Environment Canada
Water Science and Technology Directorate

Direction générale des sciences et de la technologie, eau
Environnement Canada

Binding of Methylnaphthalenes to Aqueous Humic Acid

By:

Dale Van Stempvoort

NWRI Contribution # 99-236

Binding of Methylnaphthalenes to Aqueous Humic Acid

Corresponding Author:

Dale R. Van Stempvoort

National Water Research Institute

P.O. Box 5050, Burlington, ON, Canada L7R 4A6

phone: 905-319-6917

fax: 905-336-4400

e-mail: dale.vanstempvoort@cciw.ca

Total Number of Words: 6,200

BINDING OF METHYLNAPHTHALENES TO AQUEOUS HUMIC ACID:

SIGNIFICANCE FOR SUBSURFACE REMEDIATION

Dale R. Van Stempvoort and Suzanne Lesage

National Water Research Institute

P.O. Box 5050, Burlington, ON, Canada L7R 4A6

MANAGEMENT PERSPECTIVE

Title: Binding of Methylnaphthalenes to Aqueous Humic Acid: Significance Re Humic Acid Carriers in Subsurface Remediation

Author(s): D. R. Van Stempvoort and S. Lesage

NWRI Publication #: 99-236

Citation: submitted for publication in Environmental Toxicology & Chemistry.

EC Priority/Issue: This laboratory work was conducted at NWRI. It was funded by both PERD, Hydrocarbon Task, and Environment Canada under the Clean Environment (Toxic) Issue.

Current Status: The work was conducted as part of a project the development of a groundwater remediation method for the treatment of petroleum compounds in groundwater. A collaborative project funded by CRESTech (University of Waterloo) is evaluating the possibility of modeling the processes that occur when humic acids are used to remediate diesel fuel. In order to be successful the modeling effort requires data on the solubilities of the components of diesel, and their binding to humic acid, which are not available in the literature. These are provided in this paper.

Next Steps: The results of this research will be compared to data generated in a multi-year pilot scale test (future publication) and will be used to validate the computer model generated at Waterloo, which will be marketed by Waterloo Hydrogeologic.

Abstract

Binding of hydrophobic organic contaminants by humic acids controls their mobility and bioavailability in the environment. The use of aqueous commercial humic acids (HA) to enhance the solubilization and mobilization of contaminants in subsurface remediation is an active area of research. This paper presents the first published data on the binding of methylnapthalenes (MNs) by HA (Aldrich). These polycyclic aromatic hydrocarbons are important components of diesel fuel and other petroleum mixtures. Two techniques were employed to measure the binding: comparison of MN solubility in water and HA solution, and solid-phase microextraction. Apparent binding coefficients ($K_{oc, app}$, mL/g) were similar for these techniques over two orders in magnitude of dissolved MN. Values of $K_{oc, app}$ increased over several days, indicating that delayed sorption was important. Consistent with earlier studies, $K_{oc, app}$ decreased with increases in aqueous HA, but appeared to approach constant values above 1 g/L HA. Using a 10 g/L solution of Aldrich HA in subsurface remediation would result in the following enhanced solubilization: 3 to 4 fold for 1-MN, 7 to 8 fold for 1,3-diMN, 12 to 16 fold for 2,3,5-triMN.

Key Words

humic   methylnaphthalene   PAH   binding   solubility

INTRODUCTION

The chemical binding of hydrophobic organic compounds (HOCs) by humic substances is a key environmental process. By this mechanism, natural humic substances play an important role in controlling the mobility [1-3] and bioavailability [4,5] of hydrophobic contaminants in the environment. To take advantage of this binding behavior, some investigators have conducted laboratory tests of the use of commercial humic acid (HA) as a aqueous carrier to increase the efficiency of subsurface remediation of hydrophobic contaminants [6-14].

In this paper, we report the binding of methylnaphthalenes (MNs) by Aldrich HA. The MNs are very important PAH components of some hydrocarbon mixtures. For example, together with BTEX, they are the major water-soluble components of diesel fuel [15], hence posing an important groundwater contamination hazard. There are apparently no published data on the binding of MNs by aqueous humic substances. Previous investigators have focused on higher molecular weight PAHs such as phenanthrene, pyrene, fluoranthene and anthracene.

The binding of HOCs by aqueous humic substances is often modeled as partitioning (i.e., solid-phase dissolution), following a linear isotherm [16]. Changes in the extent of binding with pH and other chemical parameters have been documented. Nonlinear sorption of HOCs to HS has often been modeled using the Langmuir or Freundlich equations [17-19]. The binding of HOCs to aqueous HS may be competitive [17-19].

Various methods have been used to quantify the binding of HOCs by aqueous humic substances. Advantages and disadvantages of the various techniques have been described [20-23]. Previous investigations of the binding of PAHs by Aldrich HA have often employed the fluorescence quenching (FQ) technique [21,24-26]. However, it is doubtful that this technique could be used at the elevated HA concentrations (1 to 10 g/L) used in this study. Further, the FQ technique "is hindered by experimental difficulties" [22] and may overestimate the binding coefficient [21]. Engebretson and von Wandruszka

[27] observed fluctuations in pyrene fluorescence that were not related to the level of binding, but to slow changes in the structures of HS molecules or aggregates in response to the introduction of Mg^{2+}.

Another approach to measuring the binding is to compare the aqueous solubility of a HOC, S_w, and its "apparent solubility", S^*_w, in the presence of aqueous humic substances [16]. In this paper this approach will be referred to as the S* method. The apparent binding coefficient ($K_{oc, app}$, mL/g) can be calculated, based on Equations 1 to 3:

$$c_{oc} = (S^*_w - S_w)/(c_{HA} \times f_c)$$ (Equation 1)

$$c_w = S_w$$ (Equation 2)

$$K_{oc, app} = c_{oc}/c_w$$ (Equation 3)

where

c_{oc} is the bound MN per mass of organic C in the HA (μg/g);

c_w is the dissolved MN (μg/mL), assumed to be at saturation;

c_{HA} is the HA concentration (g/L)

and f_c is the weight fraction of carbon in Aldrich HA, reported as 0.382 g/g [24].

Such an apparent binding parameter, $K_{oc, app}$, does not imply either a linear sorption (binding) isotherm or equilibrium [28]. These binding coefficients can be used in computer modeling of the enhanced transport of MNs in the presence of Aldrich HA.

