overline{s}$	$\log \overline{K_{OC}}$	$\overline{s}$
sorbed to Fe_2O_3 (pH 4.5)	3.78	0.22	3.46	0.40	3.56	0.43	4.21	0.26	4,78	0,07
freely dissolved (pH 4.5)	3.82	0.20	3.68	0.27	3.37	0.57	4.23	0.15	4,64	0,06
flocculated (pH 5.5)	3.76	0.22	3.66	0.24	3.45	0.30	4.18	0.18	4,68	0,05
freely dissolved (pH 5.5)	3.97	0.17	3.97	0.20	3.57	0.32	3.88	0.10	4,49	0,07
	$\log \overline{K_{Min}}$	$\overline{s}$	$\log \overline{K_{Min}}$	$\overline{s}$	$\log \overline{K_{Min}}$	$\overline{s}$	$\log \overline{K_{Min}}$	$\overline{s}$	$\log \overline{K_{Min}}$	$\overline{s}$
Fe_2O_3 blanc (pH 4.5)	rcn. with matrix		0.98	0.71	no sorption		rcn. with matrix		0.78	1.06
$Fe(OH)_3$-flocculate blanc	2.22	1.08	2.12	1.07	no sorption		rcn. with matrix		1.99	0.78

[1] Tetrahydrothiophene and acenaphthylene reacted with the blanc hematite surfaces, no acceptable standard deviations could be obtained, data where omitted.

(naphthalene through phenanthrene) as well as tetrahydrothiophene and 2,2,4-trimethylcyclopentanone was spiked to each of the flasks from acetonic solution to give a concentration of 100 μg L^{-1} per compound. After equilibrating the multiphase systems for one day, SPME fibres (7 μm PDMS coating) were pierced through an PTFE-coated septum and placed in the headspace above the solution. An SPME sampling time of 18 h was maintained (typical overnight procedure to ensure equilibrium conditions in the headspace SPME; see [65]. Each measurement was carried out in four replicates.

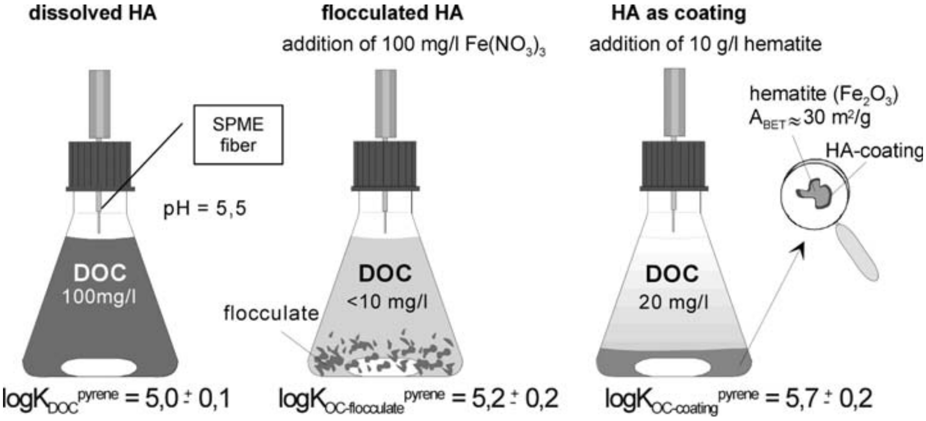


Figure 5. Determination of sorption coefficients by means of headspace SPME on DOM, flocculated HOM, and mineral-associated HOM.

The results, which are summarized in Table 6, give strong evidence that there is no significant deviation in sorption data for a given solute dependent on the state of HOM "aggregation". Therefore, the findings in [79] and [80] are assumed to be associated with peculiarities of the fluorescence quenching technique. A methodological comparison of this technique and our SPME approach [54, 67, 83] confirmed that K_{DOC} data of different PAHs measured by FQT were up to one order of magnitude higher than data obtained by using SPME. These methods differ in their definition of the sorbed state. In sorption experiments with dissolved sorbents, FQT includes all solute molecules which are sufficiently close to the sorbent that their fluorescence signal is quenched. When the sorbent is in the particulate state, the sorbed fraction of the solute and the particular sorbent are separated from the solution phase. The concentration of the freely-dissolved fraction of the solute is determined by a fluorescence measurement. With the FQT approach the sorbed state is method defined [67]. In comparison, SPME is an activity-based method, where all effects caused by the sorbent which contribute to a decrease in the thermodynamic activity of the solute are defined as sorption or sorptive interaction, regardless of the mechanism, strength or life-time of binding. Whether the sorbent is in the dissolved or particulate state does not change this principle. Therefore, we evaluate the SPME approach described above to be more reliable for a comparison of the sorption potential of OM in its different states (dissolved versus particulate).

