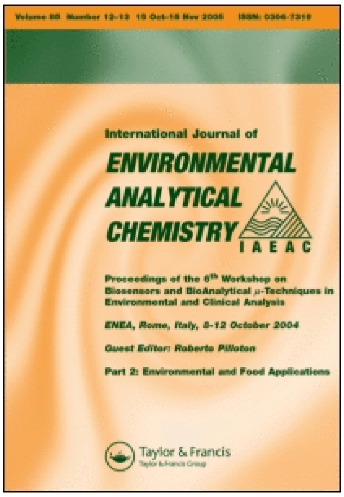

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Linn Persson[a]; Tomas Alsberg[a]; Göran Odham[a]; Anna Ledin[b]
[a] Institute of Applied Environmental Research, Stockholm University, 106 91 Stockholm, Sweden [b] Environment & Resources DTU, Technical University of Denmark, Denmark

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MEASURING THE POLLUTANT TRANSPORT CAPACITY OF DISSOLVED ORGANIC MATTER IN COMPLEX MATRIXES

LINN PERSSON[a,*], TOMAS ALSBERG[a], GÖRAN ODHAM[a] and ANNA LEDIN[b]

[a]*Institute of Applied Environmental Research, Stockholm University, 106 91 Stockholm, Sweden;*
[b]*Environment & Resources DTU, Technical University of Denmark, Denmark*

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Dissolved organic matter (DOM) facilitated transport in contaminated groundwater was investigated through the measurement of the binding capacity of landfill leachate DOM (Vejen, Denmark) towards two model pollutants (pyrene and phenanthrene). Three different methods for measuring binding capacity were used and evaluated, head-space solid-phase micro-extraction (HS-SPME), enhanced solubility (ES) and fluorescence quenching (FQ). It was concluded that for samples with complex matrixes it was possible to measure the net effect of the DOM binding capacity and the salting out effect of the matrix. It was further concluded that DOM facilitated transport should be taken into account for non-ionic PAHs with $\lg K_{\mathrm{OW}}$ above 5, at DOM concentrations above 250 mg C/L. The total DOM concentration was found to be more important for the potential of facilitated transport than differences in the DOM binding capacity.

Keywords: Leachate; Groundwater; Dissolved organic matter; Solid-phase micro extraction; Fluorescence quenching; Enhanced solubility

INTRODUCTION

Polluted water bodies often contain a large variety of different pollutants. Wastewater from households and industries are water samples with complex matrixes, resulting in analytical difficulties in the monitoring of concentration levels and pollutant transport processes. The leachate originating from landfills is an extreme case of polluted water with a complex matrix.

There are large numbers of landfills in the world without protecting underlying barriers for collection of leachate. The remediation of such sites is expensive and it is therefore important to know whether the contaminants stay within the leachate plume close to the site, or if they are transported into the groundwater system. There is also a need to know more about the processes governing subsurface transport in order to create criteria for the termination of post-closure monitoring of landfill sites that are left unremediated [1,2].

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[*] Corresponding author. Fax: +46-8-6747637. E-mail: linn.persson@itm.su.se

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The leachate from a landfill deposit contains a large variety of different substances, both inorganic and organic. Usually there is a high content of dissolved organic matter (DOM). The DOM can be mobile in aquifers [3], either truly dissolved or in colloidal forms. Colloids may even move faster than a conservative tracer in certain aquifer systems, owing to size-exclusion effects [4]. The pollution of groundwater from sources such as landfills is a long-term problem since groundwater contaminant transport is characterized by long time lags [5]. DOM has been shown to facilitate the transport of metals [6,7], radio nuclides [8,9] and organic pollutants [10–12].

Thus, DOM facilitated transport may be of importance for pollutant fate. However, our ability to predict the magnitude of the transport in specific cases is limited [11]. The extent of the DOM facilitated transport of pollutants in a groundwater system will depend on various parameters, e.g., the properties of the pollutant in question, and the amount and quality of the DOM present [13], as well as the hydrology, geology and water chemistry. Furthermore, heterogeneities in the aquifer and the presence of preferential flow paths may increase the complexity of the transport process.

It was concluded in a laboratory study that the mobile load of perylene was doubled due to the presence of groundwater DOM at 1 mg C/L close to a recharge facility [14], and the concentrations of several investigated polycyclic aromatic hydrocarbons (PAHs) were elevated owing to the presence of colloids in groundwater close to a coal-tar site [15]. Magee *et al.* [16] observed facilitated transport of phenanthrene through natural soils in column experiments. Johnson and Amy [17] reported significant reduction of the retardation through quartz sediment of benz[*a*]anthracene in the presence of Suwannee river humic and fulvic acids.

On the other hand Larsen *et al.* [18] suggested that DOM will not increase the transport of hydrophobic pollutants, based on the results of batch experiments with different aquifer materials and landfill leachate. They observed partitioning of hydrophobic pollutants into the DOM of the leachate. Concurrently the leachate interacted with the aquifer material and thereby increased the affinity of the sorbent for the pollutants. In a landfill with a stationary plume, where a steady state has developed, there may be less sorption of DOM to the aquifer material, and consequently the transport may increase. This was seen by McCarthy *et al.* [3] when performing field-scale transport studies of natural organic matter. After two weeks of injections of brown water at their field site they reported an apparent steady-state situation where the initial retardation of the organic matter was no longer taking place and the organic matter was exhibiting considerable mobility.