The solid-phase microextraction (SPME) technique [22,23] measures the "free" dissolved HOC, c_w, which is generally less than S_w. The total aqueous concentration of an HOC in a SPME test solution, c_t, can also be measured directly (in this study, by HPLC), and used to infer c_{oc}:

$$c_t = c_w + c_b$$ (Equation 5)

$$c_{oc} = c_b/(c_{HA} \times f_c)$$ (Equation 6)

where c_b is the bulk, aqueous concentration of bound MN.

Then based on Equation 3, the SPME results can be used to calculate $K_{oc,\,app}$.

In this study, the S* method and SPME were used to measure the binding of MNs by Aldrich HA. Given the various problems that may be associated with FQ, the use of S* and SPME appear to be good alternatives, which can be applied to a wider range of HA levels. In particular, the use of the SPME technique, which was introduced relatively recently, appears to offer several key advantages. Unlike S*, it does not require the use of an immiscible liquid mixture, where tiny suspended droplets may be inadvertently measured as dissolved phase. In comparison to another recently developed method, complexation-flocculation [21], SPME causes minimal disturbance to the test solution.

In this paper, solubility enhancement is operationally defined as S^*_w/S_w. This term provides a quantitative measure of the enhancement of solubility or "solubilization" that would be anticipated in a subsurface remediation application. The S* method provides a direct measure of solubility enhancement. Assuming that a binding coefficient determined by SPME applies for the case $c_w = S_w$ (i.e., linear sorption), solubility enhancement can be calculated using Equations 1 to 3, rearranged as Equation 7:

$$S^*_w/S_w = (K_{oc,\,app} \times c_{HA} \times f_c) + 1 \qquad \text{(Equation 7)}$$

In this way, the SPME technique can also be applied to predict the enhancement of the solubility of HOCs in HA solutions for subsurface remediation applications.

The results reported in this study are complementary to the first documented pilot-scale test of the use of a humic acid to remediate hydrophobic contaminants in groundwater [9-11]. In the pilot scale test, diesel fuel was the "residual-phase" contaminant. In these bench-scale binding tests, we used pure phase MNs, rather than diesel. This allowed us to determine binding coefficients for individual isomers, while

avoiding analytical interferences by other isomers or hydrocarbons. Also, the use of pure-phase MNs allowed much higher aqueous concentrations of MNs in the batches. Previous studies [9,29] indicated that the aqueous concentrations of trimethylnaphthalenes derived from diesel are near the detection limit.

EXPERIMENTAL PROCEDURES

All experiments were conducted at room temperature (23 ± 2°C) using analytical grade reagents. The comparative solubility (S*) tests were used to investigate binding of two pure phase isomers, 1-MN (methylnaphthalene) and 1,3-DMN (dimethylnaphthalene). Solid-phase microextraction (SPME) was used to examine the binding of the same isomers and three others, 2-MN , 1-7 DMN, and 2,3,5-TMN (trimethylnaphthalene).

Solubility of methylnaphthalenes in water and Aldrich HA: S* results

Nominal 1 g/L Aldrich HA "solution" was prepared by adding sodium humate (Aldrich Chemicals, Milwaukee) HA to Milli-Q water. This was the same as used in pilot-scale tests, and is a kind of mixture that could easily be prepared in large volume for field-scale remediation applications. The HA solution was stirred for ~ 12 h. Minor particulate HA settled over the next 24-48 h, and the supernatant was removed by peristaltic pump. Based on filtration and centrifugation tests, this nominal 1 g/L HA "solution" contained both dissolved and colloidal HA, and perhaps some remaining suspended, particulate HA. Milli-Q water and the nominal 1 g/L Aldrich HA were sparged with Ar (~1 min per 100 mL) to remove O_2, and placed in an anaerobic chamber. The O_2 was removed to minimize subsequent biodegradation and photooxidation of PAHs. Then, for each test, 100 mL of either HA and Milli-Q was transferred to a glass serum bottle, and pure NAPL-phase 1-MN or 1,3-DMN (Sigma-Aldrich Canada Ltd., Mississauga, ON) was added in excess of the anticipated saturation. The mixtures were sealed with Teflon-lined septa, placed on an orbital shaker for 16 to 24 hours, returned to the anaerobic chamber,

then sampled by glass syringe (after 1, 2, 5 and 12 d) and filtered to remove residual NAPL or solid phase MN. Filters had been prepared by packing glass beads (0.60 - 0.85 mm diam.) between silanized glass wool plugs in a disposable Pasteur pipette. During preliminary testing, the first 6 filtrates showed gradual increases in concentrations and were therefore discarded. Subsequent samples were diluted 50 % in methanol (HPLC grade, Ar-sparged) and analyzed by HPLC, using a Waters® system (600E multisolvent delivery system, 700 WISP autosampler, and 470 Scanning Fluorescence Detector). The chromatographic column selected for these analyses was a RP-8 Spheri-10 Brownlee® cartridge (Perkin-Elmer Corp., Norwalk, CT). The eluent was a mixture of methanol and Milli-Q water (65/35 % by vol.). Preliminary testing was conducted to determine whether aqueous Aldrich HA interfered with the analyses of total MNs.

SPME tests of the binding of methynaphthalenes by HA

SPME fiber assemblies (with film of 100 µm polydimethylsiloxane) and a manual sampling holder were purchased from SUPELCO Chromatography Products (Oakville, ON). The fiber was cut to reduce the length from 1 cm to 0.2 cm. In the anaerobic chamber, MNs were added from a stock (50 mg/L each of 1-MN, 1,3-DMN and 2,3,5-TMN in methanol) to 100 mL of either Milli-Q water (pH adjusted with NaOH to 8, Ar-purged) or nominal 1 g/L Aldrich HA (Ar-purged) in 120 mL glass serum bottles, to prepare final concentrations of between 100 to 1500 µg/L of each MN. These bottles were sealed and placed on an orbital shaker for 30 min. Then, within the chamber, portions (20 mL) of these solutions were transferred to glass vials (25 mL) and capped by septa for analysis by SPME. An internal standard could not be added to the batch solutions because it would bind to the HA. Thus, it was decided to try a sequential immersion technique. The SPME fiber was first immersed for 10 min with stirring in a 500 µg/L phenanthrene standard (in 4 mL of Milli-Q), then for 5 min in the 20 mL sample to be analyzed, again with stirring. A desorption test showed that there was neglible loss of phenanthrene to the sample. After sample immersion, within 1 min the fiber was manually inserted into a Hewlett Packard GC/MSD (Model 5890A GC, 5970 MSD). The GC column was a DB-1 (J & W Scientific Inc., Folsom, CA: 30 m long, 0.32 mm OD, 0.25 µm film thickness), and the carrier gas was helium. The fiber was held in place for at least

5 min at 250°C. The GC oven was held at 50°C for 5 min, then increased at a rate of 20°C/min to 250°C.

