Binding of Hydrophobic Organic Contaminants to Humalite-Derived Aqueous Humic Products, with Implications for Remediation

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In order to assess the potential of commercial humic products in environmental remediation, their binding to heptachlor, hexachlorobenzene, hexachloroethane, 1,2,4-trichlorobenzene and n-hexane was measured. The binding was similar in tests with two colloidal-phase humic products prepared from humalite (naturally occurring, oxidized organic deposits found adjacent to coal) from Alberta, Canada (Luscar Ltd.). There were minor or negligible changes in binding strength for these two products over the full range of aqueous concentrations tested (1.67 to 33.4 g organic C/L), and for Aldrich humic acid. Aldrich humic acid was a stronger binder of the hydrophobic organic compounds than the two Luscar humic products, by factors of approximately 3 to 7. The binding of hydrophobic organics to the two Luscar humic products was similar in strength to that predicted for humic substances that occur in natural aquatic environments. Our binding data suggest that the use of concentrated Luscar humic products as colloidal-phase flushing agents would increase the aqueous concentrations of some hydrophobic organic contaminants in soils or aquifers by up to several hundred fold.

Key words: humic, humalite, binding, hydrophobic, remediation

Introduction

Aqueous humic substances bind hydrophobic contaminants, and thus exert control on their mobility and toxicity in the environment. This phenomenon is the basis for the current research into the potential use of commercial humic products as remediation products. Some investigators have examined the potential use of commercial humic products as sequestering agents (Shimizu 1998; Sanjay et al. 1999; Poerschmann and Balcke 2000). More often, researchers have considered the use of mobile, aqueous-phase humic substances as flushing agents to clean up contaminated soils and aquifers (Abdul et al. 1990; Xu et al. 1994; Ding and Wu 1997; Lesage et al. 1995; Rebhun et al. 1996; Johnson and John 1999; Boving and Brusseau 2000; Van Stempvoort et al. 2002; Molson et al. 2002). Most published data on the binding of organic contaminants by commercial aqueous humic products are studies with Aldrich humic acid (HA). The research with Aldrich HA, including studies over the past
8 years at our institute (Xu et al. 1994; Van Stempvoort and Lesage 2002), have focused on binding of PAHs, PCBs and pesticides (e.g., Burkhard 2000; Krop et al. 2001). Given the considerable attention that has been devoted to understanding the binding properties of Aldrich HA, it is not surprising that virtually all previous investigations into the use of commercial aqueous humic products (AHPs) as contaminant flushing agents have used Aldrich HA (see above references).

Although some have reported nonlinear behaviour (e.g., Xu et al. 1994; Chiou et al. 2000; Yuan and Xing 2001; Laor and Rebhun 2002), in many studies the binding of organic contaminants to aqueous humic substances is modeled as linear partitioning:

$$K_{oc} = \frac{C_b}{C_w}$$  \hspace{1cm} (1)

where $K_{oc}$ is the partitioning coefficient (L/g organic C), $C_b$ is the humic-bound contaminant concentration (mass of bound contaminant, $M_b$, per unit concentration of humic organic carbon, $C_{oc}$), and $C_w$ is the dissolved contaminant concentration in water. We prefer to use the term $K_{oc}$ in equation 1, rather than $K_{doc}$ which some authors (e.g., Burkhard 2000) have used to designate the humic-dominated aqueous organic matter as “dissolved organic carbon.” However, the bulk of aqueous humic substances form a polydisperse mixture of suspended colloids, between 1 nm and 1 µm in diameter. Such an aqueous colloidal dispersion can be referred to as a hydrosol (Olson et al. 1988).