Consequently, considering our concept of generating a mineral-associated HOM barrier, we expect that the sorption potential of the HOM remains completely preserved after the immobilization of HOM.

5. Engineering Procedures for Immobilization of HOM on Selected Aquifer Materials

In this section we describe HOM-coating procedures under flow-through conditions. We present lab scale study results and proposed field applications for HOM sorption barriers.

5.1. LAB-SCALE

To simulate the suggested remediation approach, a set-up was developed which is schematically depicted in figure 6 and briefly described in the following: Salt solutions were passed through glass columns (5) (length 20 cm, diameter 2.2 cm) filled with the carrier material under study, with flow from the bottom to the top. The flux was adjusted to about 50-100 mL per day (which is about 34 to 68 cm/d linear velocity). The flux is adjusted by the level of the potential vessel (2). To keep the potential constant, the potential vessel is connected to a reservoir (1) via an overflow and a peristaltic pump (4). Anoxic conditions are preserved by a gas barrier (3) and by gas frits to flush the vessels with argon (7). The set-up in figure 6 is thought to be quite universal for investigation of the immobilization of the HOM as well as the retardation of the HOC on the immobilized coatings.

In the latter case, a conventional solid phase extraction (SPE) cartridge (6) filled with 200 mg C18 and 200 mg SDB-2 material (both from Baker) allows to monitor the breakthrough of organic analytes of a wide range of polarity. For studying the HOC breakthrough the peristaltic pump is not activated to prevent sorption of HOC onto the tubing. 200 mg L^{-1} NaN_3 was added to the influent in order to suppress biodegradation of the HOC under investigation.

To demonstrate the principle functioning of an HOM-barrier under flow-through conditions we first had to build up a ferric iron barrier. Lacking representative aquifer materials from polluted sites in native condition (e.g., ferrous iron surface species, exclusion of oxygen, undisturbed texture), we injected ferric iron solutions to precipitate ferric hydroxide onto mineral surfaces.

The suggested procedure depicted schematically in figure 1 includes the following steps

- injection of ferric iron salt solutions ($FeCl_3$) and precipitation as ferric hydroxide as a result of increased pH or reaction with phosphate buffer (alternative to ferrous iron oxidation)
- injection of dissolved HOM resulting in its immobilization
- examination of the retardation of HOC on the sorptive/reactive barrier.

In succeeding to build up a ferric iron coating we passed a 0.1 M $FeCl_3$-solution (pre-titrated to pH 2.5) alternating with either 0.1 mM NaOH (A) or 0.5 M phosphate buffer (pH 6.5) (B) through the columns. Several experiments with a pre-cleaned quartz sand (fraction 200-630 µm, BET(N_2)-surface = 0.4 m²/g, porosity = 0.356) led to 0.7 mg Fe/g sand when precipitated by NaOH and 2.2 mg Fe/g sand when phosphate buffer was added.

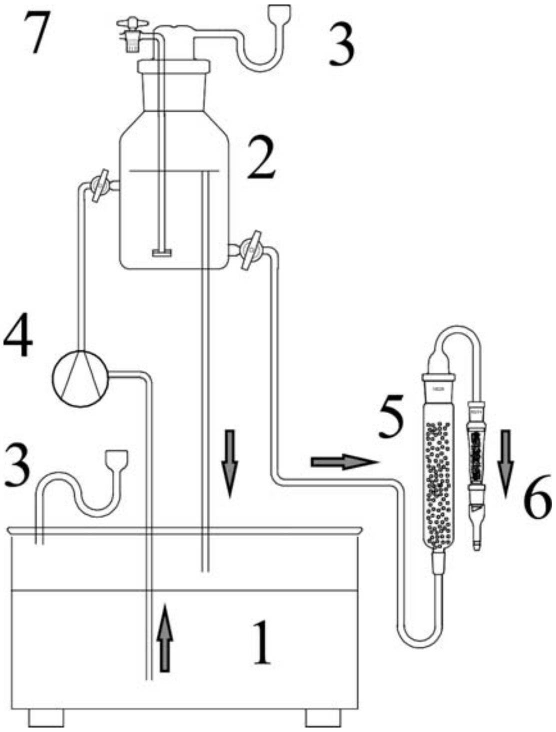


Figure 6. Apparatus for immobilization of HOM under bench scale flow through conditions. Numbered components are explained in the text.