The aim of this study was to compare different techniques for the determination of the binding capacity of landfill leachate DOM in order to improve our ability to predict DOM facilitated transport in contaminated groundwater. A landfill site where the groundwater gradient offered a range of DOM concentrations and varying quality was chosen for the study.

When measuring the binding capacity of DOM (K_{DOC}) the challenge lies in measuring without interfering with the process studied. In general, techniques that do not separate the phases reduce the effect of measurement on the binding [19]. We therefore chose to work with three different techniques that measure the partitioning without separation of the phases, head-space solid-phase microextraction (HS-SPME), fluorescence quenching (FQ) and enhanced solubility (ES). HS-SPME has been used to measure partitioning of hydrophobic pollutants to isolated humic materials [20–24] and to whole water DOM samples [25]. The ES technique has also been used to measure partitioning of hydrophobic pollutants in many studies [26–28], and so has FQ [14,19,29]. However, to the best of our knowledge none of the techniques have previously been used for leachate samples, or other water samples of similar composition.

EXPERIMENTAL

Model Compounds

Two hydrophobic aromatic hydrocarbons (PAHs) were used as model compounds, pyrene and phenanthrene (99+%, Aldrich-Chemie, Steinheim, Germany), with lg K_{OW} of 5.13 and 4.57, respectively [30]. Both compounds have been used in many studies of K_{DOC} measurements of DOM of different origin thus offering possibilities for comparison with literature values.

Field Site

A landfill site that has been thoroughly studied earlier [31–35], including characterization of the DOM [36,37], was chosen for the study. In an earlier study most of the colloids were found to be small (primarily in the fraction between 0.010 and 0.001 μm), and to a large extent consisting of organic matter [38]. Intact water samples were analyzed, since isolation of the DOM may change its properties resulting in a different binding capacity [12]. The waste disposal at the Vejen landfill started in 1962 and terminated in 1981 and included both municipal and industrial waste. There is no leachate collection system and a substantial fraction of the leachate has been leaking into a shallow unconfined sandy aquifer since approximately 1973 [31]. The pore flow velocity has been estimated to 150–200 m/year [32].

Samples were collected from five different locations (Fig. 1 and Table I) downstream from the landfill as described elsewhere [33,37]. The samples were transported to the laboratory under anaerobic conditions in refrigerated boxes. Until analysis the samples were stored in the dark, under water, at 4°C. Prior to analysis the samples were aerated, 0.1% NaN_3 (J.T. Baker B.V., Deventer, The Netherlands) was added in order to prevent bacterial growth and the samples were filtered through 0.45-μm GHP filters (Waters, Milford, MA, USA). The content of phenanthrene and pyrene in the leachate prior to the experiment was below the limit of detection as measured with SPME (the limits of detection were 20 and 60 ng/L of phenanthrene and pyrene, respectively).

Nordic reference humic and fulvic acids (NRHA and NRFA, obtained through the International Humic Substances Society) were also included in the study. These were dissolved in Milli-Q water (from a Milli-Q cartridge system, Millipore, Bedford, MA, USA) but otherwise treated as the samples.

HS-SPME

SPME measures the activity of an analyte in the sample. The binding capacity of the sample DOM may be calculated from the reduced activity of the analyte. The advantage of using SPME in the head-space mode, instead of immersing the fiber into the samples, is that the possible adsorption of DOM, which may degrade the fiber and

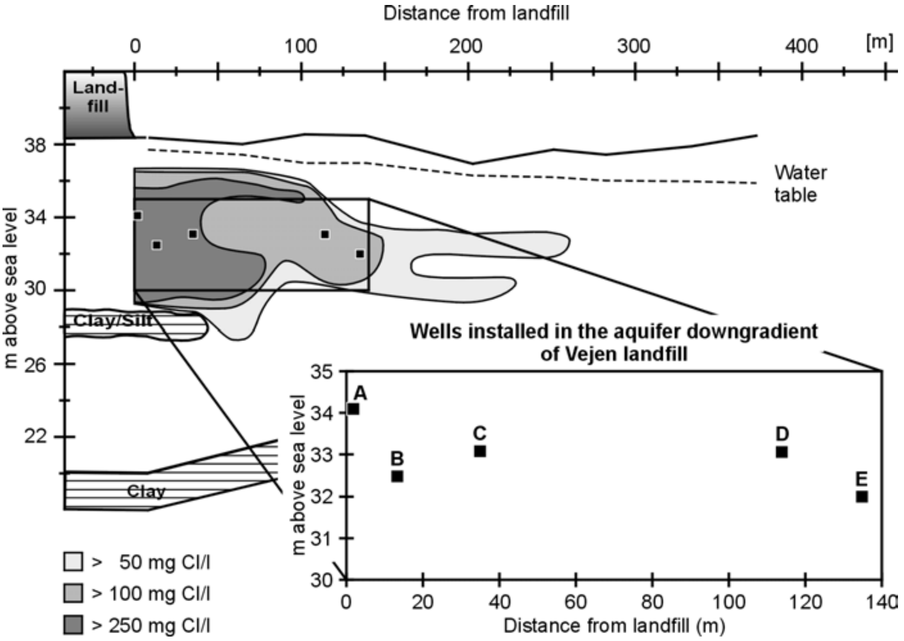


FIGURE 1 Map of leachate plume and sampling locations.