Researchers have found that Aldrich HA is generally a stronger binder of hydrophobic organic contaminants than most natural aqueous humic substances, whether derived from soils or surface waters (e.g., Chiou et al. 1987; Chin et al. 1997; Doll et al. 1999). Burkhard (2000) has recently compiled information on the binding of nonionic organic compounds to aqueous humic substances. He provided summary equations to predict the relationship between $K_{oc}$ (his $K_{doc}$) to hydrophobicity, as measured by octanol-water partitioning. For Aldrich HA, the summary equation is:

$$\log(K_{oc}) = 0.85(\pm 0.03)*\log(K_{ow}) + 0.27(\pm 0.20)$$ \hspace{1cm} (2)

where $K_{ow}$ is the 1-octanol/water partitioning coefficient for the organic compound. For naturally occurring aqueous humic substances (“DOC”), the weaker binding is described by the following Burkhard equation:

$$\log(K_{oc}) = 0.85(\pm 0.06)*\log(K_{ow}) - 0.25(\pm 0.34)$$ \hspace{1cm} (3)

Although equations 2 and 3 have been presented by Burkhard as being applicable for hydrophobic organic contaminants in general, most of the experiments on which these equations are based were tests with aromatic compounds (see Results and Discussion).
Most binding tests with Aldrich HA have been conducted at low humic concentrations. With Aldrich HA levels between 0.001 and 0.020 g OC/L (where OC = organic C), most studies have indicated that the binding of contaminants tends to decrease in strength (factor of ~2–3), measured as K<sub>oc</sub>, with increasing humic concentration (Carter and Suffet 1982; Landrum et al. 1984; Yin and Hassett 1986; Li et al. 1997). In contrast, for a similar range in Aldrich HA concentrations, Chiu et al. (1987) inferred relatively constant K<sub>oc</sub> values. For all of these tests, the HA levels were much too low to be practical for efficient flushing in remediation applications.

Studies at higher concentrations of Aldrich HA (>0.02 g OC/L) have given mixed results regarding the HA concentration effect on K<sub>oc</sub> values. Using a headspace technique, Resendes et al. (1992) found relatively constant K<sub>oc</sub> values for the binding of chlorobenzenes to Aldrich HA over an HA range up to ~0.3 g OC/L. Similarly, using batch solubilization and solid phase microextraction (SPME), respectively, Xu et al. (1994) and Doll et al. (1999) indicated relatively constant binding strength for phenanthrene to Aldrich HA over a combined range up to ~0.8 g OC/L HA. Doll et al. noted a slight decrease in binding strength with increasing HA. Using batch solubilization, Johnson and John (1999) inferred relatively constant binding strength for tetrachloroethene at Aldrich HA concentrations up to ~6 g OC/L. Using SPME, Van Stempvoort and Lesage (2002) found that the apparent K<sub>oc</sub> values for methylated naphthalenes (important PAHs in diesel and other petroleum products) decreased by a factor of ~2 to 3 when the Aldrich HA increased from 0.30 to 0.97 g OC/L, but were similar at 0.97 and 3.15 g OC/L.

In notable contrast to the above studies, a batch solubilization study by Guetzloff and Rice (1994) suggested that purified Aldrich HA formed micelles at levels above ~3 to 4 g OC/L (they reported the critical level as 7.4 g/L total HA), and that the strength of the binding of the organic pesticide DDT was greatly enhanced above this critical micelle concentration (CMC). However, in a follow-up study, the same authors (1996) found no evidence for the same effect of the CMC on the binding of pyrene to Aldrich HA. Thus, there is not firm evidence for the existence of a consistent, predictable CMC for Aldrich HA.

This study is a continuation of research at the National Water Research Institute (NWRI) in Canada on the potential use of AHPs in environmental remediation. Previous testing at the bench and pilot scale with Aldrich humic acid (HA) yielded promising results (Xu et al. 1994; Lesage et al. 1995; Van Stempvoort et al. 2000, 2002; Van Stempvoort and Lesage 2002). Given that Aldrich HA is a relatively expensive laboratory reagent, we decided to shift the focus of our research in order to investigate more affordable commercial humic products that might be used in full-scale field applications.

In our search for commercial AHPs that can be used in full-scale contaminant remediation applications, the goal was to find one or more prod-
ucts that have contaminant-binding properties similar to those of Aldrich HA, but that are more cost-effective for use in field applications. This led to the current research initiative with AHPs provided by Luscar Ltd. of Edmonton, Alberta, Canada. The quotes that we obtained (2002) indicate that the current cost for bulk quantities of BlackEarth™, a dry, powder form, “soluble” humic product produced and marketed by Luscar Ltd., is about one-fifth of the cost for bulk, technical grade sodium-form Aldrich® HA (both per bulk weight basis).

