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Sorption of Methylated Naphthalenes by
Winter Sand, a Model Aquifer Material
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Part 4, Report to PERD*

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MANAGEMENT PERSPECTIVE

The work was conducted as part of a project for 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 modeling the various chemical and biological processes that occur when humic acids are used to remediate diesel fuel. This paper (Part 4 of a 4 part Report to PERD) provides data on the sorption of the diesel components (e.g., PAHs) to the aquifer materials. These are not available in the literature, but are required for the numerical modeling .

The methods described in this paper will be applied in future pilot scale field tests of the remediation method.

Sorption des méthylnaphthalèmes par le sable d'hiver, un matériau d'aquifère type

SOMMAIRE À L'INTENTION DE LA DIRECTION

Ces études en laboratoire effectuées à l'INRE étaient financés par le PRDE (hydrocarbures) et Environnement Canada, dans le cadre du secteur d'activité Un environnement sain (substances toxiques).

On a effectué ces travaux dans le cadre d'un projet de développement d'une méthode d'assainissement des eaux souterraines pour le traitement des composés de pétrole dans les eaux souterraines, un projet en collaboration financé par CRESTech (Université de Waterloo). On a modélisé les divers processus chimiques et biologiques qui interviennent lorsqu'on utilise des acides humiques pour l'assainissement de zones contaminées par du carburant diesel. Ce document (dernière tranche d'un rapport en 4 parties présenté au PRDE) présente des données sur la sorption de composants du carburant diesel (p. ex. les HAP) par les matières de l'aquifère. Ces données inédites sont requises pour la modélisation numérique .

On doit appliquer les méthodes décrites dans ce document à des études pilotes sur le terrain prévues pour cette méthode d'assainissement.

Abstract

Information on the sorption of methylated naphthalenes (PAHs) to Winter Sand was required for numerical modeling of a pilot scale test of a diesel contaminant plume in groundwater. Batch tests that contained humic acid-conditioned Winter Sand, water and three methylated naphthalenes provided apparent sorption isotherms at 2 h, 5 h, 70 h and 25 d. The aqueous concentrations of the methylated naphthalenes decreased over this 25 d period, approaching apparent equilibrium values. The apparent K_d values (mL/g) at 25 d for 1-methylnaphthalene and 1,3-dimethylnaphthalene were 3.3 and 5.3 respectively. Based on these results, the sorption of methylated naphthalenes to Winter Sand includes a significant slow component (between 10 to 25 % of total). Numerical simulation of this sorption process must take into account this information on kinetics.

RÉSUMÉ

Des informations sur la sorption des méthylnaphthalènes (HAP) dans le sable d'hiver sont requises pour la modélisation numérique de l'étude pilote d'un panache de carburant diesel contaminant des eaux souterraines. Des essais par lots avec du sable d'hiver humique à traitement acide, de l'eau et trois méthylnaphthalènes ont donné des isothermes de sorption apparente pour des périodes de 2 heures, 5 heures, 70 heures et 25 jours. Les concentrations aqueuses des méthylnaphthalènes diminuaient au cours de cette période de 25 jours, approchant des valeurs d'équilibre apparentes. Après 25 jours, les valeurs de K_d apparent (mL/g) du 1-méthylnaphthalène et du 1,3-diméthylnaphthalène étaient de 4,1 et de 7,2, respectivement. Selon ces résultats, la sorption des méthylnaphthalènes dans le sable d'hiver comporte une phase lente significative (pour 10 à 25 % de la quantité totale). Les simulations numériques de ce processus de sorption doivent prendre en compte ces informations cinétiques.

INTRODUCTION

In a pilot scale test aquifer at the Canada Centre for Inland Waters in Burlington, Ontario, methylated naphthalenes (MNs) were detected at elevated levels (tens to hundreds µg/L) in a diesel contaminant plume (Lesage et al., 1997; Van Stempvoort et al., 2001). Concentrated Aldrich humic acid (HA) (nominal 1 g/L) had been added to the model groundwater as a flushing agent, causing significant increases in the total aqueous concentrations of MNs, and other polycyclic aromatic hydrocarbons (PAHs). This paper reports batch experiments ($23 \pm 2°C$) that were conducted in order to quantify the sorption of aqueous phase MNs to the model aquifer material. The apparent sorption parameters determined in these batch experiments are applied in the numerical modeling of the pilot scale experiment (Molson et al., 2000, 2001).

The model aquifer material that was used in the pilot test and in the batch experiments reported here is Winter Sand. This aggregate product (Preston Sand & Gravel Co. Ltd. of Kitchener, Ontario) is a carbonate-rich (77 ± 2 weight % as $CaCO_3$) sediment, composed mainly of medium to very coarse sand, granules and pebbles (Van Stempvoort et al., 2000).

Background

Hydrophobic organics are important contaminants in many subsurface environments (soils, sediments, groundwater). The behavior of these contaminants is strongly affected by sorption to the solid media in which they occur. The sorption of hydrophobic organic compounds (HOCs) by soils/sediments has been examined in many studies. The sorption mechanism is often modeled as partitioning (i.e., solid-phase dissolution), following linear isotherm behavior:

$$K_d = C_s/C_w, \hspace{4cm} \text{(Equation 1)}$$

where K_d is the sorption distribution coefficient, C_s is the concentration of HOC that is sorbed to the soil/sediment (per mass or surface area), C_w is the concentration of the HOC in water.