TABLE I Hydrochemical parameters of the samples

Sample	*Distance from landfill* (m)	*DOC* (mg/L)	*Chloride* (mg/L)	*Dilution factor*[a]	*pH*	*ε254*[b] (L/mol cm)	M_w (Da)[b]
A	0	278	1000	1	6.48	603	5800
B	18	144	674	1.5	6.57	447	5100
C	35	71	489	2.1	6.49	313	4000
D	114	55	177	6.3	6.34	642	4700
E	135	17	78	17	6.33	934	3900

[a] Calculated using chloride as conservative tracer, as described in Baun *et al.* [34].
[b] From Persson *et al.* [37].

which may also give an underestimation of the K_{DOC}, is excluded [23,39]. The extracted amount of analytes should not exceed 5% of the concentration [40], in order not to influence the partitioning process. In this study, the extracted amount was 2–3% for phenanthrene and 1–2% for pyrene. Pyrene and phenanthrene standards were dissolved in water. The aqueous standards were prepared in three different concentrations by evaporation of hexane standard solutions to dryness in test tubes followed by addition of Milli-Q water and ultrasonication. 1 mL of PAH standard solution in water was added to 10-mL of sample in 22-mL vials with PTFE/silicon septa (Supelco, Bellefonte, PA, USA), giving a final concentration of 0.8–13 µg/L of each PAH. The analytes were equilibrated between the water and the headspace for three days at room temperature in the dark (measurements showed that after three days equilibrium was reached). Between 12 and 16% of the added pyrene, and 1–4% of the added phenanthrene was adsorbed to the vial walls. A manual holder SPME device with an 85-µm Polyacrylate SPME fiber (Supelco, Bellefonte, PA, USA) was used in the headspace of the vial (5 min adsorption) while stirring with Teflon-coated magnetic stir bars. Teflon-coated stir bars are usually not recommended since they may adsorb PAHs (e.g., ref. [41]). However, blank values were compared with those obtained using glass stir bars, and they were similar. It was therefore chosen to work with the mechanically more stable Teflon magnets. The short extraction time applied (5 min) meant that the sampling was carried out under non-equilibrium conditions. Therefore the sampling conditions were always carefully kept the same (stirring rate, room temperature and position of the SPME fiber).

The fiber was desorbed for 4 min in the GC injector, and the analysis performed with GC-MS (Saturn 3 Ion trap mass spectrometer with a Star 3400 CX GC, Varian Inc., Palo Alto, CA, USA). The injector temperature was 250°C. The SPME fiber was conditioned in another GC injector for 7 min at 280°C between injections to avoid memory effects.

Enhanced Solubility

An acetone solution of phenanthrene and pyrene was added to test tubes in amounts exceeding their solubilities in water (7900 ng of phenanthrene and 3900 ng of pyrene), corresponding to concentrations of 564 and 279 μg/L respectively. The solvent was allowed to evaporate completely before the test tubes were filled with sample or Milli-Q water. The tubes were left to equilibrate for six days after which they were shaken and centrifuged for 20 min at 2000 rpm. 10 mL of sample was transferred to another test tube and internal standards of perdeuterated pyrene and perdeuterated phenanthrene (98% Cambridge Isotope Laboratories, Inc., Andover, MA, USA), 80 ng of each, dissolved in 1 mL of cyclohexane (HPLC grade, Labscan Ltd., Dublin, Ireland) were added. The tubes were rotated for 20 h to allow the internal standard and the analytes to equilibrate with the water phase. 3 mL of cyclohexane was added and the test tubes were rotated for another 20 h, after which they were centrifuged and the organic phase was withdrawn. The extraction was repeated with 3 mL of cyclohexane. The liquid-phase extraction with cyclohexane was considered to extract all PAH bound to the DOM [17], as well as the dissolved PAH, thus giving the total amount of PAH in the water phase. The cyclohexane was concentrated under nitrogen and analyzed with GC-MS (Jeol Automass System II from Unicam Analytical Systems, France, with a HP 5890 Series II GC-instrument) without further treatment.

Fluorescence Quenching

The FQ technique is based on the observation that PAHs fluoresce in aqueous solution but not when associated with DOM. The fraction of PAH associated with DOM may thus be determined directly from the fractional decrease in fluorescence when DOM is added [19]. Using intact water samples requires a few extra concerns to be addressed [14]. Firstly, other quenchers apart from the DOM may be present in the sample. However, the high DOM concentrations in the landfill samples would require other quenchers to be present in very high concentrations if they were to influence the results. The possible presence of other quenchers was therefore considered negligible in the samples of this study. Sorption of the analytes to laboratory vessels has been reported earlier for pyrene [12], but was not seen for phenanthrene [14]. This was handled by measuring the fluorescence shortly (15 min) after the addition of the PAHs, starting with the wavelength of the most hydrophobic analyte, pyrene, to minimize the losses to the vessel walls. The partitioning of PAH between fulvic acid and water has been shown to be complete within a few minutes [42]. Furthermore, the quenching efficiency may not be 100% for all types of organic carbon capable of binding PAHs in a natural sample. Earlier studies have shown that 60% of the leachate DOM consists of fulvic and humic substances [36], therefore the dominating part of the leachate DOM is believed to have humic-like behavior and quench PAHs to 100%.