This report provides results of an investigation of the binding of volatile or semi-volatile organic contaminants to highly concentrated AHPs using a headspace technique. The advantages of this technique were that we could investigate the binding of contaminants to aqueous humic products at very high aqueous humic concentrations (up to 33.4 g OC/L), and we did not have to contend with matrix interference of the analyses, because we analyzed samples of the equilibrated headspace air, rather than the AHP hydrosols.

We tested the binding of four chlorinated organic compounds: heptachlor, hexachlorobenzene, hexachloroethane and 1,2,4-trichlorobenzene, as well as a representative petroleum hydrocarbon, n-hexane. Because of their hydrophobic nature, these five compounds bind strongly to AHPs, and their moderate to high volatility made them suitable for GC analyses using the headspace technique. The four chlorinated compounds are toxic and persistent organic pollutants (POPs) of global concern. Heptachlor and hexachlorobenzene, formerly in wide use as pesticides, are 2 of the 12 POPs targeted to be banned under the international Stockholm Convention on Persistent Organic Pollutants (May 22, 2001).

**Theory and Equations for the Headspace Technique**

Headspace sampling is commonly used to measure the concentrations of volatile organic compounds in water. Theory underlining practical applications of the headspace technique to examine the binding of contaminants to aqueous humic substances have been provided by Yin and Hassett (1986), Resendes et al. (1992) and others. The specific procedures and equations that we used at NWRI pertain to sampling the headspaces of static batches (see Materials and Methods section).

A basic assumption of all headspace techniques is Henry’s law, which describes the equilibrium partitioning behaviour of a solute between two solvent phases, in this case a (semi-)volatile organic contaminant between water and air. In the case of static batch tests with dilute solutions, the activity of each solute in each phase is assumed to be proportional to the concentration of the solute in that phase and independent of the presence of other solutes (i.e., activity coefficients = 1). Assuming ideal behaviour in dilute solutions at a constant temperature, this relationship can be expressed as follows:
where $H$ is the dimensionless Henry’s law coefficient, and $C_a$ and $C_w$ are the concentrations of the contaminant in the headspace (air) and water, respectively. In static batch tests, $C_a$ can be defined as $M_a/V_a$, and $C_w$ as $M_w/V_w$, where $M_a$ is the mass in the headspace, $V_a$ the headspace volume, $M_w$ the mass in the water, and $V_w$ the volume of water. In the headspace technique, $C_a$ is analyzed, generally by gas chromatography (GC). Using the above relationships:

$$H = \frac{C_a}{C_w}$$  (4)

$$C_a = \frac{H*M_t}{(V_w + H*V_a)}$$  (5)

where $M_t$ is the total mass of contaminant added, the sum $M_a + M_w$. If reliable values of $H$ are not available, they can be determined in paired batch tests, “1” and “2”, by varying the ratio of $V_a$ to $V_w$ and applying the $C_a$ measured for each (Lincoff and Gossett 1984):

$$H = \frac{[(C_{a1}/C_{a2})*V_{w1}-V_{w2}]/[V_{a2}-(C_{a1}/C_{a2})V_{a1}]}{[(C_{a1}/C_{a2})*V_{w1}-V_{w2}]/[V_{a2}-(C_{a1}/C_{a2})V_{a1}]}$$  (6)

The use of equation 6 assumes a linear relationship between the detector response for the analysis (e.g., peak area for GC analyses) and $C_a$.

For headspace batch tests with AHPs, the binding of the contaminant to humic substances (equation 1) also has to be taken into consideration. The volatile or semi-volatile organic contaminant partitions between three phases, air, water (free dissolved) and the aqueous humic product (bound). In this case, $M_t = M_a + M_w + M_b$, and the following relationship holds:

$$C_a = \frac{(H*M_t)/(V_w*(1 + X))} {[(1 + H*V_a)/(V_w*(1 + X))]$$  (7)

where $X = K_{oc}*C_{oc}$.

In tests with high concentrations of AHPs (up to several weight %), the activity of the water is lower, by perhaps several percent compared to tests with only water. Consequently, the use of equation 7, which assumes ideal behaviour, results in small errors. Lower water activity in the presence of the AHPs is numerically equivalent to decreasing the value of $V_w$ in equation 7. Accordingly, the calculated $K_{oc}$ values reported in this paper, which are based on equation 7, may underestimate this binding coefficient by up to several percent at the higher AHP concentrations.