The variability of the phenanthrene results indicated that this was not a suitable internal standard. Results for the MNs were therefore reported as uncorrected. Batches analyzed by SPME-GC/MS were also analyzed by HPLC, but without prior dilution in methanol (see previous section), to measure the total concentrations of MNs, and by comparison, to determine the binding of the MNs to HA. As a check for negligible depletion by SPME, 1 µL volumes of MN in hexane were injected manually into the GC, and the detector response per mass of MN determined. Based on these results, the approximate fractions of each aqueous MN that had sorbed to the fiber per SPME test were on the order of 1-2 % (1-MN, 1,3-DMN, 2,3,5-TMN).

Subsequently, the SPME-GC/MS technique was also used to determine binding coefficients at two higher Aldrich HA concentrations: 3 g/L and 10 g/L. The same procedures were followed except that larger quantities of MNs were added (2500 - 7500 µg/L) and the aqueous mixtures of MNs and HA were shaken for approximately 15 h prior to the initial analyses. The latter change was made to provide more consistent results, given that larger quantities of MNs were added to the 3 and 10 g/L solutions. For HPLC analyses of MNs, samples of the 3 and 10 g/L HA batches were diluted in methanol (1:5, H_2O:MeOH).

RESULTS

Solubility Enhancement of Methylnaphthalenes in the Presence of Aldrich HA

For 1-MN, the aqueous solubility, S_w, was found to be 30.0 ± 1.7 mg/L (n = 40). This result compares well with published values (Table 1). For 1,3-DMN, the S_w was found to be 8.2 ± 0.4 mg/L (n = 24), also close to a previously published value (Table 1).

The apparent solubilities, S^*_w, of 1-MN and 1,3-DMN in 1 g/L HA solutions were measured by HPLC. In the first S^* batch test using 1 g/L HA, a large excess of NAPL phase 1-MN was added (2 g/L) yielding very high S^*_w results (119 to 196 mg/L), with values increasing over 5 days (Table 2). Based on these results, the solubility enhancement was ~ 4 to 6, much higher than expected, based on related tests (e.g., see SPME results). It was suspected that these high S^*_w results may have been affected by NAPL phase breakthrough during filtering.

In the second S^* test, a much smaller excess of 1-MN was used (0.2 g/L). After one day the S^*_w was 56.5 mg/L (Table 2). It increased to 63.1 mg/L after 5 days and 87.5 mg/L after 12 days.

The S^*_w of 1,3-DMN in 1 g/L HA as measured by HPLC was 50.4 mg/L after one day, and then decreased to 45.1 mg/L after 2 days (Table 2). Overall, the data indicated an approximately six fold solubility enhancement.

The $K_{oc, app}$ values were calculated for 1-MN and 1,3-DMN using Equations 1 to 3, as shown in Table 3. For 1-MN, the S^* data indicated that a large proportion of the apparent sorption was a slow-phase or "delayed" component. The $K_{oc, app}$ values are approximately an order in magnitude smaller than binding coefficients that have been inferred for slightly water soluble (> 0.3 mg/L) PAHs, such as fluoranthene, anthracene and pyrene, to less concentrated aqueous Aldrich HA, typically ≤ 100 mg/L [21]. However, the $K_{oc, app}$ determined for 1,3-DMN in this study (1.18 to 1.35 x 10^4 mL/g) is similar to previous K_{oc} values for binding of moderately soluble phenanthrene (Table 1) to Aldrich HA, as determined by complexation-flocculation (1.47 to 1.66 x 10^4 mL/g) [21].

Binding of Methylnaphthalenes by Aldrich HA - SPME Results

The SPME tests using 1 g/L Aldrich HA indicated that after the MNs were added, their free dissolved concentrations declined steadily over the first six hours (Figure 1). The $K_{oc, app}$ values for MNs in 1 g/L

HA were determined at several time intervals using the SPME results for the free dissolved concentrations and HPLC results for total aqueous concentrations (Table 4, Figure 2). The sequential SPME results indicate that further binding of MNs to Aldrich HA occurred after the initial 6 hours. However, in contrast to the S* results, the trend in $K_{oc, app}$ as measured by SPME is not well defined. The SPME data suggest that there is little net binding of MNs to HA between day 2 and day 7.

Compared with S* results, the SPME technique yielded similar apparent binding coefficients for 1-MN and 1,3-DMN in 1 g/L Aldrich HA (Figure 2; Tables 3 and 4). Thus, the apparent binding coefficients determined for these two MNs in 1 g/L Aldrich HA were found to be similar over approximately two orders of magnitude in dissolved MN concentrations (e.g., ~ 200 µg/L (SPME) to 30 mg/L (S*) for 1-MN). However, the standard deviations for the $K_{oc, app}$ values determined by SPME-GC/MS were considerably higher than for S*. Higher standard deviations for the SPME-GC/MS technique can be attributed to a number of factors. This technique has larger analytical errors (by ~ 2 to 3 times) compared to HPLC (by Figure 3) because the SPME-GC/MS injections were performed manually, and an internal standard for the GC-MS could not be included. Also, some final dissolved concentrations in SPME batches were significantly lower than calibration standards. The different ages of the nominal Aldrich HA solutions used for the SPME technique (2 days to several weeks) may also have had some influence on the magnitude of the binding coefficient.

There is strong evidence that the chemical properties of aqueous Aldrich HA change with age. Over two weeks following the preparation of nominal 1 g/L HA solution, the pH declined from 9.3 to 7.3, perhaps in part due to episodic exposure to the atmosphere of the anaerobic chamber, which contains 5% CO_2. The absorbance of 1 g/L nominal standard HA solution declined by about 15 % over approximately 100 d following its preparation (Figure 3). A detailed examination of the aging of aqueous Aldrich HA and its effect on the binding of PAHs is outside the scope of this study.