The samples were diluted with a carbonate buffer solution of 25-mM $NaHCO_3$ (pa, Merck, Darmstadt, Germany) with the addition of 210 mg/L of NaCl and 210 mg/L of NaN_3, adjusted to pH 7.0 with HCl. The sample closest to the landfill was diluted about 10 times, and the sample furthest away twice. A standard solution was prepared by adding pyrene and phenanthrene dissolved in acetone (Suprasolve, Merck, Darmstadt, Germany) to a glass flask. The acetone was evaporated and carbonate buffer solution was added to the flask. The flask was ultrasonicated and kept at room temperature in the dark until used. The concentrations were 119 and 185 µg/L of pyrene and phenanthrene, respectively (the concentration should be close to the solubility limit to maximize fluorescence intensity relative to the background [19]). Each sample was further diluted with buffer solution to give four different concentrations of DOM between 1 and 23 mg C/L. The diluted sample was added to buffer solution containing PAH standards. All measurements were performed on duplicate samples, the F_0 medium (carbonate buffer solution) measurements on triplicates. Fluorescence measurements were carried out on a Jasco FP-777 spectrofluorometer (Japan Spectroscopic co. Ltd., Tokyo, Japan) using 334-nm excitation and 394-nm emission for pyrene and 250-nm excitation and 350-nm emission for phenanthrene (10-nm bandwidth, medium PMT Gain, 1-cm quartz cuvettes). The inner filter effect was corrected for according to Gauthier *et al.* [19]. The correction factors were always below 1.9 for pyrene, which is below the recommended maximum of 3 [25]. For phenanthrene, however, the correction factors were as high as 6.0 for some samples (those data were not used, see discussion below). The absorbance of each sample at the four wavelengths was measured on a Hitachi U-3200 (Hitachi Ltd., Tokyo, Japan) for the inner filter effect calculations.

Separation of DOM for the Salting-out Experiment

In order to separate the DOM from the sample matrix the samples were run through solid-phase extraction anion-exchange columns (5 g Isolute SAX, International Sorbent Technology, Mid Glamorgan, UK). The columns were first solvated with 8 mL MeOH (HPLC grade, Merck, Darmstadt, Germany) and then rinsed with 2.5 L of de-ionised water. The content of organic matter in the last 20 mL of rinsing water was between 17 and 26 mg C/L. Reduced pressure (7 mm Hg) was applied to elute the columns. 100 mL of sample was run through the column, the first 7 mL of the eluate was discarded, the rest was collected and used for the measurement of the salting-out effect. The sample matrix contained between 12 and 41 mg C/L. The conductivity of the sample matrix was between 6 and 15% higher than in the intact samples.

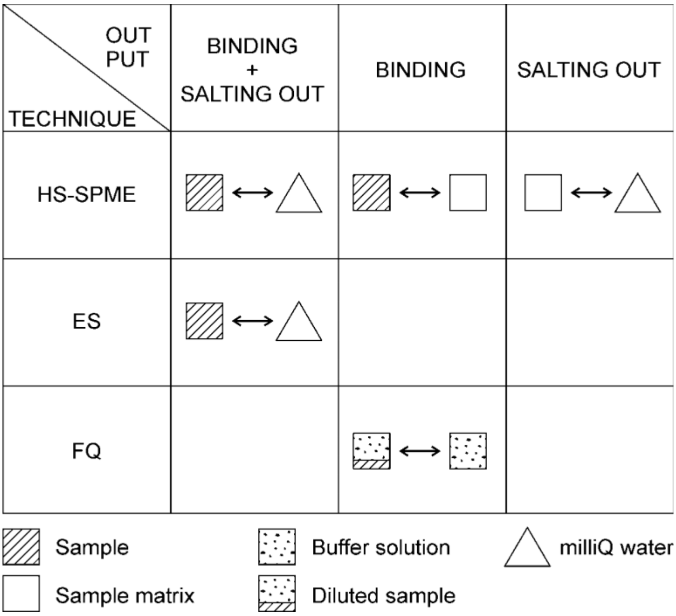
RESULTS AND DISCUSSION

Analytical Considerations

Measuring K_{DOC} in highly polluted samples demands special precautions. Adopting an analytical strategy includes the choice of how to deal with the matrix effect. In all methods for measuring binding capacity, the binding of a compound is measured by comparison to a reference where the sorbent is not present. The reference may be the sample matrix without sorbent or, for instance, a buffer solution. Figure 2 gives an overview of the measurements included in this study. Two experiments measured the net effect of the binding and the salting-out effect of the sample matrix. Those were HS-SPME and ES experiments with MilliQ-water as the reference. When the HS-SPME technique was used with sample matrix as the reference, this allowed the measurement of the binding only. Also in the FQ experiment the binding alone was measured. The FQ may not be used with high DOM concentrations owing to the DOM absorption of the fluorescence. Therefore the samples were diluted with carbonate buffer solution. The buffer was adjusted to be similar to the Vejen aquifer, which is dominated by the carbonate system. Lastly, the HS-SPME technique was used with the sample matrix as the sample and MilliQ-water as the reference, which allowed quantification of the salting-out effect of the matrix.