According to these results the immobilization of a reference HOM (200 mg L^{-1} commercial humic acid, Roth Ltd., Germany) resulted in 0.26 mg OC/g sand (A) and 0.35 mg OC/g sand (B). The iron and HOM precipitates dyed the sand homogeneously and did not lead to clogging effects, most likely due to a high portion of voids and very little dispersivity of the applied sand grains. Yet, batch coating experiments confirmed that iron covers the quartz surface only on “hot spots” in cleavages and surface cracks. XPS investigations also revealed less than 5% iron at the quartz surface on an atomic scale.

The HOC mixture applied in the retardation studies represented typical coal pyrolysis contaminants as they occur e.g. downstream the above mentioned tar factory site in Rositz, Germany [3]. The compounds which were used cover a log K_{OW}-range from 1.79 to 4.46 and include compound classes like ketones, phenols, pyridines, quinolines, and PAHs. Each compound was spiked into a 0.1 M NaCl feed solution (pH 6.5) to give a concentration of 100 µg L^{-1}. Analysis of the solid phase extracts at the outlet of the columns was performed by GC/MS in SIM mode.

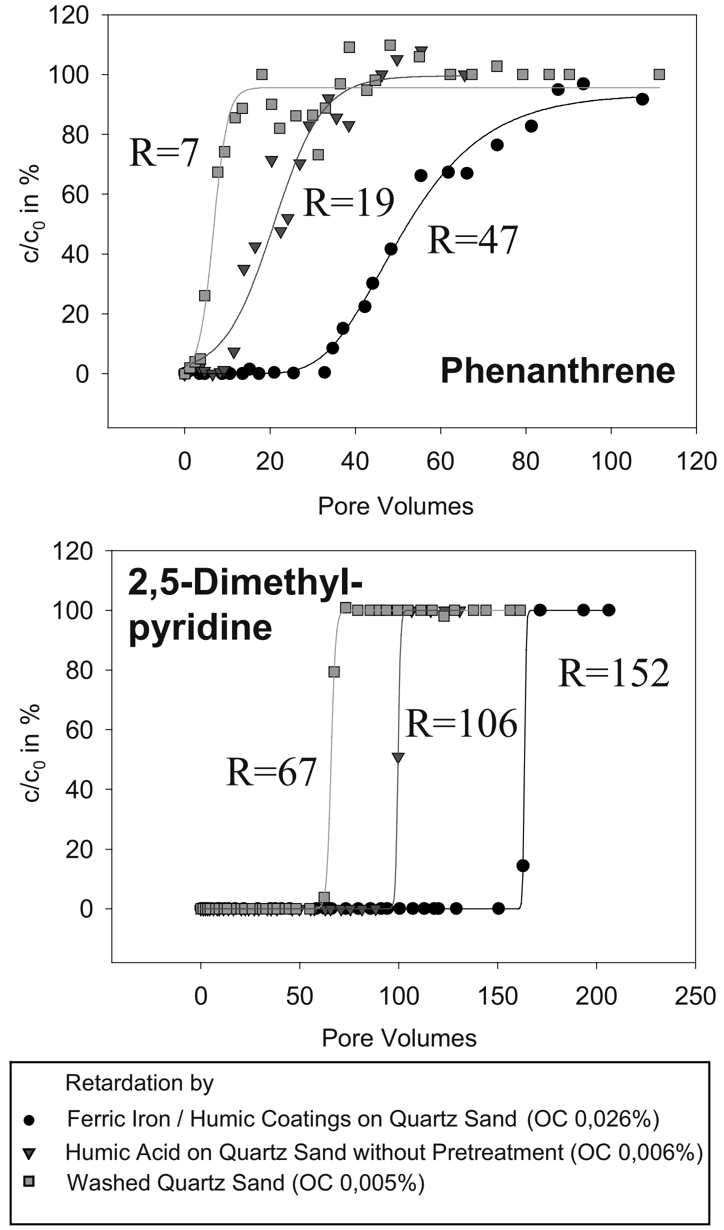


Figure 7. Breakthrough curves of two HOC in columns of quartz sand coated with Roth humic acid. c/c$_0$ denotes the ratio of the HOC concentration at the outlet of the column and its initial concentration in the reservoir. The total pore volume of a column was determined to be 21 mL.