Results after one day equilibration in 1 g/L Aldrich HA for two other isomers, 2-MN and 1,7-DMN yielded very similar apparent binding coefficients compared to 1-MN and 1,3-DMN respectively (Table 4). These

results suggest that the apparent binding coefficients for the pure-phase isomers determined in this study are reasonably representative of the complex mixtures of isomers that are present in natural hydrocarbon products, such as diesel fuel.

Table 5 provides a list of $K_{oc, app}$ values determined for MNs in 3 and 10 g/L Aldrich HA. For these batch tests, the total aqueous MN concentrations, c_t, were based on the amounts added, given that HPLC indicated quantitative recoveries (see following section). A comparison of Tables 4 and 5 indicates that there is a general decline in $K_{oc, app}$ values with the increase in Aldrich HA concentration from 1 to 3 g/L. For example, the $K_{oc, app}$ values determined by SPME at 1 day for 3 g/L HA were approximately 40 % of those determined at 1 day for 1 g/L HA. In contrast, the $K_{oc, app}$ values determined for 10 g/L HA were very similar to those for 3 g/L HA (Table 5; Figure 2). These data suggests that at elevated levels of HA (i.e., > 1 g/L Aldrich HA), the binding coefficient approaches a constant value, in spite of concomitant changes in pH.

Unlike the time trends observed for the 1 g/L Aldrich HA tests (Table 4), the $K_{oc, app}$ values did not change perceptibly between days 1 and 3 for the 3 and 10 g/L Aldrich HA batch solutions (Table 5). The lack of evidence for a delayed sorption component in these tests may be related, at least in part, to the fact that these solutions were shaken longer (15 h) than the 1 g/L solutions (0.5 h) following the addition of MNs. The lower relative standard deviations for the $K_{oc, app}$ values determined in 3 and 10 g/L HA, as opposed to those in 1 g/L HA, reflect at least two factors: i) less variation in the age of the HA solutions used, ii) the c_w/c_{oc} ratio decreased as the HA concentration increased, and the larger analytical error was associated with determining the c_w by SPME-GC/MS.

Tests for Interference by HPLC

Testing indicated that aqueous Aldrich HA did not interfere with the HPLC analyses of total aqueous MNs ("free" plus HA-bound fractions) in anaerobic batch solutions aged < 1 d (MNs in 1 g/L HA). However, in subsequent HPLC analyses to support the SPME technique, for batches aged up to 7 days, the peak

areas for MNs tended to decline over time: there were ~ 20 to 40 % declines in apparent total concentrations by 100 to 150 h . Sometimes "shoulders" appeared on the leading edge of the MN peaks on the HPLC chromatograms. Such results suggested that a fraction of HA-bound MN was no longer readily recoverable by HPLC after several days, and/or eluted as a distinct fraction.

In subsequent SPME tests, samples taken, at 1 and 3 days after MNs addition to 3 and 10 g/L Aldrich HA, were diluted in methanol (1: 5) several hours prior to their analyses by HPLC. In these tests the MNs were recovered quantitatively (> 96 % in majority of analyses). These results suggest that the methanol dilution step may be required to recover a significant fraction of slowly-desorbing MNs for HPLC analysis.

DISCUSSION

Previous applications of SPME have included the quantification of binding of various HOCs, including PAHs by natural aqueous humics [22], and the binding of chlorinated HOCs by Aldrich HA [23]. In this study, the SPME technique was used to examine binding of PAHs in solutions that contained up to 10 g/L Aldrich HA. Previous investigators of the binding of HOCs by HA have generally looked at relatively low HA concentrations ($\leq$ 200 mg/L or $\leq$ 100 mg/L as C). Notable exceptions were the studies by Guetzloff and Rice [34] and Johnson and John [14], who, respectively, examined binding of DDT and PCE in solutions containing up to 10 g/L or more Aldrich HA, using the S* technique. We found that SPME analyses were relatively time efficient compared to S*, because mixtures containing up to three isomers could be analyzed. Also, SPME was more flexible than S* in terms of its ability to test binding at various dissolved MN levels.

This study confirms earlier results [20,35,36] that have indicated that the binding of HOCs by HA decreases as the HA concentration increases. Previous observations of this trend were conducted at much lower HA concentrations, typically < 50 mg/L. Landrum et al. [20] suggested that this $K_{oc, app}$

versus HA concentration trend might be related to the formation of larger aggregates or associations of humic acid at higher HA concentrations. Similarly, Li et al. [36] attributed this trend to increased aggregation at higher HA concentrations, leading to fewer available exposed binding sites. Our results suggest that the concentration effect on binding becomes negligible at elevated levels of Aldrich HA (i.e., "nominal levels > 1 g/L). The reason for this pattern requires further investigation.

Guetzloff and Rice [34] reported that above 7.4 g/L, aqueous Aldrich humic acid (HA) formed micelles, which greatly enhanced its ability to dissolve DDT. In contrast, Johnson and John [14] found no evidence for enhanced solubilization of PCE by micellar Aldrich HA at concentrations > 7.4 g/L. Similarly, our results do not support the inferred critical micellar concentration (7.4 g/L) for Aldrich HA. For binding of MNs to Aldrich HA, the coefficients (apparent) are nearly identical for 3 and 10 g/L HA.

The dependence of the apparent solubility of 1-MN on the initial NAPL/aqueous solution ratio (Table 2) may have been an artifact, due to breakthrough of NAPL phase during filtering. Alternatively, it is possible that the large excess in NAPL-phase 1-MN (2 g/L) changed the conformation and/or association/aggregation properties of the aqueous Aldrich HA, which in turn changed the extent of binding of dissolved phase 1-MN by the HA. Perhaps, similar to the effects of other added organic phases [37], the presence of abundant NAPL-phase 1-MN causes a reduction in HA aggregation, which, as for elevated HA (see above), may lead to an enhancement in binding.

The S* results indicate a significant delayed component of sorption for 1-MN over 12 days (Table 3). Xu et al. [29] also used the S* technique and observed a similar delayed component for the binding of phenanthrene to Aldrich HA over a 36 day period. Others [36,38] have also reported delayed sorption of HOCs to HA. Delayed sorption may be related to the slow rate of diffusion within the humic acid molecules and/or to activation energies of sorption/desorption [38]. Alternatively, the slow-phase of sorption may also be related to ongoing changes in the aggregation or association of the HA molecules, as influenced by the presence of NAPL-phase 1-MN.

