Sorption of humic substances on aquifer material at artificial recharge of groundwater

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Abstract

Experiments in batch equilibrium system were carried out to evaluate the importance of physical and chemical factors determining the sorption efficiency of humic substances (HS) on aquifer material, which has been used for artificial recharge of groundwater (ARG) in drinking water production. Results showed that an increase of the amount of clay in the aquifer material and a decrease of pH in water increased the sorption efficiency. The sorption of higher molecular weight, more hydrophobic and aromatic HS (Aldrich and forest soil humic acids) were greater than the sorption of acidic HS (river fulvic acids), either on the aquifer material or to its representative sorbing phases, clay and organic matter. The sorption on the aquifer material was largely due to physical sorption (hydrophobic attractions). This study showed the importance of HS composition on their removal during ARG and contributed to an understanding of the HS sorption mechanisms in this process.

Keywords: Humic substances; Sorption; Artificial recharge of groundwater; Aquifer material; Drinking water

1. Introduction

Artificial recharge of groundwater (ARG) is achieved by putting surface water in basins or other facilities where it infiltrates into the ground and moves through porous media downwards to recharge aquifers. In this process, without adding any reagents, suspended particles and human pathogens are effectively removed from the water (Huisman and Olsthoorn, 1983). Therefore, in areas where permeable aquifers are available, ARG has been used for drinking water production for more than 150 years. Nowadays, it is recognized that removing humic substances (HS) (humic acids (HA) and fulvic acids (FA)) from drinking water is important because they impart a yellow colour to water and may lead to the formation of carcinogenic by-products during disinfections (Rook, 1974) as well as undesirable bacterial biofilm growth (Ellis et al., 2000) in distribution systems. The removal efficiency of HS during ARG varies from place to place; the causes of these variations are often not understood. Thus, more knowledge about the mechanisms involved in removing HS is of interest.

Due to partially colloidal properties (Jones and Bryan, 1998) and its ability to associate with inorganic colloids (Burba et al., 2001), straining and interception in porous media both in solid–water and gas–water interface may be involved in HS retention during the ARG. However, sorption to aquifer material (hereafter filtersand) (McCarthy et al., 1993) followed by microbial degradation are the most important mechanisms.
Because HS are relatively resistant to degradation whereas attachment to surfaces may increase their availability for bacteria (Camper, 2002), sorption is most likely a limiting step for HS removal during ARG. The mechanisms of HS sorption to filtersand have not been widely studied. However, given the similarity in composition of material, these mechanisms are assumed to be similar to those occurring in soils (Jacks and Fryeklund, 1995), river sediments, and natural aquifer materials. Among the different mechanisms proposed, ligand exchange (chemisorption), hydrophobic attraction, and electrostatic attraction (physical sorption) are considered the most important for removal of HS by surfaces (Stumm, 1992) because HS has both acidic functional groups (carboxyl and phenol) and hydrophobic moieties. Due to the carboxyl groups, HS may participate in ligand exchange or electrostatic interaction with oxide surfaces, whereas hydrophobic properties allow HS to accumulate on surfaces because of their incompatibility with water, which is more polar than the surface (Lai and Chen, 2001). The importance of these mechanisms can be evaluated by comparing the sorption of FA (i.e. more acid fraction of HS) with HA (i.e. more hydrophobic fraction of HS). In addition to the type of HS, the physical–chemical properties of sorbing material (e.g. texture, surface area, amounts of oxides groups) and of water (e.g. pH, ion strength, concentration of divalent metals) govern the sorption mechanisms.

In the present study the sorption of FA and HA on the filtersand and its major composing phases participating in the sorption (i.e. iron and aluminium oxides, organic matter) was evaluated in laboratory batch equilibrium systems. The objective of the study was to investigate how the composition of the filtersand and HS influence sorption efficiency of HS on the filtersand, and to evaluate importance of the sorption mechanisms in removal of HS during ARG.