Net Effect of the DOM Binding and the Salting Out of the Sample Matrix

Measurements with HS-SPME and ES using MilliQ water as the reference showed the net effect of the DOM binding capacity and the salting-out effect of the



OUT PUT / TECHNIQUE	BINDING + SALTING OUT	BINDING	SALTING OUT
HS-SPME	▨ ⟷ △	▨ ⟷ □	□ ⟷ △
ES	▨ ⟷ △		
FQ		▤ ⟷ ▒	

▨ Sample
□ Sample matrix
▒ Buffer solution
▤ Diluted sample
△ milliQ water

FIGURE 2 Schematic overview of the experiments. Three different set ups were used measuring: the net effect of salting out and DOM binding; binding only; salting out only. The sample (left side of the arrow) and the reference (right side of the arrow) used in each set of experiments are shown.

sample matrix. In the HS-SPME analysis pyrene showed net binding to the leachate DOM only in the sample closest to the landfill (sample A). The binding capacity is given as $SPME_0/SPME$, where $SPME_0$ is the peak area of pyrene in the gas chromatogram from the SPME analysis of the Milli-Q reference, and $SPME$ is the peak area of pyrene in the sample chromatogram. Phenanthrene did not bind to the DOM to a detectable degree in any of the samples (Fig. 3). Results for pyrene and the five samples with ES and HS-SPME are compared in Fig. 4. ES showed the same results as HS-SPME with a detectable binding only for pyrene in sample A, and no increased apparent solubility of phenanthrene in any of the leachate samples compared to the pure water (phenanthrene ES results not shown).

The HS-SPME and ES data were used to calculate estimated K_{DOC} values for pyrene, denominated ${}^{\mathrm{est}}K_{\mathrm{DOC}}$. These are considered as estimates since they are based on only one concentration of DOM and pyrene and not calculated from isotherms. They are based on measurements at the actual DOM concentration in the aquifer, and the two techniques together represent a pyrene concentration interval of one order of magnitude, which strengthens the estimation. The calculation was based on Eq. (1) [25] for SPME results and the corresponding Eq. (2) [43], for ES results. ES is the total concentration of pyrene in the sample and ES_0 in the MilliQ reference,

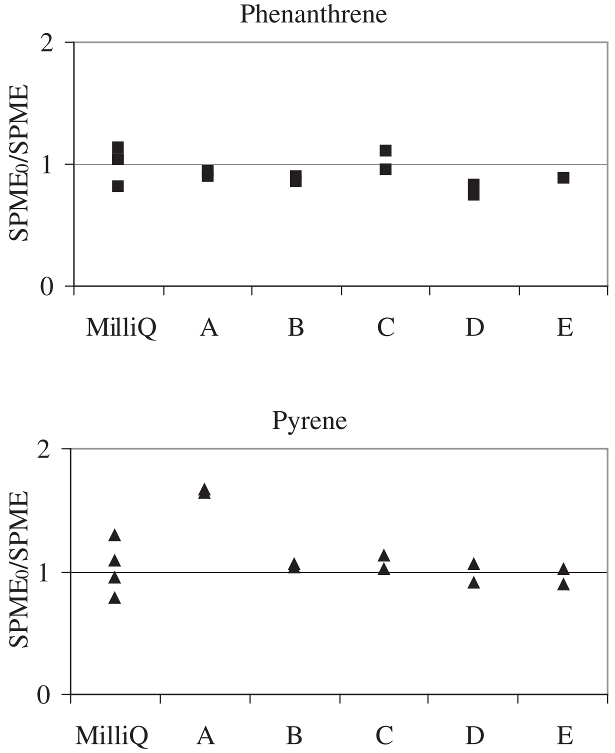


FIGURE 3 Net effect of binding and salting out as measured with HS-SPME using Milli-Q water as the reference ($SPME_0/SPME$). Duplicate samples are shown for sampling points A–E, and four replicates for the reference Milli-Q water.

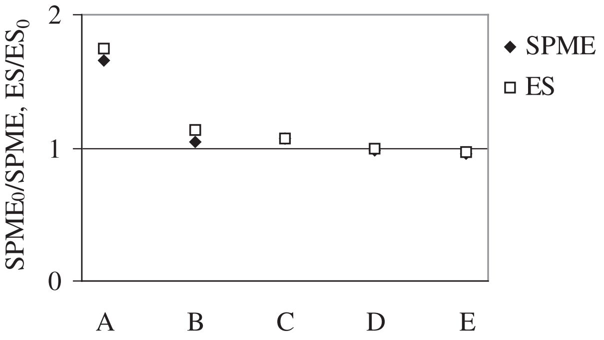


FIGURE 4 Binding capacity of pyrene as measured with HS-SPME and ES, using Milli-Q water as the reference. The HS-SPME results are shown as $SPME_0/SPME$ and the ES results as ES/ES_0, on the y-axis. Duplicate samples shown.