The SPME results suggest a shorter period of delayed sorption. In 1 g/L Aldrich HA, the free dissolved MN concentrations declined steadily over the first six hours (Figure 1), and sorption increased further by day 2 (Table 4). Using the complexation-flocculation technique, Laor and Rebhun [21] reported similar trends for time-dependent binding of pyrene and phenanthrene to Aldrich HA (filtered 0.45 μm) and inferred approximate equilibrium after 20 h. In contrast, some previous studies have indicated very rapid sorption kinetics, reaching apparent equilibrium in several minutes, for the binding of HOCs to natural HS [22,39], and for binding of benzo[a]pyrene to aqueous Aldrich HA (filtered 0.3 μm) [40].

The apparent aging of Aldrich HA solution observed in this study was not anticipated. This factor must be considered during further testing and field applications of Aldrich HA in subsurface remediation. Apparent aging of anaerobic NAPL-MN/water mixtures, without HA, were also observed. For reason(s) yet unexplained, after one week the HPLC analyses of such mixtures (not shown) tended to exhibit gradual declines in the mean concentrations of aqueous MNs over time. These aging effects should be examined further.

Currently, there is a large amount of research devoted to the complex and dynamic conformation and aggregation properties of aqueous humic substances. Some recent studies have challenged the conventional models and assumptions [27,37,41]. The results of this study reinforce the need to continue such basic research.

Significance for the use of humic acid carriers in subsurface remediation

The apparent binding coefficients observed for the concentrated Aldrich HA batches can be used to infer the enhanced solubilization (S^*_w/S_w) by nominal Aldrich HA solutions in subsurface remediation applications (see Introduction). Under ideal conditions there would be equilibrium dissolution of MNs from a NAPL contaminant hydrocarbon mixture, and the binding of MNs by aqueous HA would follow the $K_{oc,\ app}$ values reported in this paper. Given these assumptions, one would anticipate that in a 10 g/L Aldrich HA "treatment solution", the enhanced solubilization would be 3 to 4 fold for 1-MN, 7 to 8 fold for

1,3-DMN,and 12 to 16 fold for 2,3,5-TMN. It is anticipated that there would be even greater enhanced solubilization for more hydrophobic PAHs, such as pyrene, anthracene and others, given that the $K_{oc, app}$ value is related to the hydrophobicity of the PAH [16,40]. However, accurate modeling of the enhanced solubilization and mobilization of PAHs in subsurface remediation applications will also require data on the sorption of aqueous PAHs and Aldrich HA by the soil and/or aquifer materials, and on concurrent biodegradation of the PAHs. The environmental impact of the use of concentrated Aldrich HA solutions will also have to be considered. Some of these topics will be discussed in related papers.

ACKNOWLEDGEMENTS

REFERENCES

1. McCarthy, JF, Zachara, JM. 1989. Subsurface transport of contaminants. *Environ Sci Technol* 23:496-502.

2. Dunnivant FM, Jardine PM, Taylor DL, McCarthy JF. 1992. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environ Sci Technol* 26:360-368.

3. Johnson-Logan LR, Broshears RE, Klaine SJ. 1992. Partitioning behavior and the mobility of chlordane in groundwater. *Environ Sci Technol* 26:2234-2239.

4. Friedig AP, Garicano EA, Busser FJM, Hermens, JLM. 1998. Estimating impact of humic acid on bioavailability and bioaccumulation of hydrophobic chemicals in guppies using kinetic solid-phase extraction. *Environ Toxicol Chem* 17:998-1004.

5. Ma H, Kim SD, Cha DK, Allen HE. 1999. Effects of kinetics of complexation by humic acid on toxicity of copper to *Ceriodaphnia dubia*. *Environ Toxicol Chem* 18:828-837.

6. Abdul AS, Gibson TL, Rai DN. 1990. Use of humic acid solution to remove organic contaminants from hydrogeologic systems. *Environ Sci Technol* 24:328-333.

7. Magee, BR, Lion LW, Lemley AT. 1991. Transport of dissolved organic macromolecules and their effect on the transport of phenanthrene in porous media. *Environ Sci Technol* 25:323-331.

8. Liu, H, Amy G. 1993. Modeling partitioning and transport interactions between natural organic matter and polynuclear aromatic hydrocarbons in groundwater. *Environ Sci Technol* 27:1553-1562.

9. Lesage S, Novakowski KS, Xu H, Bickerton G, Durham L, Brown S. 1995a. A large scale aquifer model to study the removal of aromatic hydrocarbons from the saturated zone. *Proceedings, Solutions '95, International Association of Hydrogeologists Congress*, Edmonton, AB, Canada, June 4-10, 1995, 6 p.

10. Lesage, S, Xu, H, Novakowski, K. S, Brown, S. and Durham, L. 1995b. Use of humic acids to enhance the removal of aromatic hydrocarbons from contaminated aquifers. Part II: Pilot Scale. *Proceedings*, 5th Annual Symposium on Groundwater and Soil Remediation, Toronto, ON, Canada, Oct. 2-6, 1995, 10 p. (CD-ROM)

11. Lesage S, Li, WC, Brown S, Liu D. 1997. Effect of humic acids on the bioremediation of polycyclic aromatic hydrocarbons from aquifers contaminated with petroleum. *Proceedings*, 6th Annual Symposium on Groundwater and Soil Remediation, Montréal, QC, Canada, March 18-21, 1997, pp. 325-338.

12. Johnson WP, Amy GL. 1995. Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons (PAH) by natural organic matter (NOM) in aquifer sediments. *Environ Sci Technol* 29:807-817.

13. Johnson WP, Amy GL, Chapra SC. 1995. Modeling of NOM-facilitated PAH transport through low-f_{oc} sediment. *J Environ Eng* 121:438-446.

14. Johnson WP, John WW. 1999. PCE solubilization by commercial humic acid. *J Contam Hydrol* 35:343-362.

15. Thomas, DH, Delfino JJ. 1991. A gas chromatographic/chemical indicator approach to assessing groundwater contamination by petroleum products. *Ground Water Monitoring Review* Fall:90-100.

16. Chiou CT, Malcolm RL, Brinton TI, Kile DE. 1986. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ Sci Technol* 20:502-508.

17. Murphy EM, Zachara JM, Smith, SC, Phillips, JL, Wietsma TW. 1994. Interaction of hydrophobic organic compounds with mineral-bound humic substances. *Environ Sci Technol* 28:1291-1299.