**Materials and Methods**

Aqueous humic products (AHPs) L-155 and L-160 were provided by Luscar Ltd. (1600 Oxford Tower, 10235-101 Street, Edmonton, Alberta, Canada T5J 3G1). These Luscar test products are derived from humalite deposits in Alberta, Canada. Humalite, which is similar to leonardite, is a
naturally occurring, highly oxidized organic material, found adjacent to sub-bituminous coal, with high concentrations of humic acids (Hoffman et al. 1993). Recently, Schnitzer et al. (2001) and Dinel et al. (2001) have characterized the chemistry of similar Luscar humic products derived from the same humalite deposits in Alberta. Concentrated Aldrich HA was obtained for comparative testing, by adding between 13.25 and 99.38 g of the sodium salt (tech., product no. H16752, Lot No. 16206AN, Aldrich Chemicals, Milwaukee, Wis.) per L of Milli-Q water. When portions of the Aldrich HA hydrosols were taken for batch testing, the precipitate fractions (~20% of HA) were excluded. The AHPs were diluted in Milli-Q water as required, and their total organic carbon measured with a Shimadzu TOC-5050 analyzer.

The organic chemicals to be tested were obtained as reagent-grade heptachlor, 1,2,4-trichlorobenzene (TCB) and n-hexane from Sigma Aldrich Canada Ltd. (Oakville, Ontario), hexachlorobenzene (HCB) and hexachloroethane (HCA) from Supelco (Oakville, Ontario). Stock solutions were prepared in methanol (1 or 5 ppm HCA with 100 or 500 ppm TCB; 1167 ppm n-hexane) or 50/50 ether and methanol (HCB with heptachlor, 5 or 100 ppm each). These stock solutions were stored at 5°C in the dark in 4-mL glass vials sealed with teflon-lined septa, diluted in methanol and/or mixed as required. For each batch test, a small quantity (1.5 to 100 µL) of a stock solution or a derivative thereof was transferred by microsyringe through a teflon-lined butyl rubber septum into a 60 mL (160 mL for n-hexane) glass serum bottle containing either Milli-Q water or an AHP (full strength or diluted), with a headspace. In preliminary tests, batches placed on an orbital shaker at ~100 rpm (New Brunswick Scientific, G-33) required approximately 48 hours to reach steady Ca values, inferred to indicate equilibrium between aqueous (dissolved, humic-bound) and headspace phases for the contaminants. All batch tests were conducted at 23 ± 2°C.

For each batch, the volume of water or AHP was determined gravimetrically, using density corrections for AHPs. Headspace volumes were determined gravimetrically by topping up each batch with Milli-Q water after analysis. Volumes of water or AHPs for the batch tests varied between 3 and 55 mL, depending on the volatility of the contaminant tested. For the tests with water for determination of H values, and for later tests with AHPs, at least 2 different ratios of V_a/V_w were used. For each equilibrated batch, 100 µL of headspace air was sampled by Hamilton gastight microsyringe and injected into an SRI 8610A gas chromatograph, equipped with a DB-1, DB-5 or DB 624 column. For the chlorinated compounds, Henry’s law coefficients were determined using equation 6; for n-hexane, the Henry’s coefficient was based on a literature value (see Results and Discussion). Tests with Milli-Q water were used to calibrate the Ca in tests with AHPs. In the latter tests, we applied equation 7, using iteration to solve X, matching calculated and measured C_a, as analyzed by GC. With this X value, K_{oc} could be calculated, since C_{oc} was known.
Results and Discussion

Henry’s Law Coefficients

As determined in headspace batch experiments with Milli-Q water, Henry’s law coefficients for the four organochlorine contaminants are shown in Table 1. These coefficients are within the ranges previously reported (Mackay et al. 1992; Sander 1999). Our values for hexachloroethane (HCA) and heptachlor are within 5% of values in the summary tables of Mackay et al. (1992, Vol. III and V). The value obtained for TCB is approximately 25% higher than a recent value reported by Dewulf and Van Langenhove (2001). The published values for HCB vary by 4 orders of magnitude (Sander 1999). For n-hexane, we chose a literature H value of 74. The majority of the values compiled by Makay et al. (1992, Vol. III) and Sander (1999) are within 15% of this value.