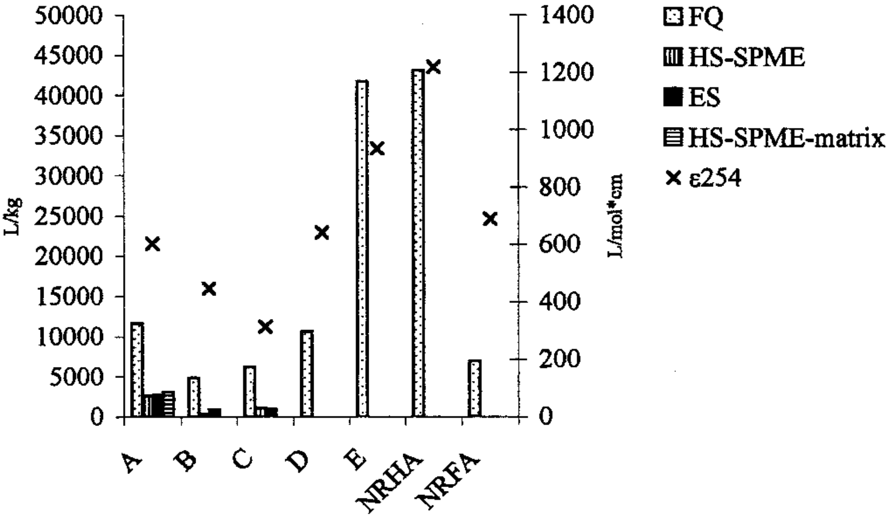


FIGURE 5 Comparison of binding capacity of DOM in samples A–E as measured with different techniques and different references. Fluorescence quenching data are also given for NRHA and NRFA. The aromaticity of the samples is given as the specific absorbance at 254 nm (ε254). The binding capacity is given as K_{DOC} for FQ results, $^{\mathrm{est}}K_{\mathrm{DOC}}$ for HS-SPME and ES, and K_{H} for HS-SPME$_{\mathrm{MATRIX}}$.

respectively. DOM is the concentration of organic carbon. $^{\mathrm{est}}K_{\mathrm{DOC}}$ values are shown in Fig. 5.

$$SPME_0/SPME = 1 + {}^{\mathrm{est}}K_{\mathrm{DOC}}DOM \tag{1}$$

$$ES/ES_0 = 1 + {}^{\mathrm{est}}K_{\mathrm{DOC}}DOM \tag{2}$$

DOM Binding

HS-SPME was also used to measure the binding without the influence of the salting-out effect for the sample closest to the landfill (sample A), by using sample matrix without DOM as the reference. In the case of phenanthrene there was a very small difference between the sample matrix and the whole sample, whereas for pyrene the binding to DOM was clearly seen (Fig. 6). The K_H value for pyrene and phenanthrene in sample A was calculated using the Henry equation, Eq. (3) [25], where μ is the loading of pyrene on the DOM in micrograms per kilogram of organic carbon and β is the equilibrium concentration of pyrene in microgram per liter.

$$\mu = K_H \beta(\mathrm{pyr}) \tag{3}$$

K_H was found to be 3100 and 120 for pyrene and phenanthrene, respectively. K_H can theoretically be shown to be equal to K_{DOC} [25], when using the same concentrations of analytes and DOM. The small binding of phenanthrene indicated in this measurement was completely hidden in the previous experiment where the net effect of binding and salting out was measured.

Earlier studies of the samples have shown that the aromaticity of the DOM was highest in the sampling point furthest away from the landfill, indicating a higher binding capacity at that point [37]. The ES and SPME experiments were therefore complemented with fluorescence quenching (FQ), a technique suitable for samples with lower content of organic carbon, in order to be able to measure K_{DOC} for pyrene in samples B–E. Since the samples were diluted for the FQ experiment, and a buffer solution was used as the reference, this experiment measured the binding only. K_{DOC} results for pyrene measured with FQ are shown in Table II. The pyrene isotherms (based on the Stern–Volmer

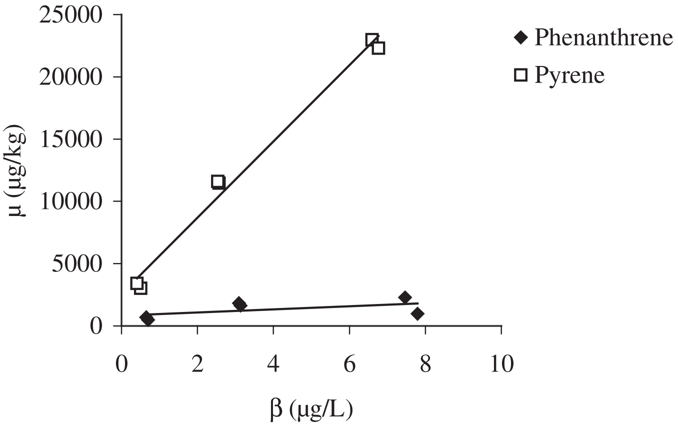


FIGURE 6 HS-SPME measurements of pyrene and phenanthrene in sample and sample matrix for sample A. Duplicate samples shown. Regression gives the K_H value for pyrene and phenanthrene.