Taking hydrophobic partitioning as a basis to describe sorption of HOC on OC-coated aquifer materials retardation factors (R) can be calculated according to equation 4 [84].

$$R = 1 + \frac{\rho}{\Theta} K_{OC} f_{OC} = \frac{\bar{u}}{\bar{u}_{HOC}} \qquad (4)$$

Where ρ is the density of the wet aquifer matrix (in our case 1.695 g cm^{-3}), Θ – the porosity of the sand (in our case 0.356), and K_{OC} – the distribution coefficient of the HOC between HOM and the aqueous phase, normalized to the OC contents of the HOM, and f_{OC} – a factor representing the OC content in the water saturated sand. For calculation of R we used the K_{FOM}-values listed in the paragraph above. R is also experimentally accessible by relating the average velocity of an inert tracer ($\bar{u}$) to the migration velocity of an HOC ($\bar{u}_{HOC}$).

The breakthrough curves of two selected compounds are shown in figure 7.

The environmental behaviour of phenanthrene as an representative of the class of PAHs is mainly determined by hydrophobic partitioning (log K_{OW} = 4.46). When comparing the breakthrough curves for this compound on pure quartz sand and HOM-coated sand with the breakthrough of an inert tracer (KNO_3, not shown) a significant sorption enhancement on HOM coated sand is noticed (R_{exp} = 47, see table 7). However, a small retardation effect is observed also for a “clean” quartz sand surface (R_{exp} = 7).

2,5-Dimethylpyridine (2,5-DMPy), a more polar compound of the Rositz plume (log K_{OW} = 1.8), is even more retarded (R_{exp} up to 150) by the barrier than the much more hydrophobic phenanthrene. The reason for this surprising observation cannot be explained only by hydrophobic interactions. Specific interactions of the N-base with mineral surfaces may account for this effect. The fact that the columns prepared by the phosphate method completely loose their ability to retard 2,5-DMPy as compared with a clean quartz also supports this idea. Phosphate sorbed on the surface of ferric hydroxide may block reactive Fe-binding sites, which are assumed to be responsible for strong interactions with 2,5-DMPy.

Tables 7 and 8 represent measured and calculated retardation factors for several HOC studied. Table 8 outlines considerable decreases in pollutant mobility for highly hydrophobic or specifically interacting pollutants when quartz sand is coated by HOM albeit the immobilized OC is fairly low (f_{OC} = 0.001). Consequently, measured R-values smaller than those calculated according to eq. 4 based on established partitioning equilibrium may imply restricted accessibility of immobilized HOM for the permeating HOC (dead end voids, stagnant water, pore exclusions by clogged ferric iron precipitates etc.).

Moreover, the iron/phosphate-HOM barrier showed significantly less HOC retardation even if the OC-contents were higher than in HOM-barriers prepared by $FeCl_3$/NaOH. These results suggest a dependency of HOC-sorption on the accessibility of humic organic carbon [85].

Table 7. Breakthrough behaviour of 5 HOC on HOM-coated quartz sand columns – Experimentally determined retardation factors.

Coating Procedure	Naphthalene	Acenaphthylene	Phenanthrene	2,5-Dimethyl-pyridine	2,6-Dimethyl-quinoline
Precipitation of $Fe(OH)_3$ by OH^-	2.9	6.7	43	152	>189
Precipitation of $Fe(OH)_3$ by OH^-	n.d.	7.6	47	123	>189
Precipitation of $Fe(OH)_3$ by phosphate	2.0	4.0	35	ca.100	189
Precipitation of $Fe(OH)_3$ by phosphate	1.7	3.1	18	75	>189
No coating (pure quartz)	1.6	1.7	6.6	67	>189

Table 8. Calculated retardation factors according to pure hydrophobic partitioning based on the OC values given in the text.

Coating Procedure	Naphthalene	Acenaphthylene	Phenanthrene
Precipitation of $Fe(OH)_3$ by OH^-	4.5	19.7	60.3
Precipitation of $Fe(OH)_3$ by OH^-	4.2	18.3	55.7
Precipitation of $Fe(OH)_3$ by phosphate	5.7	26.2	80.8
Precipitation of $Fe(OH)_3$ by phosphate	4.0	16.9	51.1
No coating (pure quartz)	1.7	4.6	12.4

5.2. FIELD SCALE

The *in situ* construction of permeable HOM barriers to retain dissolved contaminants comprises several considerations that need to be addressed here.