18. Xing B, Pignatello JJ. 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ Sci Technol* 31:792-799.

19. Chiou, CT, Kile DE. 1998. Deviations from sorption linearity on soils of polar and nonpolar organic compounds at low relative concentrations. *Environ Sci Technol* 32:338-343.

20. Landrum PF, Nihart SR, Eadie BJ, Gardner WS. 1984. Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters. *Environ Sci Technol* 18:187-192.

21. Laor Y, Rebhun M. 1997. Complexation-flocculation: A new method to determine binding coefficients of organic contaminants to dissolved humic substances. *Environ Sci Technol* 31:3558-3564.

22. Poerschmann J, Zhang Z, Kopinke FD, Pawliszyn J. 1997. Solid phase microextraction for determining the distribution of chemicals in aqueous matrices. *Anal Chem* 69:597-600.

23. Urrestarazu Ramos E, Meijer SN, Vaes WHJ, Verhaar HJM, Hermens JLM. 1998. Using solid-phase microextraction to determine partition coefficients to humic acids and bioavailable concentrations of hydrophobic chemicals. *Environ Sci Technol* 32:3430-3435.

24. Gauthier TD, Seitz WR, Grant CL. 1987. Effects of structural and compositional variations of dissolved humic materials on pyrene K_{oc} values. *Environ Sci Technol* 20:1162-1166.

25. Backus, DA, Gschwend PM. 1990. Fluorescent polycyclic aromatic hydrocarbons as probes for studying the impact of colloids on pollutant transport in groundwater. *Environ Sci Technol* 24:1214-1223.

26. Rav-Acha C, Rebhun M. 1992. Binding of organic solutes to dissolved humic substances and its effects on adsorption and transport in the aquatic environment. *Water Research* 26:1645-1654.

27. Engebretson RR, von Wandruszka R. 1998. Kinetic aspects of cation-enhanced aggregation in aqueous humic acids. *Environ Sci Technol* 32:488-493.

28. Cornelissen G, van Noort PCM, Govers HAJ. 1998. Mechanism of slow desorption of organic compounds from sediments: A study using model sorbents. *Environ Sci Technol* 32:3124-3131.

29. Xu H, Lesage S, Durham L. 1994. The use of humic acids to enhance removal of aromatic hydrocarbons from contaminated aquifers. *Proceedings*, 4th Annual Symposium on Groundwater & Soil Remediation, Calgary, AB, Canada, Sept. 21-23, 1994, pp. 635-645.

30. Eganhouse RP, Calder JA. 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of aromatic hydrocarbon co-solutes and salinity. *Geochim Cosmochim Acta* 40:555-561.

31. Chen CSH, Delfino, JJ, Rao PSC. 1994. Partitioning of organic and inorganic components from motor oil into water. *Chemosphere* 28:1385-1400.

32. Mackay D, Shiu WY. 1977. Aqueous solubility of polynuclear aromatic hydrocarbons. *J Chem Eng Data* 22:399-402.

33. Burris DR, MacIntyre WG. 1986. A thermodynamic study of solutions of liquid hydrocarbon mixtures in water. *Geochim Cosmochim Acta* 50:1545-1549.

34. Guetzloff TF, Rice JA. 1994. Does humic acid form a micelle? *Sci Total Environ* 152:31-35.

35. Carter CW, Suffet IH. 1982. Binding of DDT to dissolved humic materials. *Environ Sci Technol* 16:735-740.

36. Li AZ, Marx KA, Walker J, Kaplan DL. 1997. Trinitrotoluene and metabolites binding to humic acid. *Environ Sci Technol* 31:584-589.

37. Conte P, Piccolo A. 1999. Conformational arrangement of dissolved humic substances. Influence of solution composition on association of humic molecules. *Environ Sci Technol* 33:1682-1690.

38. Pignatello JJ, Xing B. 1996. Mechanism of slow sorption of organic chemicals to natural particles. *Environ Sci Technol* 30:1-11.

39. Schlautman MA, Morgan JJ. 1993. Effects of aqueous chemistry on the binding of polycyclic aromatic hydrocarbons by dissolved humic materials. *Environ Sci Technol* 27:961-969.

40. McCarthy JF, Jimenez BD. 1985. Interactions between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation. *Environ Sci Technol* 19:1072-1076.

41. Schlebaum W, Badora A, Schraa G, van Riemsdijk WH. 1998. Interactions between a hydrophobic organic chemical and natural organic matter: Equilibrium and kinetic studies. *Environ Sci Technol* 32:2273-2277.

Table 1. Solubility data for selected methylnaphthalenes.

Isomer	Aqueous Solubility (S_w mg/L)	
	Literature (20, 25°C)	This Study (23±2°C)
1-methylnaphthalene	25.8[30], 27[31], 28.5[32], 30.2[33], 32.0[33]	30.0
2- methylnaphthalene	24.6[30], 25.4[32], 26[31]	22.6
1,3-dimethylnaphthalene	8.0[32]	8.2

Table 2. Apparent solubilities (S^*_w) of pure phase methylnaphthalenes in 1 g/L HA.

isomer starting NAPL/water ratio	aging of mixture days	S^*_w (mg/L) $\mu \pm \sigma$	(n)
1-MN			
2 g/L	1	119.2 ± 5.7	(36)
	2	127.3 ± 22.0	(36)
	5	196.2 ± 16.3	(24)
0.2 g/L	1	56.5 ± 1.9	(36)
	2	53.6 ± 2.2	(36)
	5	63.1 ± 3.3	(36)
	12	87.5 ± 3.8	(18)
1,3-DMN			
0.1 g/L	1	50.4 ± 1.6	(36)
	2	45.1 ± 1.4	(36)

Table 3. Apparent binding coefficients ($K_{oc, app}$ as mL per g organic C in HA) based on comparison of aqueous solubility (S_w) and apparent solubility in Aldrich HA ($S_w{}^*$). In this paper this approach is referred to as S* (see text for details).