TABLE II Pyrene K_{DOC} from FQ measurements

Sample	K_{DOC} (L/kg)
A	11 600
B	4800
C	6200
D	10 600
E	41 700
NRHA	43 100
NRFA	6900

TABLE III K_{DOC} and ${}^{est}K_{DOC}$ for pyrene (L/kg); sample A and literature values

Sample	*FQ*	K_H *(SPME)*	*SPME*	*ES*
Sample A	11 600	3100	2600	2700
WSOC[a]	4050			
SRFA[b]	100 000			
SRFA[c]	27 540			10 230
SRHA[d]	33 880			21 380
HA+FA[e]	40 000–120 000			
DOM[f]	58 000	1500	12 000	

[a] Water Soluble Organic Carbon from soil solution, Herbert *et al.* [12].
[b] Suwannee river fulvic acid, Gauthier *et al.* [19].
[c] Suwannee river fulvic acid, Danielsen *et al.* [45].
[d] Suwannee river humic acid, Danielsen *et al.* [45].
[e] Aquatic HS, Perminova *et al.* [53].
[f] Doll *et al.* [25].

equation) were linear, which indicated that there was only static quenching in the samples. However, it should be noted that deviations from non-linearity may not be apparent over limited DOM ranges [14,44]. For phenanthrene the inner filter effect correction factor was too high and the results were therefore not used (data not shown).

The binding capacity of pyrene was lowest in the middle of the gradient, and highest at the point furthest away from the landfill. The Nordic reference humic substances were also analyzed and the K_{DOC} values were in agreement with earlier published data for pyrene with isolated fulvic acid (Table III).

Comparison of the Techniques

Figure 5 shows the ${}^{est}K_{DOC}$ values together with the K_{DOC} from the FQ measurements, as well as the K_H value measured with HS-SPME for sample A. The HS-SPME and ES ${}^{est}K_{DOM}$ values are in agreement, both corresponding to the net effect of the salting out and of the binding capacity. K_H measured using the sample matrix as reference gives the binding capacity without the salting out effect. Also FQ shows results without the salting-out effect, since the analysis was carried out with the sample DOM in a buffer solution that was identical to the reference solution. However, the FQ result is four times higher for sample A. In comparison with the HS-SPME and ES results, the FQ measurements give about five times higher values for all samples.

The FQ measurements are the only experiments carried out on diluted samples, which may be one explanation for the discrepancy. Another explanation may be inherent differences between the techniques. Literature K_{DOC} values measured by FQ are generally higher than those measured by other techniques [25,45,46]. Mackenzie *et al.* [39] reported values for pyrene K_{DOC} measured with FQ four times higher than those measured with SPME. The authors explained their results by suggesting that the techniques are inevitably different, since they measure different sorption coefficients (activity-based for SPME, concentration-based for FQ). They predicted that techniques like ES should yield similar results to SPME, as was observed in this study. Compared to literature values of K_{DOC} the resulting values from the leachate DOM in this study are lower (Table III). However, most of the reported literature values are from experiments with isolated humic material and not intact water samples.

With HS-SPME and ES, DOM binding could be measured for analytes with $\lg K_{OW}$ higher than 5, and at DOM concentrations above 250 mg C/L. Using SPME, low PAH concentrations can be used, whereas the ES technique requires concentrations close to the solubility limit of the PAHs. The FQ technique measures binding capacities at low DOM levels (less than 10 mg C/L), but requires higher PAH concentrations.

It was possible to estimate the actual aquifer situation by measuring the net effect of the salting out and the DOM binding. In the aquifer both processes are active and need to be considered in, for instance, transport modeling. The FQ technique is not recommended unless demanded by a low carbon content, owing to the confirmed overestimation of K_{DOC} with this technique.

Salting-out Effects

Comparing the sample matrix to Milli-Q water allowed the measurement of the salting out of the analytes in the sample matrix in the absence of DOM. For phenanthrene the matrix had only a minor effect on the apparent solubility (data not shown). The transport potential in this aquifer of phenanthrene was thus not affected by the mobile phase being pure water or leachate since neither salting out nor DOM binding was found to be significant. In the case of the more hydrophobic pyrene the matrix effect could be measured (Fig. 7). Pyrene was approximately 25% less soluble in the matrix of the sample closest to the landfill than in pure water. This corresponds well with the results obtained by comparing K_H with the SPME-derived ${}^{est}K_{DOC}$ (3100 and 2600 L/kg, respectively), indicating that the salting out of pyrene reduces the apparent solubility by about 20%.

A theoretical calculation of the decrease in solubility expected by the salt concentrations in the Vejen aquifer (calculated from 1.0 g/L of chloride and 25 mM carbonate, using Setschenow's empirical formula and literature salting-out constants [30]) yields a decrease of 4% of the pyrene solubility in sample A. Thus, the carbonate and chloride concentrations alone do not explain the measured salting-out effect, although they are the most dominating specific ionic species in the water. The salting-out effect is therefore likely based on a cumulative effect of the various ionic species present in the leachate, in spite of low concentrations of single species. This illustrates the importance of being able to measure the salting-out effect of a certain matrix, since a theoretical prediction would at least require calculations based on time-consuming quantifications of all ionic species in a given water sample.