Assumptions built into Equation 1 include: that sorption is a reversible, equilibrium process, and that this is a linear relationship. K_d values are generally based on laboratory batch or column tests. The K_d for a given HOC-soil/sediment system can often be predicted fairly closely on the basis of two parameters: (1) the octanol-water partitioning coefficient (K_{ow}) for the HOC, and (2) the concentration of organic carbon (OC) in the soil/sediment (e.g., Karickhoff et al., 1979; Schwarzenbach and Westall, 1981).

For low HOC concentrations, Equation 1 has generally been a useful quantitative tool, and it has often been applied in numerical modeling. In reality, nonlinear sorption of HOCs by soils/sediments is common (Chiou and Kile, 1998). Nonlinear results are often modeled using the Freundlich equation (Equation 2), the Langmuir equation (Equation 3) or others (Kinniburgh, 1986; Kozak, 1996).

$$C_s = K_f C_w^{1/n} \hspace{4cm} \text{(Equation 2)}$$

where K_f = Freundlich sorption coefficient, $1/n$ = constant.

$$C_s = Q_{max} K_l C_w/(1+K_l C_w) \hspace{3cm} \text{(Equation 3)}$$

where Q_{max} = saturation sorbed HA concentration, and K_l = Langmuir sorption parameter.

Studies have generally shown that sorption of HOCs to soils/sediments is generally not completely reversible. Hysteresis is common, apparently because the activation energy required for desorption is often greater than for sorption, or other reasons (Pignatello and Xing, 1996). In many cases, even after exhaustive desorption procedures are employed, a fraction of the sorbed HOC remains "irreversibly" bound (e.g., Burgos et al., 1996; Kan et al., 1998; Lahlou and Ortega-Calvo, 1999).

The equilibrium assumption of either Equation 1 or 2 is often assumed to be valid for numerical modeling of the sorption of HOCs in the subsurface environment. The justification given is that the sorption of HOCs to sediments/soils appears to be a rapid process, compared to

the relatively sluggish movement of groundwater. Based on laboratory batch test results, the sorption of HOCs to soils and aquifer materials is generally assumed to reach equilibrium in a matter of minutes to hours. However, as reviewed by Pignatello and Xing (1996), a broad spectrum of research results have indicated that a slow or very slow component of sorption and/or desorption occurs, on the order of days to weeks. In some cases, slow to very slow sorption and desorption may be dominant (i.e., more than 50 % of total sorption). These kinetics have significant implications for the fate and remediation of HOCs in the subsurface environment.

Many observations of slow phase sorption kinetics have been reported in recent years. Such work will likely prove helpful for gaining a better understanding of sorption mechanisms (Pignatello and Xing, 1996; Cornelissen et al., 2000), and the role of diffusion in sorption kinetics (e.g., Piatt and Brusseau, 1998). Based on recent research it appears that for the sorption of HOCs to soils/sediments, a slow component is common, if not ubiquitous.

The kinetics studies have generally indicated that the rate of desorption of HOCs from soils is slower than rate of sorption (e.g., Lueking et al., 2000). A study by Cornelissen et al. (1998) indicated that the presence of mineral micropores and/or organic matter can result in slow desorption of HOCs from soils, but that the organic matter present was more important in controlling the desorption. Cornelissen et al. (2000) reported that the fractions of HOCs that desorbed rapidly from a lake sediment followed a linear isotherm, whereas slowly to very slowly desorbing fractions followed Langmuir behavior. Lueking et al. (2000) found that the type of soil organic matter had a large effect on the rates of sorption and desorption, whereas Chiou et al. (2000) found that the types of organic matter and the polarity of contaminants had a strong influence on whether sorption of the latter was linear or nonlinear.

Another factor that has to be taken into account in studies of HOC sorption to soils and sediments is the "solids effect". Previous studies have established that for batch testing, as the ratio of solids to water increases, the observed K_d value for a given HOC and soil/sediment pair decreases (e.g., O'Connor and Connolly, 1980; Voice et al., 1983). Although the reason for this trend is not fully understood, it may be related to the following factors:

1) presence of microparticles, which may be more dispersed in relatively dilute suspensions of soil/sediment (e.g., Gschwend and Wu, 1985);

2) a particle-interaction induced desorption, that becomes more significant at relatively high solids concentrations (Di Toro et al., 1986);

3) the surface area of the solids that is accessible to sorption may decrease as the solids concentration increases (Celorie et al., 1989).

Preliminary Tests and Parallel Studies

In preliminary aerobic batch tests conducted in 1998, the concentrations of aqueous MNs declined sharply over periods of one day or less, due to apparent degradation, even in solutions containing 0.1 – 0.25 % sodium azide. Thus, for the batch tests reported in this paper, care was taken to minimize any biodegradation and photodegradation by eliminating dissolved O_2. Thus, the batch solutions were sparged with Ar and then combined with Winter Sand in an anaerobic chamber.

Preliminary tests also showed that the "solids-effect" was very important (Figure 1). Thus, the batch tests reported here were designed to have solids/solution ratios similar to those of the pilot scale study.