2. Materials and methods

2.1. Isolation and analyses of humic substances

HA and FA from typical forest soil (podzolic) in Latvia and filtersand from the infiltration basin used for drinking water production at Baltezers ARG plant in Riga, Latvia were isolated by extraction with 0.1 M NaOH (Thurman, 1985). HA and FA from water of Lake Baltezers (used for ARG) and the Salaca River were isolated by the Thurman and Malcolm method (Thurman and Malcolm, 1981), which was modified by Klavins and Cinis (1990). Commercial (Aldrich Chemical Company—Milwaukee, WI) HA isolated from coal was used for comparison. The elemental composition of isolated HS was determined on a Perkin–Elmer 240 B CHN analyser. Ash content was determined by ignition of samples at 500 °C for 5 h. The content of carboxyl groups was determined using Ba(OH)$_2$ titration, and the content of hydroxyl groups was done after acetylation (APHA, 1988). Aromaticity of HS was determined based on measurement of their ultraviolet light absorption and calculated according to Chin et al. (1994). The (O+N)/C atomic ratio was used to establish hydrophilicity/hydrophobicity of HS as suggested by De Paolis and Kukkonen (1997). The higher is this ratio the more hydrophilic is the substance. Molecular weight distribution was determined with gel filtration on Sephadex G-100. Properties of the HS used are summarised in Table 1. Concentrations of HS in water were measured colorimetrically at 410 nm wavelengths using a HACH DR 2000 spectrophotometer and calculated from calibration graphs initially prepared for each HS.

2.2. Sampling, preparation and analysis of the filtersand

Filtersand was sampled at the Baltezers plant where groundwater is artificially recharged by infiltration of

<table>
<thead>
<tr>
<th>HS</th>
<th>Elemental composition (%)</th>
<th>Atomic ratio</th>
<th>$^{a}\text{C}_{\text{COOH}}$ (mmol/g)</th>
<th>$^{b}\text{C}_{\text{OH}}$ (mmol/g)</th>
<th>$^{c}\text{C}_{\text{aromaticity}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtersand HA</td>
<td>C 54.6 H 3.7 N 0.9 O 40.8</td>
<td>H/O 1.45</td>
<td>4.88</td>
<td>1.18</td>
<td>32.5</td>
</tr>
<tr>
<td>Lake HA</td>
<td>C 57.2 H 3.9 N 1.0 O 40.2</td>
<td>H/O 1.57</td>
<td>4.15</td>
<td>1.42</td>
<td>19.3</td>
</tr>
<tr>
<td>Sediment HA</td>
<td>C 52.1 H 6.0 N 4.3 O 37.5</td>
<td>H/O 2.58</td>
<td>2.43</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>River FA</td>
<td>C 46.3 H 3.7 N 2.9 O 47.1</td>
<td>H/O 1.26</td>
<td>4.45</td>
<td>0.98</td>
<td>16.3</td>
</tr>
<tr>
<td>Soil HA</td>
<td>C 49.8 H 4.7 N 2.1 O 43.3</td>
<td>H/O 1.75</td>
<td>2.21</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Aldrich HA</td>
<td>C 49.9 H 4.7 N 2.3 O 43.1</td>
<td>H/O 1.76</td>
<td>2.15</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$a$ Carboxylic groups.  
$b$ Phenolic hydroxyl groups.  
$c$ Aromaticity.
water from Lake Baltezers through the infiltration basins. The basins were excavated in quaternary deposits at the end of the 1950s. In 1997, samples were collected from the bottoms of three infiltration ponds numbered accordingly 3, 4, and 8. Samples from each basin were taken close to the periphery (A), the centre (C) of the basins and in between these sampling points (B). The surficial filtersand layer (0–4 cm) was sampled by Ekman drag, and deeper layers (4–24 cm) were taken using a core sampler and dissected into segments of 4 cm. The samples were air dried, sieved (<2 mm), and subsequently used for analyses and sorption experiments.

Particle size was estimated by dry sieve analysis or by the hydrometer method. BET surface area for minerals was determined by Micrometric FlowSorb II 2300 (30% H₂, 70% He) or Coulter SA 3100. The mineral composition was estimated using X-ray diffraction (diffractometer DRON-3). The filtersand chemical composition was determined by standard methods (APHA, 1988). For chemical analyses iron was extracted from filtersand samples (~10 g) with 25 ml conc. HNO₃, together with 5 ml 60% HClO₄. The content of organic carbon (OC) in the filtersand was determined by K₂Cr₂O₇ digestion (Methods of Soil Analysis, 1989).

2.3. Filtersand with organic matter removed

The organic matter in filtersand samples was removed by oxidation in acidic media: 500 g of the filtersand treated with a mixture of 375 ml 15% H₂O₂ and 10% CH₃COOH (55 ml) at 75 °C for 4 h, after which a new portion (100 ml) of 30% H₂O₂ was added with heating for an additional 2 h. Next, the samples were washed with 0.01 M NaCl to remove the entrained salts, then by distilled water, and dried at 105 °C (24 h).