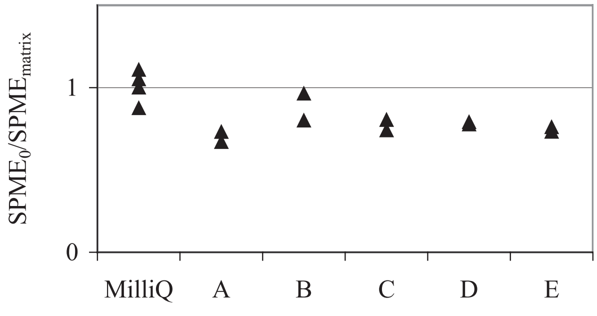


FIGURE 7 Sample matrix salting out of pyrene, using Milli-Q water as the reference, as $SPME_0/SPME_{MATRIX}$. Duplicate samples are shown for sampling points A–E and four replicates for the reference Milli-Q water.

The water chemistry affects the conformation of the DOM, thereby also affecting the K_{DOC} value [42]. For pyrene, Means [47] observed salinity effects on K_{DOC} in an estuary where sorption of pyrene increased with salinity. The findings were interpreted as a combination of salting out of pyrene from the water phase, and of the sediment organic matter being salted out, thus becoming a better solvent for aromatic molecules. Experiments with sodium chloride solutions in this study indicated that high salt concentrations increased the amount of pyrene sorbed to the SPME vials, as well as to the amount present in the gas phase, and the amount sorbed to the DOM. Whether this was due to conformational changes of the DOM, or just a salting-out effect from the water phase could not be concluded.

DOM Structure in Relation to Binding Efficiency

The binding of PAH and other aromatic nonpolar molecules to aquatic humic substances is generally attributed to hydrophobic binding [13]. Good correlations between K_{DOC} and K_{OW} have been found in many studies [e.g. 10]. However, the simple partitioning model for the binding of hydrophobic organic pollutants to organic matter has also been questioned. It has for example been proposed that it is the aliphatic components of DOM that are most important for pyrene binding [48], and for phenanthrene [49,50]. Hur and Schlautman [51] reported a higher contribution of specific interactions versus partitioning with increasing pH.

In this study a correlation between the K_{DOC} values and aromaticity measured as $\varepsilon254$ was observed (Fig. 5). Such a correlation has also been reported by others [13,27,52]. However, the correlation with molecular weight was poorer (molecular weights are decreasing along the gradient, see Table I). Perminova *et al.* [53] observed a similar pattern. They studied 26 different humic samples and their binding to pyrene and found the best correlation with aromaticity as measured with ^{13}C NMR spectroscopy, good correlation with the specific absorbance at 280 nm ($\varepsilon280$), but poor correlation with molecular weight. However, other studies have reported good correlations also with molecular weight [27,28,54]. In Vejen, the concentration of DOM varied more (17 times) than K_{DOC}, and the DOM concentration is therefore suggested to be more important than DOM quality as the determining factor for the transport process.

Implications for Groundwater Transport of Pollutants

K_{DOC} is only one of the important parameters influencing the transport of pollutants in an aquifer. DOM facilitated transport will be of importance principally to compounds that are resistant to degradation in the anaerobic leachate plume, and that have high $\lg K_{OW}$. It has been shown that there is substantial degradation of some aromatic hydrocarbons (ethyl benzene and *m*/*p*-xylene) in the anaerobic plume at the Vejen landfill [55]. Others, such as naphthalene, did not show signs of degradation along the flow-path. Baun *et al.* [34] showed degradation of several organic xenobiotics in Vejen. Exceptions were benzene, the herbicide MCPP and the DOM. Notably, also, the DOM itself influences the water chemistry of the aquifer. The DOM is the primary electron donor in the plume [55], and therefore has an important role in, for instance, the degradation pattern of xenobiotics.

The results of this study indicated that DOM facilitated transport may be of importance in the Vejen aquifer for compounds with $\lg K_{OW}$ of 5 or higher at DOM concentrations exceeding 250 mg C/L. Hence, compounds like PCB or DDT with $\lg K_{OW}$ at 6–8 would exhibit a high partitioning to the DOM. However, the most frequently found xenobiotic organic compounds in leachate are all compounds with $\lg K_{OW}$ below 5. These include aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylenes) and halogenated hydrocarbons, e.g., trichloroethene [56]. These are also the compounds found in the highest concentrations. For substances like phenanthrene with $\lg K_{OW}$ below 5, the results indicated that transport in the aquifer may be modeled without taking DOM facilitated transport into consideration.

CONCLUSIONS

It was possible to estimate the actual aquifer situation by measuring the net effect of the salting out and the DOM binding. In the aquifer, both processes are active and need to be considered in, for instance, transport modeling. ES and HS-SPME were both used to measure this net effect. HS-SPME was also used to measure the salting out as such. The earlier reported overestimation of K_{DOC} as measured by the FQ techniques was confirmed. FQ is therefore not recommended unless demanded by a low carbon content of the samples.

The salting out of pyrene by the sample matrix was found to reduce pyrene solubility by 20–25%, whereas phenanthrene was not salted out nor bound to DOM to a detectable degree. The K_{DOC} value of the landfill leachate samples were low compared to literature values of binding capacity of organic matter and K_{DOC} varied along the groundwater gradient. However, the concentration of DOM varied more (17 times), and the DOM concentration was therefore suggested to be more important than DOM quality as determining factor for the transport process in the aquifer Vejen. The results indicated that DOM facilitated transport should be taken into account for non-ionic substances, e.g., PAHs, with $\lg K_{OW}$ above 5 at DOM concentrations above 250 mg C/L.

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