Test	Day	$K_{oc, app}$ mL/g* $\mu \pm \sigma$
1-MN	1	$7.78 (\pm 0.52) \times 10^3$
(2 g/L)	2	$8.49 (\pm 1.93) \times 10^3$
	5	$1.45 (\pm 0.14) \times 10^4$
1-MN	1	$2.3 (\pm 0.22) \times 10^3$
(0.2 g/L)	2	$2.1 (\pm 0.24) \times 10^3$
	5	$2.9 (\pm 0.32) \times 10^3$
	12	$5.0 (\pm 0.36) \times 10^3$
1,3-DMN	1	$1.35 (\pm 0.05) \times 10^4$
	2	$1.18 (\pm 0.05) \times 10^4$

*assuming Aldrich HA is 38.2 % organic C [24]

Table 4. Apparent binding coefficients in 1 g/L Aldrich HA based on SPME ($K_{oc, app}$ as mL per g organic C in HA).

Test	Equilibration period (days)	Final dissolved MN conc. (μg/L)	$K_{oc, app}$ mL/g* $\mu \pm \sigma$	(n)
1-MN	1	309 - 1,079	1.7 ($\pm$ 0.92) x 10^3	(27)
	2	176 - 191	4.1 ($\pm$ 0.41) x 10^3	(3)
	6	192 - 456	5.4 ($\pm$ 1.1) x 10^3	(9)
	7	143 - 171	4.0 ($\pm$ 0.55) x 10^3	(4)
2-MN	1	410 - 977	2.1 ($\pm$ 1.1) x 10^3	(18)
1,3-DMN	1	129 - 704	4.3 ($\pm$ 1.7) x 10^3	(27)
	2	117 - 125	7.9 ($\pm$ 0.34) x 10^3	(3)
	6	138 - 292	1.0 ($\pm$ 0.17) x 10^4	(9)
	7	89 - 131	7.5 ($\pm$ 0.60) x 10^3	(3)
1,7-DMN	1	418 -699	3.7 ($\pm$ 1.2) x 10^3	(18)
2,3,5-TMN	1	88 - 439	7.9 ($\pm$ 3.9) x 10^3	(27)
	2	97 - 101	4.3 ($\pm$ 0.13) x 10^3	(3)
	6	101 - 220	1.3 ($\pm$ 0.45) x 10^4	(9)
	7	62 - 67	9.8 ($\pm$ 0.52) x 10^3	(3)

*assuming Aldrich HA is 38.2 % organic C [24]

Table 5. Apparent binding coefficients in 3 and 10 g/L Aldrich HA solutions based on SPME ($K_{oc, app}$ as mL per g organic C in HA).

Test	Aldrich HA conc. (g/L)	Equilibration Period (days)	Final dissolved MN conc. (µg/L)	$K_{oc, app}$ mL/g* $\mu \pm \sigma$	(n)
1-MN	3	1	1,269 - 1,468	7.14 ($\pm$ 1.19) x 10^2	(3)
	3	3	1,325 - 1,567	6.22 ($\pm$ 1.35) x 10^2	(3)
	10	1	1,794 - 1,804	7.85 ($\pm$ 0.13) x 10^2	(3)
	10	3	1,507 - 1,881	8.51 ($\pm$ 1.28) x 10^2	(3)
1,3-DMN	3	1	737 - 860	1.82 ($\pm$ 0.24) x 10^3	(3)
	3	3	761 - 981	1.58 ($\pm$ 0.36) x 10^3	(3)
	10	1	899 - 965	1.75 ($\pm$ 0.08) x 10^3	(3)
	10	3	799 - 964	1.86 ($\pm$ 0.21) x 10^3	(3)
2,3,5-TMN	3	1	468 - 539	3.35 ($\pm$ 0.38) x 10^3	(3)
	3	3	474 - 652	2.90 ($\pm$ 0.73) x 10^3	(3)
	10	1	573 - 622	2.88 ($\pm$ 0.13) x 10^3	(3)
	10	3	481 - 566	3.26 ($\pm$ 0.33) x 10^3	(3)

*assuming Aldrich HA is 38.2 % organic C [24]

FIGURE CAPTIONS

Figure 1. Trends in free dissolved concentrations of MNs in 1 g/L Aldrich HA, as measured by SPME. For each MN, the starting concentration was 500 µg/L.

Figure 2. Apparent binding coefficients versus time for various MN isomers, Aldrich HA concentrations and analysis techniques.