2.4. Oxides, clays and lake sediments

To determine more specifically what phases contributing to HS sorption on aquatic material, phases representing those found in aquifer material were obtained for the study. Reanal supplied Alumina (α-Al₂O₃). Goethite (α-FeOOH) was synthesised accordingly (Lattimer and Jones, 1992). Clays were collected in Latvia; their characteristics are given in Table 2. Surficial sediments layer (67% OC, BET of 1.51 m²/g, 7.37 mg/g Fe) were collected by Ekman drag from the bottom of Lake Baltezers and analysed as per the methods cited above.

2.5. Sorption experiments

Sorption studies for HS on different phases were conducted as batch experiments performed in 50 ml sealed glass bottles on a rotary shaker table for 16 h at 20 °C. In 50 ml glassware, 5, 10, 25, 50, 75, 100, and 250 mg/l solutions of HS were equilibrated with 0.5 g of sorbent until equilibrium occurred. After separation of the sorbent by filtration through filter paper, the concentration of HS in the filtrate was analysed. The quantity of HS sorbed to different phases was determined from the difference between the initial aqueous phase concentration and the concentration in solution at equilibrium. Due to the release of organic matter from the filtersand and lake sediments, the results of the sorption experiments could not be interpreted by Freundlich or Langmuir isotherms. When initially sorbed (background) organic matter needs to be considered, the initial mass approach (Nodvin et al., 1986) is useful. This approach was also used in this study. In the initial mass approach, the concentration of a substance retained or released (normalized to sorbent mass) is plotted as a function of the initial concentration of the substances (also normalized to sorbent mass).

3. Results

3.1. Composition of the filtersand

Mineralogical analysis using X-ray diffraction spectroscopy revealed that the filtersand, regardless the sampling location and depth, was dominantly composed of SiO₂ (quartz) with some admixture of aluminium silicate (labradorite plagioclase). An absence of iron oxide minerals (e.g. celadonite and glauconite) indicated that iron, detected by chemical analyses, (Table 3) presumably infiltrated in via surface water. The texture of the aquifer material ranged from clay to fine sand. Typical concentrations of clay in filtersand ranged between 1% and 3% (basins no. 8 and 3), whereas it was as
higher in basin no. 4 close to that found in soils, see Table 3. The amount of OC was about 0.5%.

3.2. Composition of humic substances

Soil HA and commercially available (Aldrich) HA, were more aromatic and contained less from the carboxyl groups than river FA, Table 1. The (O + N/C) atomic ratios for Aldrich HA and soil HA were significantly lower than for river FA (Table 1) and indicated that both HAs were more hydrophobic than the FA. The molecular mass of the aquatic FA was lower (500–1000 Da) than for both HAs (500–3000 Da).

3.3. HS sorption on filtersand and related phases

Sorption of Aldrich HS increased with increased amounts of clay and decreased with increased amount of OC in the filtersand, Figs. 1 and 2. Sorption was heterogeneous among samples, but generally increased with the depth below the basins, Fig. 2. Sorption experiments of different HS on clays revealed that HS sorption exceeded the FA sorption, while it was better on smectite (the expandable clays) compared to kaolinite, Table 2. Sorption to the filtersand from which organic matter was chemically removed was low or negative. At the same pH,
Aldrich and soil HA were sorbed better than river FA to typical filtersand (basins no. 3 and 8) from Baltezers plant, Fig. 3. Regardless of the filtersand composition, the lowering of pH significantly increased the sorption efficiently of HS, Fig. 4. To understand the influence of different phases composing the filtersand, the sorption of HA and FA to iron, aluminium oxides, and organic rich sediments were tested. HA were always better or similarly sorbed to all filtersand components except iron oxide, which instead better sorbed FA (Fig. 5).
4. Discussion

Shen (1999) suggested that chemisorption (ligand exchange) is the dominant mechanism for sorption of HS to soil. Jardine et al. (1989), after observing temperature independency of HS sorption to soil, suggested that physical sorption driven by entropy changes (hydrophobic attraction) is more important. Gu et al. (1994) argued that due to fact that most of positively charged sites (e.g. iron oxides, broken edges of clay surfaces) are occupied with organic matter, the ligand exchange is unlikely to be a dominant interaction in the soil system.

The composition of the filtersand used for ARG systems was similar to that of soils but with lower amounts of clay and iron oxide (Table 3), the surfaces bearing major binding sites for sorption of HS. A relatively high amount of OC (Table 3) indicated that a large proportion of these sites had already been occupied with organic matter making their surfaces negatively charged (Day et al., 1994), and thus unavailable for ligand exchange. The quartz was a major constituent of the filtersand. Ligand exchange of HS with quartz surfaces is minor, as proven in experiments by Spark et al. (1997), in which no proton consumption was observed in the interaction between the quartz and HS. Thus, under conditions where filtersand has a limited number of binding sites, ligand exchange is probably not the dominant process for removing HS during ARG.