Contaminant Binding to AHPs

For the five contaminants, the masses of each added to the batches, and the resulting free dissolved concentrations were similar, except for HCA (Table 2). Given the relatively high volatility of HCA, as indicated by Table 1, and its very high response factor on the electron capture detector, less of this compound was added to each batch in order to fit the range of linear responses for the detector. The headspace concentration of n-hexane was much higher than for the other contaminants, because of its very high volatility, and the much different response of the flame ionization detector. The partitioning and binding of heptachlor and HCB were very similar (Table 2). For comparable ranges of dissolved TCB and hexane, the binding of these contaminants to L-155 was similar (Table 2).

The contaminant binding coefficients, $K_{oc}$, obtained for the batch tests with L-155, L-160, and Aldrich HA, are shown in Tables 3, 4 and 5, respectively. More data was acquired for L-155 than the other AHPs. For the majority of the $K_{oc}$ data, standard deviations are within 25% of the means. The $K_{oc}$ for each contaminant is relatively consistent over the ranges in humic concentrations tested. These results suggest that the H values that we used were accurate. Errors in H values would be incorpo-

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu \pm \sigma$ (n)</th>
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<tbody>
<tr>
<td>hexachloroethane</td>
<td>0.34 ± 0.03 (16)</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>0.25 ± 0.06 (18)</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>0.20 ± 0.04 (12)</td>
</tr>
<tr>
<td>heptachlor</td>
<td>0.15 ± 0.05 (9)</td>
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Table 2. Ranges in results for equilibrated batch tests with selected contaminants and Luscar aqueous humic product L-155

<table>
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<tbody>
<tr>
<td></td>
<td>µg (Mt)</td>
<td>µg/L (Ca)</td>
<td>µg/L (Cw)</td>
<td>µg/g organic C (Mb/Coc)</td>
<td>µg/L (Cw + Mb/Vw)</td>
</tr>
<tr>
<td>heptachlor</td>
<td>1.5–10.7</td>
<td>0.09–1.4</td>
<td>0.6–6.3</td>
<td>10.5–88.8</td>
<td>51.3–1051</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>1.5–10.7</td>
<td>0.26–1.7</td>
<td>1.1–6.8</td>
<td>10.5–88.7</td>
<td>51.1–1048</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>0.5–3.1</td>
<td>0.9–8.3</td>
<td>4.4–41.4</td>
<td>2.6–25.5</td>
<td>14.9–287</td>
</tr>
<tr>
<td>hexachloroethane</td>
<td>0.005–0.031</td>
<td>0.01–0.25</td>
<td>0.08–0.3</td>
<td>0.01–0.10</td>
<td>0.13–2.5</td>
</tr>
<tr>
<td>n-hexane</td>
<td>18.5</td>
<td>492–2977</td>
<td>11.5–40.2</td>
<td>3.16–10.6</td>
<td>38.1–110</td>
</tr>
</tbody>
</table>

Table 3. $K_{oc}$ (L/g) values, $\mu \pm \sigma$ (n), measured in this study for the binding of various organic contaminants (left column) to Luscar product L-155, at 5 humic concentrations

<table>
<thead>
<tr>
<th>Humic organic C conc. (g/L)</th>
<th>1.67</th>
<th>3.34</th>
<th>6.68</th>
<th>16.7</th>
<th>33.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptachlor</td>
<td>16.4 ± 2.6 (8)</td>
<td>18.3 ± 3.4 (6)</td>
<td>15.2 ± 2.1 (8)</td>
<td>11.4 ± 4.0 (6)</td>
<td>14.5 ± 2.3 (6)</td>
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<tr>
<td>hexachlorobenzene</td>
<td>17.0 ± 3.5 (10)</td>
<td>17.4 ± 2.0 (6)</td>
<td>11.8 ± 1.4 (7)</td>
<td>16.0 ± 4.9 (6)</td>
<td>8.16 ± 1.63 (6)</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>0.63 ± 0.20 (9)</td>
<td>0.60 ± 0.12 (6)</td>
<td>0.79 ± 0.16 (5)</td>
<td>0.32 ± 0.05 (6)</td>
<td>0.29 ± 0.07 (6)</td>
</tr>
<tr>
<td>hexachloroethane</td>
<td>0.41 ± 0.19 (13)</td>
<td>not det.</td>
<td>0.14 ± 0.04 (5)</td>
<td>0.27 ± 0.04 (6)</td>
<td>0.26 ± 0.02 (6)</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.26 ± 0.03 (6)</td>
<td>0.26 ± 0.02 (6)</td>
<td>0.26 ± 0.02 (6)</td>
<td>0.26 ± 0.02 (6)</td>
<td>0.26 ± 0.02 (6)</td>
</tr>
</tbody>
</table>
rated into calculations by equation 7, enlarging the variances of the resulting $K_{oc}$ over the $C_{oc}$, $V_a$ and $V_w$ ranges that were tested.