Parallel studies indicated that substantial fractions of dissolved MNs bind to aqueous Aldrich humic acid (HA) (Van Stempvoort and Lesage, 2001), and that a significant amount of the aqueous HA (up to ~ 0.4 mg/g) is sorbed by the Winter Sand (Van Stempvoort et al., 2000). The sorbed HA may exert a strong influence on the (co)sorption of MNs by the sand. Aqueous HA that becomes sorbed to mineral surfaces is tightly bound. Desorption is generally minimal, unless the pH is changed sharply (Avena and Koopal, 1998). Thus, for the batch tests reported here, "HA-conditioned" Winter Sand was sampled from the pilot scale model aquifer at the Canada Centre for Inland Waters described by Lesage et al. (1997) and Van Stempvoort et al. (2001). This sand had been in contact with model groundwater containing ~1 g/L Aldrich HA for four years.

MATERIALS AND METHODS

PAHs

Three pure phase methylated naphthalenes were obtained from Sigma-Aldrich Canada Ltd. (Mississauga, ON): 1-methylnaphthalene (1-MN), 1,3-dimethylnaphthalene (1,3-DMN) and 2,3,5-trimethylnaphthalene (2,3,5-TMN).

Shaker tests

The HA-conditioned sand was sampled from just below water table of the pilot scale model aquifer, using a split spoon coring device. Residual HA solution was purged from ~ 400 g of this sand sample in the following way. First, ~ 150 mL of solution with pH of ~ 7.9 (dilute NaOH) was placed in a 7 cm diameter sediment column constructed with stainless steel and glass. This pH value, 7.9, was approximately the same as that of the HA solution in the model aquifer. Then the sand was added to the column, and approximately 300 mL of the same "pH 7.9" solution was passed through it at a rate of approx. 0.35 mL/min, using a Model A-30-S Eldex Precision Metering Pump. After purging, the porewater in the column was allowed to drain by gravity. Then more of the remaining porewater was removed by transferring the sand to a glass vacuum filtration apparatus, and applying a vacuum through a 47 mm diameter Gelman glass fiber filter (Type A). This filtrate had very little colour, indicating that there was little remaining HA in solution. The water content of a sample of the filter-evacuated sand was determined by air-drying.

The prepared HA-conditioned sand sample was placed in an anaerobic chamber. In same chamber, three "start" solutions of MNs were prepared by adding stock (1 % 1-MN, 0.5 % 1,3-DMN and 0.1 % 2,3,5-TMN) to pH 7.9 solution and then purged by Ar. Portions of the prepared HA-conditioned sand were added to 9 pre-weighed 40 mL glass vials, which were reweighed and placed in the anaerobic chamber. The 9 vials were placed in 3 groups of 3. For each group, a different start solution was added to each vial such that, when stirred with a stainless steel spatula to remove trapped air, the resulting batch was water-saturated with a slight excess (approx. 1 - 2 mL) of solution (Table 1). The batches were sealed with septa and caps, removed from the anaerobic chamber, weighed again, shaken for 1.5 h (orbital) and then placed back in the anaerobic chamber. After approximately 1 h of settling, the "supernatant" in each batch was sampled by glass pipette and transferred to a 4.8 mL vial, in which approx. 2 mL of Ar-purged methanol had been added. The mass of each component was determined by pre-weighing the vial, re-weighing with methanol, and finally weighing again with the sample. The concentrations of MNs in the samples were analyzed by HPLC. Samples of the start solutions were prepared and analyzed in the same way. The start solution concentration for each batch was adjusted, taking into account the initial water content of the prepared sand that had been added.

Further testing with the same batches was conducted to provide information on the kinetics of the sorption process. Approximately 1 h after the first sampling event, ~ 5 mL of the pH 7.9 solution was added to each batch, which was then resealed, removed from the chamber and placed on an orbital shaker for approx. 70 h. Then the batches were again allowed to settle for approximately one hour and samples were prepared for analyses by HPLC (Table 2). Glass sample vials (4.8 mL capacity) were prepared by the following steps: pre-weighing, placing them in the anaerobic chamber, adding 2 mL (approx.) of the methanol to each, sealing with septa, removing from the chamber, reweighing, and placing them back in the chamber.

Finally, for direct qualitative evidence re the fate of the fraction of each methylated naphthalene that had apparently "sorbed" to the Winter Sand, a method was used to try to desorb this fraction. Approximately 5 mL of methanol were added to each batch, which was turned upside down twice to mix the methanol and water, then shaken for 1 h, allowed to settle, then sampled and analyzed, as above.

Static Tests

The above shaker batch tests with HA-conditioned sand had relatively low solution/sand ratios (0.21 to 0.29 by weight) in order to avoid the "solids" effect that was observed in preliminary tests with more dilute batch tests. However, with these low ratios, the sand was tightly packed into the vials and as a result, active mixing of the batches during shaking appeared to be limited. In particular, there was some doubt concerning the efficiency of mixing between the "excess" solution above the sand with the porewater within the sand. Further, it could be argued that the shaking technique would not yield results that are representative of the pilot-scale experiment, at least in terms of the sorption kinetics. As a result, further batch tests were designed in order to avoid the potential problem of inefficient batch solution mixing, without the use of shaking.