HOM barriers can be created on native or artificially coated mineral surfaces of the aquifer. One general recipe to build up an HOM barrier cannot be given. The way the barrier needs to be constructed is rather site dependent. Firstly; an extended geological survey of the polluted aquifer is required. This survey should include geohydraulic tests, information about the grain size distribution, clay, chalk, OC and iron content, dissolved ferrous iron concentration, and mineral surface textures. If clays are present, they frequently form indigenous surface coatings with increased HOM retention potential.

Laboratory results implied (see above) that metal ion surface precipitates must be generated in case the majority of the aquifer material is made of low surface quartz and other silicate materials.

If the groundwater is rich in dissolved ferrous iron, aeration technologies may attribute ferric iron coatings in advance to provide for a better HOM sorption onto the aquifer material. Field tests are needed to confirm the stability of such barriers at shutoff of the oxygen supply.

As with the mediator, the HOM-coating must be long-term stable and withstand leaching in the specific anoxic groundwater environment. For aluminium hydroxide coatings may not be allowed by the local authorities, iron coatings may be more suitable instead. Here the redox instability of iron and the potentially associated barrier leaching at reduction of ferric iron must be taken into consideration. Assuming the pH is kept in the neutral range, the supply of phosphate may assist in generating milieu stable ferrous phosphate surface coatings which in turn are highly susceptible to bind HOM.

In order to avoid bypassing of the pollutant plume, the original hydrodynamic conditions have to be preserved as best as possible. In this respect, thin and uniform mediator and HOM coatings on the aquifer matrix are to be pursued. Hence, we would like to suggest to create sorptive/reactive areas of moderate OC content within an aquifer rather than barriers of spatially high HOM content. The production of tailored HOM for this specific field of application might be considered; e.g. the introduction of chelating groups into the HOM backbone to retard heavy metal contaminations or the enhancement of the HOM's hydrophobicity when considering HOC as targets.

A locally controlled precipitation of the injected HOM can potentially be achieved in the field by two methods.

First, we will consider the case where HOM shows non-conservative flow behaviour, as occurring especially in aquifers with significant contents of inorganic surface precipitates and clays [3, 86, 87]. The concept in this case is either to directly flush the HOM solutions into the aquifer, if the aquifer grains are already coated with ferric iron or clay precipitates, or to use solutions of polyvalent cations (such as Ca^{2+}), that show almost conservative flow behaviour, subsequent to HOM injections which is retarded due to interactions with the mineral surfaces of the aquifer material. As a consequence of the different flow velocities the HOM becomes caught up by the polyvalent cations and flocculated. Studying the velocities of both reactants in the aquifer the barrier can be placed that way at a desired spot [88]. While the latter method should result in high local

OC spots, uncontrolled flocculation of the HOM in the voids of the aquifer may result in an undesirable decrease in hydraulic conductivity [Balcke, unpublished].

The approach preferred in this study is to coat the mineral surfaces of the aquifer with polyvalent ion precipitates so the sorption affinity towards HOM increases. Ferric iron surface coatings can be established in practice by temporary groundwater oxygenation if the aquifer carries enough dissolved ferrous iron or ferrous precipitates, such as siderite or pyrite. In chalk-rich aquifers or those of high alkalinity dilute acidic ferric iron solution injections will be neutralized and dispersed finally precipitating ferrous oxyhydrates onto the aquifer mineral surfaces rendering them more susceptible for sorption of HOM. If the aquifer contains neither chalk nor a sufficient clay content, based on an intensive geological survey the utilization of transverse mixing of two spatially separated injections into the aquifer may be possible. These could include mixing of solutions of different density (e.g., high salinity ferric iron solution, low salinity dilute sodium hydroxide solution) or mixing of solutions by transverse dispersion with precipitation in the contact mixing zone.

In a future project we intend to investigate the construction and effectiveness of a HOM barrier adapted to the specific conditions of a contaminated site. The field study site will be the grounds of a former wood preserving plant that is contaminated by tar oil. The main groundwater contaminants consist of HOC suitable to be retarded/fixed by a HOM barrier (PAHs and their metabolites as well as heterocyclic compounds). Within this pilot scale field test the HOM barrier will be created according to both previously mentioned strategies.

In summary, we may conclude that HOM sorption/ reactive barriers possess a high potential to retard dissolved environmental pollutants in comparison to the groundwater flux. Even small effective retardation coefficients (e.g., order of magnitude 10), caused by low OC enrichment, will give rise to relevantly longer exposure to microbial attacks and covalent fixation to surface bound HOM.

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