Figure 3. Changes in absorbance for 1 g/L Aldrich HA standard over time.
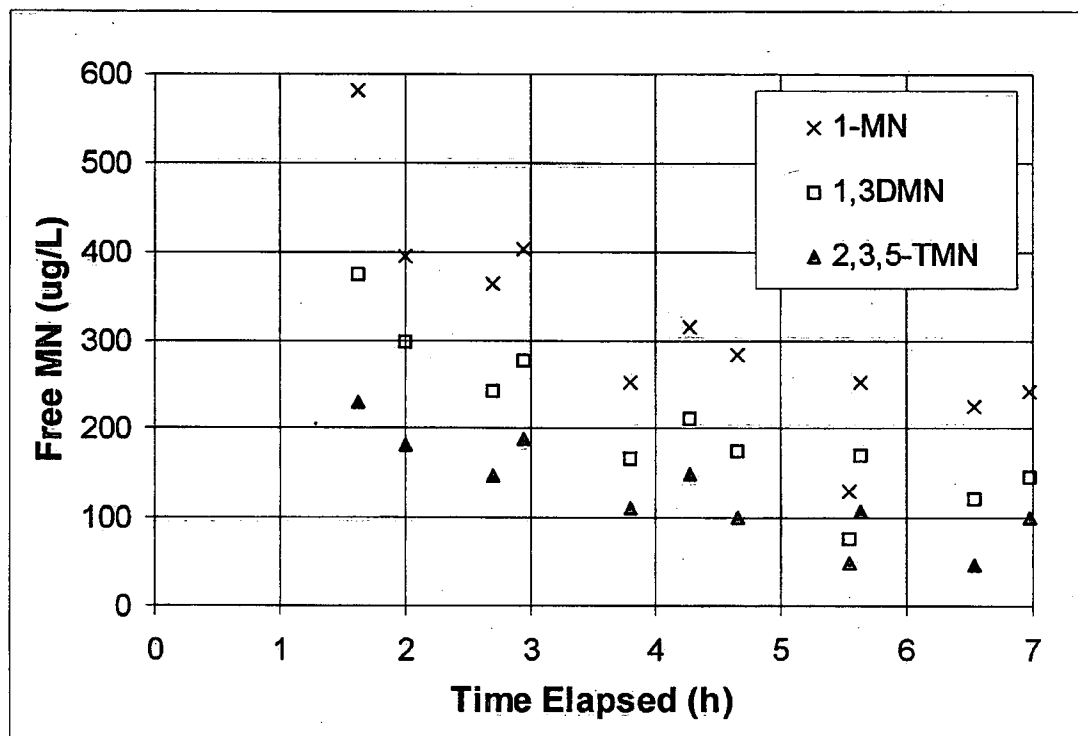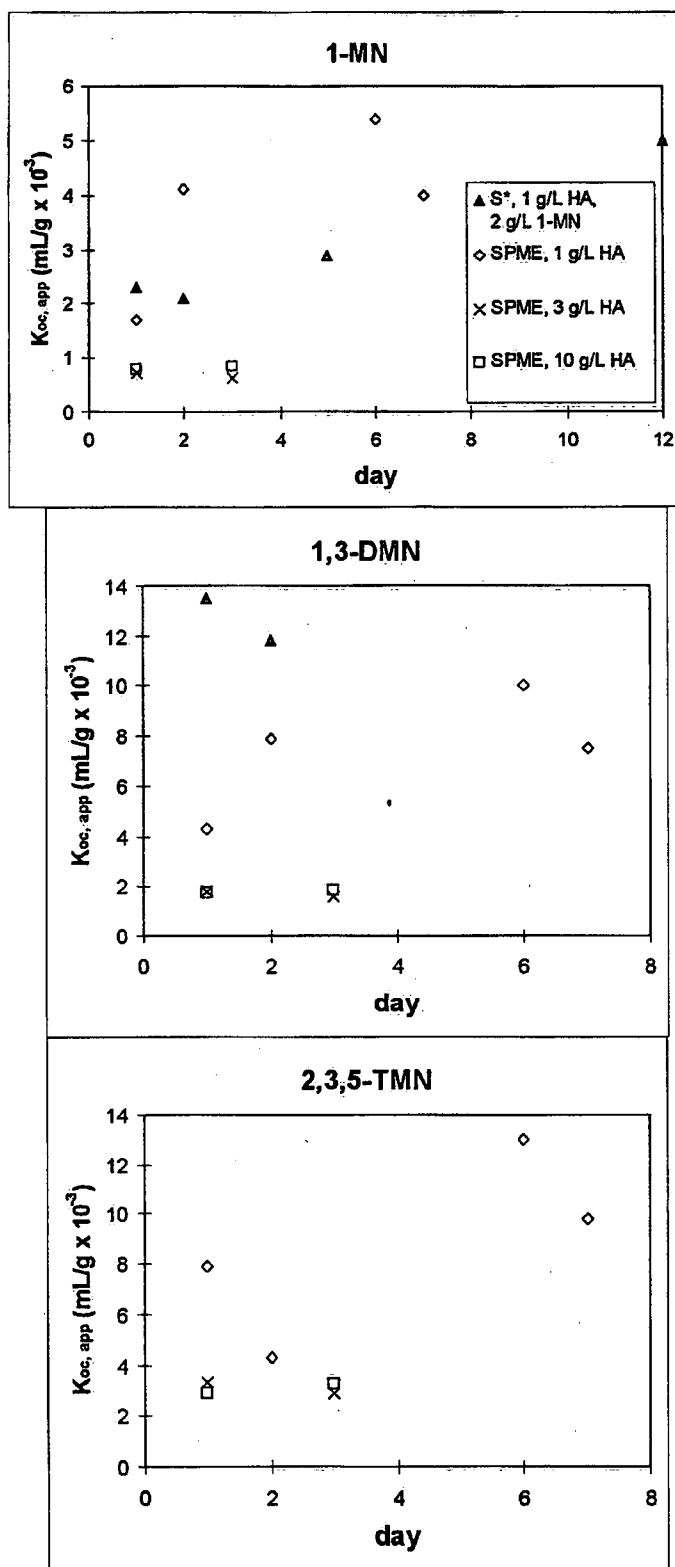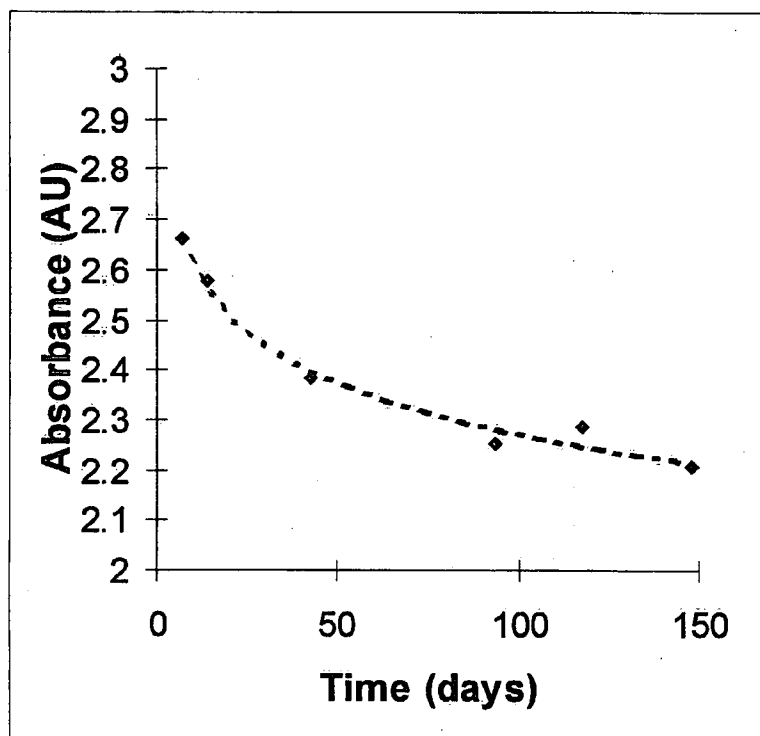
Figure 1.

Figure 2.

Figure 2 contains three plots:

1-MN — $K_{oc, app}$ (mL/g $\times 10^3$) vs day, with legend:
- ▲ S*, 1 g/L HA, 2 g/L 1-MN
- ◇ SPME, 1 g/L HA
- ✕ SPME, 3 g/L HA
- ☐ SPME, 10 g/L HA

1,3-DMN — $K_{oc, app}$ (mL/g $\times 10^3$) vs day

2,3,5-TMN — $K_{oc, app}$ (mL/g $\times 10^3$) vs day

Figure 3.