As for the shaker tests, another ~ 5 kg of HA-conditioned Winter Sand was sampled from the pilot scale model aquifer at a point just below water table, using a split spoon coring device. This time, due to the larger sample size, the residual HA solution was not purged in a column, but was allowed to drain by gravity, and then more was removed by transferring the sand to a glass vacuum filtration apparatus, and applying a vacuum through a 10 μm mesh stainless steel screen. The water content of a sample of the filter-evacuated sand was determined by air-drying, and was assumed to be present as residual 1 g/L HA solution. The vacuum-prepared sand was placed in 4 open plastic bags within the portal of the anaerobic chamber and subjected to 4 vacuum-N_2 atmosphere cycles (5 to 25 min per step), in order to remove O_2.

Nine 500 mL Mason jars with lids, and nine stainless steel mini-screens for batch sampling (Van Stempvoort et al., 2000), were cleaned, weighed (jar, lid + screen) and placed in the anaerobic chamber. Three start solutions were prepared as in previous test phases. As before, each of the start solutions was added to three batches: in each Mason jar, approximately 100 mL of one start solution was added. The jars with solutions and mini-wells were sealed, removed from the chamber, re-weighed, and placed back in the chamber. Then prepared sand was added to each batch, using a plastic reagent boat, until there was negligible excess solution, with the sand at ~ 100 % saturation with solution, and the mini-well inserted for sampling. Care was taken to prevent sand from entering through the top, open end of the mini-well. During addition of the sand, trapped air was eliminated as required by stirring with a stainless steel spatula, and the sand was compacted by striking the base of the jar on the bottom surface of the chamber.

These static batches were left in the anaerobic chamber, and were sampled at several time intervals: approximately 2 h, 5 h, 70 h and 25 d. The resulting concentrations of MNs in the samples were total, including dissolved phase and the fraction bound (sorbed) to aqueous HA. In order to calculate the "free" concentration, C_w, the residual solution in the sand after filter-evacuation was assumed to be 1 g/L HA. The calculation used was based on Equation 4:

$$C_w = C_t/(K_{oc, app} \times c_{HA} \times f_c + 1) \hspace{3cm} \text{(Equation 4)}$$

where C_t is the measured total aqueous methylated naphthalene concentration,
$K_{oc, app}$ is the apparent binding coefficient for the methylated naphthalene, per organic C in the HA,
c_{HA} is the inferred concentration of the HA in the solution,
and f_c is the fraction of organic C in the HA (0.301).

Apparent coefficients ($K_{oc, app}$, L/g) for the binding of MNs to aqueous Aldrich humic acid were based on previous testing (SPME tests with 1 g/L Aldrich HA: Van Stempvoort and Lesage, 2001), as follows: 2.2 for 1-MN, 5.1 for 1,3-DMN and 9.8 for 2,3,5-TMN.

RESULTS

Shaker Tests

Based on the results of the shaker tests, the apparent isotherms indicate weakest sorption to Winter Sand by the 1-MN, moderate sorption by 1,3-DMN, and strongest sorption by the 2,3,5-TMN, and approximately linear behavior over the concentration ranges tested.

The concentrations of the MNs in the samples of batch solutions are shown in Tables 1 and 2. Apparent isotherms based on these results are given in Figures 2a, b and c. The 1.5 h shaker batch test results with HA-conditioned sand yielded similar results to the preliminary 1 h tests using fresh Winter Sand (not shown), suggesting that the presence of HA sorbed to the sand had relatively little effect on the sorption of MNs to the same sand.

Compared to the 1.5 h tests with HA-conditioned sand, the 70 h shaker tests indicated a significant amount of delayed sorption of MNs, resulting in unique isotherms with much steeper slopes (Figures 2 a,b,c). However, based on the data in Tables 1 and 2, in most batches the large majority of the sorption had occurred within the first 1.5 h of shaking.

For the shaker tests results shown in Figures 2 a, b and c, apparent sorption coefficients, $K_{d, app}$, based on Equation 1 are shown in Table 3. Calculation of these apparent sorption coefficients does not imply that the actual sorption process is either a linear or equilibrium process (cf. Cornelissen et al., 1998). In fact, the isotherms appear to be slightly non-linear, and this, in part, apparently accounts for the relatively large standard deviations shown in Table 3.

The data for sorption of 1-MN and 1,3-DMN, as shown in Figures 2a and b, suggest non-linearity, with a decrease in the strength of sorption as the aqueous concentrations increase. Thus they were also fitted to the Freundlich equation (Equation 2), using a curve fitting program (CurveExpert Version 1.37). The results are shown in Table 4. As for Table 3, Table 4 should be interpreted as apparent sorption parameters, without implying that equilibrium had been achieved. Because of large scatter, Freundlich curves were not fit to the 2,3,5-TMN data.

The desorption tests were conducted following the 70 h sampling episode. In the majority of these tests, approximately 30 to 40 % of the sorbed 1-MN and 1,3-DMN was extracted to the methanol/water solutions (Table 5). The results for 2,3,5-TMN were similar but less consistent. Given the relatively short duration of these desorption tests (1 h), and the fact that infinite-sink techniques were not applied (cf. Lueking et al., 2000), these results should be viewed as indicators of incomplete desorption, rather than exhaustive desorption. Based on the literature, we suspect that larger fractions of the MNs would have been extracted if more rigorous recovery techniques were used.