The results showed that sorption of HS increases with an increase the fraction of clay in the filtersand. Due to small size the clay particles have a large specific surface area that, depending of chemical and physical properties of clay (not identified herein), can be conductive for either physical or chemical sorption to occur. The results from this study showed that HA, more aromatic and with higher molecular mass fraction of HS were better removed than FA, more acidic fraction with higher amounts of functional groups, Fig. 3. This might indicate that physical interaction rather than ligand exchange between HS and the filtersand are important. However, this should be carefully considered since lower sorption efficiency of HS with a higher amount of functional groups (e.g. FA) is not always indicative of a lack of coordinative interaction (ligand exchange). HS are macromolecules which behave like polyelectrolytes; thus their sorption is determined not only by the availability of sites, but also by lateral interaction between themselves and the steric arrangements of the macromolecule (Kaiser and Zech, 1997; Vermeer et al., 1998). Due to a high amount of functional groups, HS stretches (due to lateral repelling between the functional groups) and when becomes sorbed on the surfaces occupies a large area that makes overall sorption efficiency of FA lower than of HA. This is also demonstrated by the finding that HS, with high amounts of aromatic groups and lower amounts of carboxyl groups, can be preferably sorbed to the surface with high amounts of binding sites such as iron or aluminium oxides (Evanko and Dzombak, 1999; Meier et al., 1999). This occurs even though ligand exchange is the dominant mechanism of interactions of HS with those surfaces (Tipping, 1981; Day et al., 1994; Gu et al., 1994; Edwards et al., 1996; Tombacz et al., 2000).

In the sorption process HS replaced nearly all previously retained HS before any sorption could occur, Fig. 3. This indicates that HS were weakly sorbed on the bare filtersand, perhaps as a result of physical interaction. Elemental analyses showed an insignificant increases of oxygen and carboxyl groups in the filtersand HS compared to HS of the water used for recharge. Thus, chemisorption, which generally contributes to higher level of these moieties in the sorbed HS, was not significant.

A change of pH affected both HS and filtersand properties. A decrease of pH should increase the positive charge of oxides, thereby making an electrostatic attraction with negatively charged HS molecules possible. However, at acidic pH HS become more hydrophobic, thus increasing the possibility for hydrophobic attraction. Since the filtersand contained low amounts of iron and clay, the strong positive effect of sorption (Fig. 4) that was due to a lowering of pH, was perhaps also due to a hydrophobic effect rather than an increase of electrostatic attraction. Therefore, the sorption may be dominated not so much by the forces between the filtersand surface and HS, but rather by the intermolecular association forces between HS and its incompatibility with water.

However, we observed that background organic matter also plays an important role. HS is better attracted to organic rich sediments than to filtersand, which had a relatively lower amount of OC. Elemental analyses revealed that filtersand showed significantly lower H/O ratio compared to sediments, Table 1. The H/O ratio indicates the humification degree of HS (De Paolis and Kukkonen, 1997). Thus, the higher ratio indicated that HS in sediments were more humified than the filtersand HS, which apparently also increases the ability to remove HS from water.

From this discussion, we conclude that due to low amounts of binding sites in filtersand, a hydrophobic fraction such as HA is preferably removed over more acidic fraction such as FA. This may lead to a fractionation of HS during ARG where large hydrophobic and aromatic molecules are removed in the earlier in the process, though FA are conserved unless the aquifer is rich with iron oxides or clay. The conclusion reached from this laboratory scale study is consistent with earlier findings from full-scale studies presented by McCarthy et al. (1993) and Schwarzenbach et al. (1983).
The aromatic fractions of HS are a major source of by-products and colour, thus ARG decreases the risk of carcinogenicity and improves the aesthetic quality of surface water. If filtersand, through which ARG is accomplished, is poor in iron oxide minerals or clay, the removal of FA would be low even after long infiltration distances.

5. Conclusion

Sorption experiments showed that clay content increased whereas organic matter decreased the sorption of HS to filtersand at ARG. Organic matter was released because it was not chemically bound and completely stabilized. More aromatic, hydrophobic fractions of HS (HA) were to a higher extend sorbed than acidic fractions of HS (FA). Chemisorption appears to be less important than physical sorption (hydrophobic sorption enhanced by polyelectrolytic effect) for HS removal during ARG.

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References