Static tests

In the static batch tests, the bulk of the sorption occurred during the first 5 hours, reducing concentrations to 10 - 25 % of starting values (cf. Tables 6 and 7; Figure 3). However, the concentrations of aqueous MNs in the samples continued to decrease over time (Table 7, Figures 4 a,b,c). Similar to the shaker tests, these results indicate that the kinetics of the sorption of MNs to the sand include a "delayed" or slow phase. Although it is possible that ongoing reaction/degradation of MNs also occurred, the anaerobic conditions of the batches probably limited such processes. However, as in the case of the shaker tests, the possibility that some biodegradation occurred, associated with reduction of Fe-oxides and/or other electron acceptors, cannot be ruled out at this time.

For 1-MN and 1,3-DMN, the apparent isotherms for the static tests were approximately linear (Figures 4a,b). For these two MNs, the apparent sorption isotherms at 70 h for the shaker and static tests were similar (Figures 4a,b), suggesting that the results were reproducible. As for the shaker tests, apparent binding parameters, $K_{d, app}$, based on the static tests were calculated using Equation 1 as shown in Table 3. Again, the static test results for 2,3,5-TMN were scattered. This is probably due, at least in part, to the relatively large measurement errors in these tests. The final concentrations were often < 50 µg/L, close to the detection limit of ~ 20 µg/L. Thus, the estimated $K_{p, app}$ values for 2,3,5-TMN, as shown in Table 3, should be considered as semi-quantitative indicators.

As for the shaker tests, the 1-MN and 1,3-DMN static test data suggest non-linearity (decreasing sorption strength with increasing aqueous concentrations) and were fitted to the Freundlich isotherm equation (Table 4). However, the R^2 for the Freundlich parameters were

generally large compared to those for the shaker tests. These statistics suggest that there were larger measurement errors in the static tests. Perhaps this was due, at least in part, to errors in corrections applied to the dissolved concentrations, based on the inferred coefficients for binding of MNs to aqueous HA. In particular, the low R^2 values for the 25 d test data indicate that the resulting Freundlich parameters are of limited value for numerical modeling.

DISCUSSION

The parameters given in Tables 3 and 4 provide a useful basis for numerical modeling of the pilot scale test. Given that Equations 1 and 2 do not take into account the kinetics of the sorption process, it may be useful to conduct further analysis of the static batch test data, in order to calculate kinetic parameters. The parameters required for numerical modeling of the pilot scale test include those indicated in either Table 3 or 4, those related to the sorption of Aldrich HA to Winter Sand (Van Stempvoort et al., 2000), to the binding of MNs by aqueous HA (Van Stempvoort and Lesage, 2001), and others related to the hydraulic properties of the model aquifer and biodegradation of the PAHs.

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Table 1. Shaker batch test data including results of the initial sampling, after 1.5 h shaking

BATCH	air-dry sand* g	solution* g	solution/sand ratio	start 1-MN ug/L	start 1,3-DMN ug/L	start 2,3,5-TMN ug/L	end 1-MN ug/L	end 1,3-DMN ug/L	end 2,3,5-TMN ug/L
s4a	32.22	7.27	0.23	5723	2509	462	2795	759	41
s4b	31.92	7.14	0.22	5706	2502	461	2762	775	65
s4c	28.12	6.91	0.25	5877	2577	475	2963	917	91
s4d	32.21	7.99	0.25	3184	1458	272	1496	391	13
s4e	36.20	8.16	0.23	3091	1416	264	1327	368	28
s4f	35.33	7.70	0.22	3055	1399	261	1028	284	33
s4g	30.17	6.39	0.21	1561	742	129	424	94	nd
s4h	27.28	7.91	0.29	1712	814	141	711	180	24
s4i	40.44	9.58	0.24	1620	770	134	535	139	7

*corrected for moisture content of sand (5.3 % by weight)

Table 2. Shaker batch test data including results of sampling after 70 h shaking

	corrected air-dry sand	final solution amount	final solution/sand ratio	restart* 1-MN ug/L	restart* 1,3-DMN ug/L	restart* 2,3,5-TMN ug/L	end 1-MN ug/L	end 1,3-DMN ug/L	end 2,3,5-TMN ug/L
s4a-2	32.22	7.67	0.24	2278	618	33	786	205	29
s4b-2	31.92	7.79	0.24	2079	583	49	776	159	nd
s4c-2	28.12	6.90	0.25	2302	713	70	866	211	nd
s4d-2	32.21	8.47	0.26	1155	302	10	473	102	nd
s4e-2	36.20	8.68	0.24	1005	279	22	404	82	nd
s4f-2	35.33	8.87	0.25	796	220	25	285	80	nd
s4g-2	30.17	7.34	0.24	304	67	nd	113	35	nd
s4h-2	27.28	7.69	0.28	567	143	19	236	54	nd
s4i-2	40.44	9.98	0.25	429	112	6	151	34	nd

* calculated based on final conc. for previous test, sample removed and H₂O ("7.9") added

Table 3. Apparent sorption coefficients (Equation 1) based on the shaker and static batch tests.

Test	$K_{d, app}$ (mL/g)	$\mu \pm \sigma$ (n)	
	1-MN	1,3-DMN	2,3,5-TMN
1.5 h shaking	0.35 ± 0.11 (9)	0.80 ± 0.32 (9)	2.33 ± 1.35 (8)
70 h shaking	1.63 ± 0.46 (9)	3.44 ± 0.75 (9)	3.26 (1)
5 h static	0.68 ± 0.05 (8)	0.77 ± 0.12 (8)	1.75 ± 0.72 (8)
70 h static	1.13 ± 0.29 (8)	2.35 ± 0.88 (8)	1.57 ± 0.59 (7)
25 d static	3.28 ± 0.81 (8)	5.33 ± 1.40 (8)	4.59 ± 3.30 (6)

Table 4. Apparent Freundlich parameters (Equation 2) for sorption observed in the batch tests as determined by curve fitting.

Test	$K_{f, app}$ (L/g)	n	R^2
1-MN			
1.5 h shaking	6.94×10^{-3}	1.74	0.966
70 h shaking	8.47×10^{-3}	1.40	0.966
5 h static	8.31×10^{-4}	1.03	0.982
70 h static	1.28×10^{-2}	1.63	0.844
25 d static	1.07×10^{-2}	1.28	0.664
1,3-DMN			
1.5 h shaking	1.23×10^{-2}	1.94	0.985
70 h shaking	1.49×10^{-2}	1.50	0.979
5 h static	2.14×10^{-4}	0.82	0.822
70 h static	2.12×10^{-2}	1.86	0.822
25 d static	1.15×10^{-2}	1.23	0.553

Table 5. Percentages of sorbed methylated naphthalenes recovered by desorption.

Test	% 1-MN desorbed	% 1,3-DMN desorbed	% 2,3,5-TMN desorbed
s4a-3	35.9	38.6	39.2
s4b-3	37.4	40.2	33.6
s4c-3	32.7	35.9	28.9
s4d-3	28.0	31.1	10.9
s4e-3	26.4	28.3	23.7
s4f-3	25.1	28.7	8.7
s4g-3	15.8	17.5	
s4h-3	26.4	28.2	3.4
s4i-3	13.5	18.0	-11.2*
		*considered erroneous	

Table 6. Start conditions for the static batch tests.

BATCH	dry sand g	Total solution g	start* 1-MN µg/L	start* 1,3-DMN µg/L	start* 2,3,5-TMN µg/L
ss-a	694	175	1961	948	158
ss-b	695	162	1887	912	152
ss-c	698	155	1841	890	149
ss-d	760	173	3611	1611	277
ss-e	766	173	3589	1601	275
ss-f	765	170	3553	1585	273
ss-g	676	152	5664	2269	390
ss-h	600	130	5552	2225	382
ss-i	657	148	5682	2277	391

*adjusted based on measured residual water content of sand (7.4 % by weight)

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Table 7. Concentrations of dissolved methylated naphthalenes in static batches at 4 sampling times.

BATCH	1-MN µg/L				1,3-DMN µg/L			
	aging				aging			
	2 hours	5 hours*	70 hours*	25 days*	2 hours	5 hours*	70 hours*	25 days*
ss-a	740	502	284	150	361	200	52	47
ss-b	745	493	242	139	390	212	67	49
ss-c	582	389	235	106	338	196	56	38
ss-d	1349	822	673	287	634	308	172	71
ss-e	1265	890	630	254	538	324	153	74
ss-f	1218	831	634	212	643	376	189	49
ss-g	1787	1372	893	235	757	400	198	60
ss-h	2120	1250	1257	n/a	837	399	243	
ss-i	1957	n/a	1003	421	797	n/a	241	100

	2,3,5-TMN µg/L			
	aging			
	2 hours	5 hours*	70 hours*	25 days*
ss-a	43	25	28	12
ss-b	70	23	29	nd
ss-c	48	25	29	nd
ss-d	80	44	43	20
ss-e	212	30	30	14
ss-f	179	58	35	20
ss-g	109	37	41	8
ss-h	97	34	n/a	n/a
ss-i	76	n/a	nd	19

*concentrations adjusted by assuming binding to residual HA in solution (see text).
n/a = not available, nd = not detectable

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Figure 1. Illustration of the solids effect: a decrease in apparent binding coefficient as a function of sand to solution ratio of the batch test.
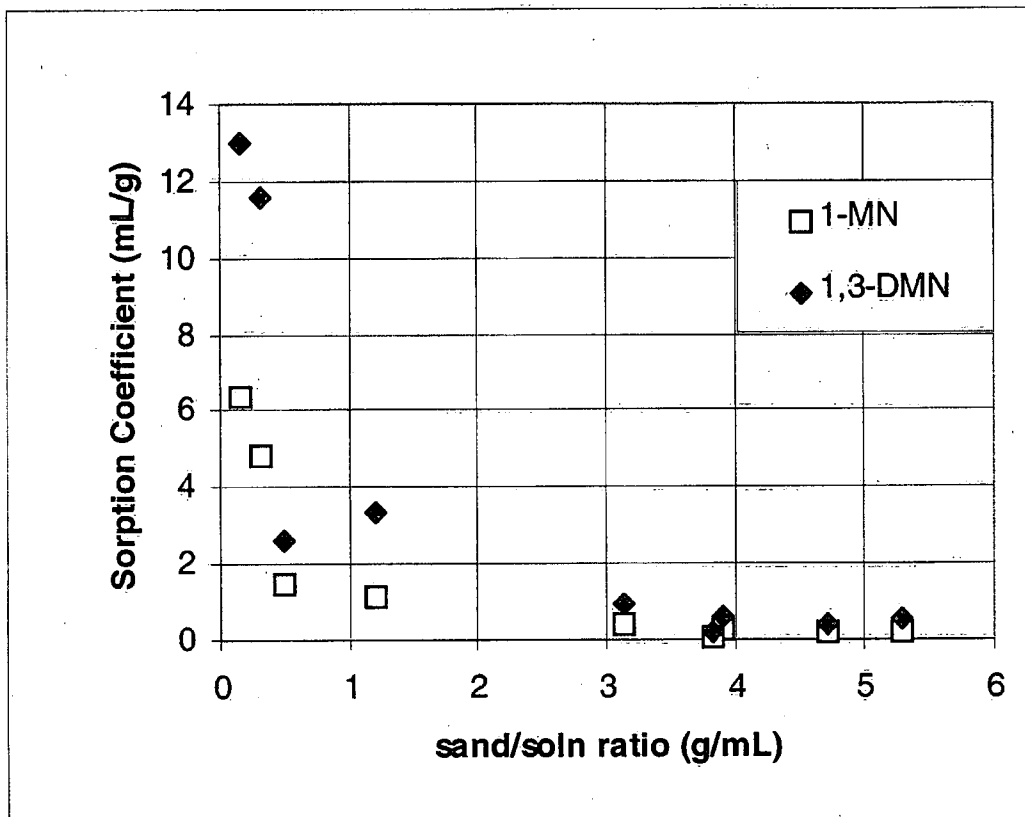
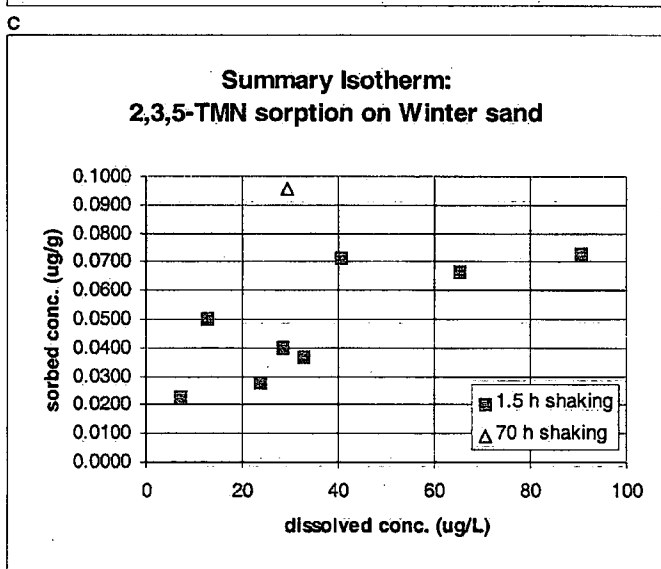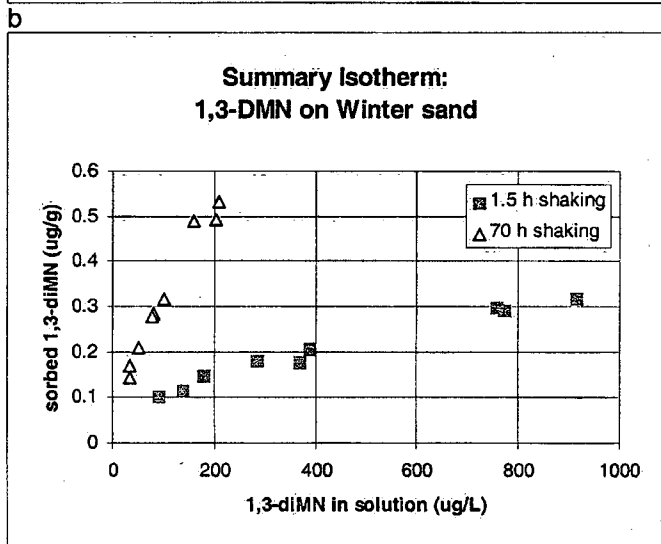Figure 2. Isotherms of sorption of methylated naphthalenes to Winter Sand, shaking tests.
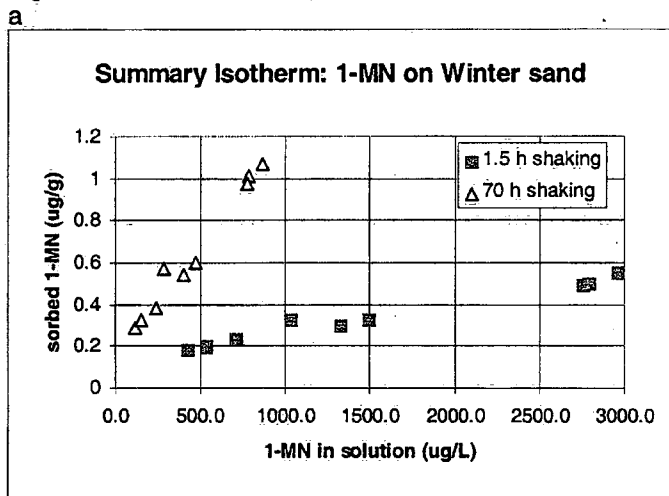
a

Summary Isotherm: 1-MN on Winter sand

Legend:
- ■ 1.5 h shaking
- △ 70 h shaking

y-axis: sorbed 1-MN (ug/g)
x-axis: 1-MN in solution (ug/L)

b

Summary Isotherm: 1,3-DMN on Winter sand

Legend:
- ■ 1.5 h shaking
- △ 70 h shaking

y-axis: sorbed 1,3-diMN (ug/g)
x-axis: 1,3-diMN in solution (ug/L)

c

Summary Isotherm: 2,3,5-TMN sorption on Winter sand

Legend:
- ■ 1.5 h shaking
- △ 70 h shaking

y-axis: sorbed conc. (ug/g)
x-axis: dissolved conc. (ug/L)

Figure 3. Example of changes in normalized dissolved aqueous concentrations of methylated naphthalenes in a batch test over time. Data shown are from batch ss-g (Tables 6 and 7).
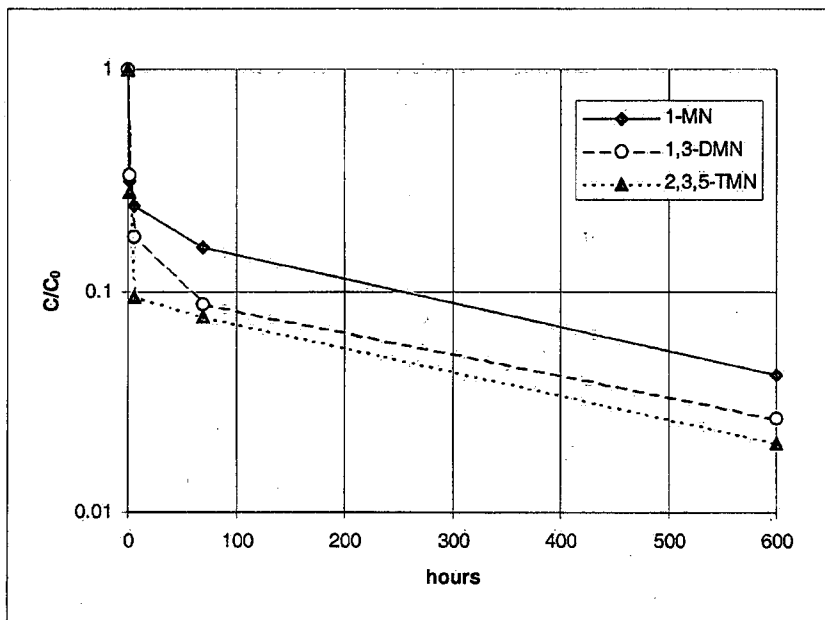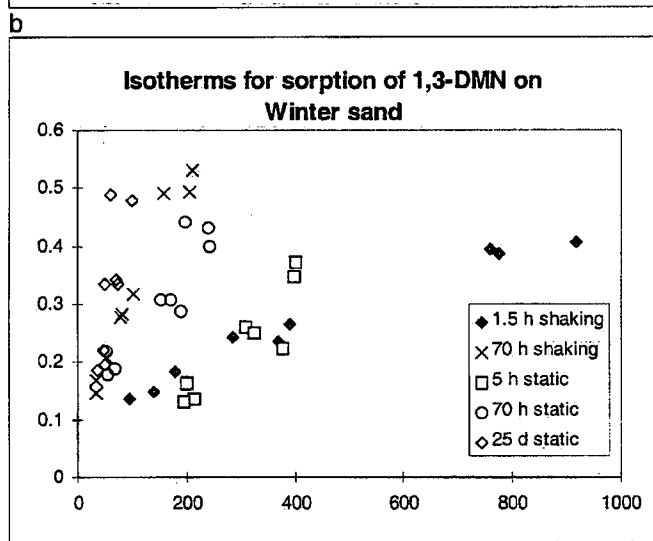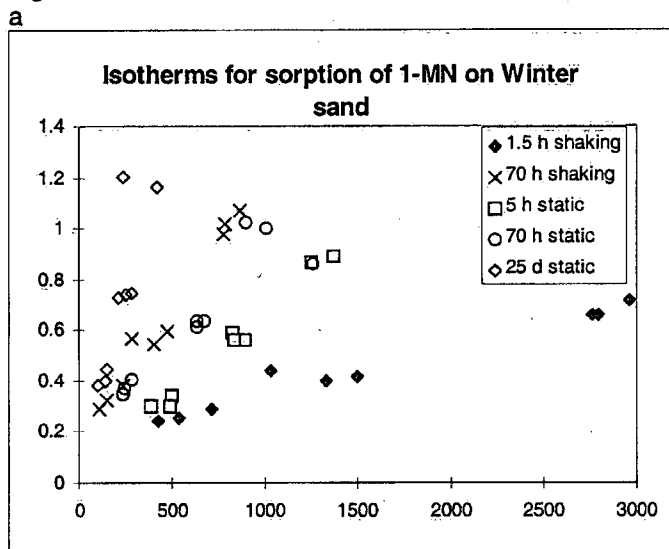
Figure 4. Isotherms for all tests, sorption of methylated naphthalenes to Winter Sand.

a

Isotherms for sorption of 1-MN on Winter sand

Legend:
- ◆ 1.5 h shaking
- ✕ 70 h shaking
- ☐ 5 h static
- ○ 70 h static
- ◇ 25 d static

b

Isotherms for sorption of 1,3-DMN on Winter sand

Legend:
- ◆ 1.5 h shaking
- ✕ 70 h shaking
- ☐ 5 h static
- ○ 70 h static
- ◇ 25 d static

c

Sorption of 2,3,5-TMN on Winter sand

Legend:
- ◆ 1.5 h shaking
- ✕ 70 h shaking
- ☐ 5 h static
- ○ 70 h static
- ◇ 25 d static