The $K_{oc}$ values for the 4 organochlorine contaminants were similar in tests with the two Luscar products L-155 (Table 3) and L-160 (Table 4). The data for L-155 were obtained over a larger range in humic concentrations. For similar ranges in humic C concentrations ($\geq 6.68$ g OC/L), there were no significant differences in the $K_{oc}$ values for each contaminant in L-155 and L-160, based on t-tests (2-tail, 0.05 level). Similar t-tests were used to compare results for the largest differences in L-155 concentrations, 1.67 and 33.4 g OC/L (Table 3). These indicated that the $K_{oc}$ values for HCB and TCB at 33.4 g OC/L were significantly lower than those at 1.67 g OC/L. In contrast, there was no significant difference in the $K_{oc}$ values for heptachlor and HCA at these two humic concentrations.

Based on t-tests as above, the marginally higher values of $K_{oc}$ for heptachlor and HCA in Aldrich HA with an increase in HA from 9.34 to

<table>
<thead>
<tr>
<th>Humic organic</th>
<th>C conc. (g/L)</th>
<th>11.6</th>
<th>29.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptachlor</td>
<td>13.0 ± 1.0 (6)</td>
<td>12.8 ± 2.8 (6)</td>
<td></td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>15.2 ± 0.9 (6)</td>
<td>13.4 ± 2.7 (6)</td>
<td></td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>0.46 ± 0.09 (5)</td>
<td>0.38 ± 0.04 (5)</td>
<td></td>
</tr>
<tr>
<td>hexachloroethane</td>
<td>0.19 ± 0.02 (5)</td>
<td>0.18 ± 0.02 (5)</td>
<td></td>
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</tbody>
</table>

| Table 4. $K_{oc}$ (L/g) values, $\mu \pm \sigma$ (n), measured in this study for the binding of various organic contaminants to Luscar product L-160, at 2 humic concentrations |

<table>
<thead>
<tr>
<th>Measured in previous studies</th>
<th>Measured in this study, $\mu \pm \sigma$ (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptachlor</td>
<td>30.2</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>93, 138, 269</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>1.29, 4.79, 10, 13</td>
</tr>
<tr>
<td>hexachloroethane</td>
<td>1.05 ± 0.10 (5)</td>
</tr>
<tr>
<td>Humic organic C conc. (g/L)</td>
<td>not reporteda</td>
</tr>
</tbody>
</table>

| Table 5. $K_{oc}$ (L/g) values for binding of various organic contaminants to Aldrich humic acid |

*a Supporting information in Burkhard (2000).
21.7 g OC/L are significant. In contrast, there were no significant changes in the $K_{oc}$ values for HCB and TCB over this range in Aldrich HA.

The data shown in Tables 3 through 5 provide no support for an earlier conclusion that, at high concentrations (above a CMC), aqueous humic substances form micelles, resulting in sharp increases in $K_{oc}$ values (Guetzloff and Rice 1994). In contrast, our results at elevated humic concentrations indicate small increases or decreases in $K_{oc}$ or negligible changes. Our results are consistent with the findings of a number of previous studies for Aldrich HA (Xu et al. 1994; Doll et al. 1999; Johnson and John 1999; Van Stempvoort and Lesage 2002) and other AHPs (Kurz et al. 1998).

A comparison of Tables 3 through 5 indicates that Aldrich HA is the strongest binder of the organic contaminants. For the four chlorinated compounds tested, the $K_{oc}$ values for Aldrich are approximately 3 to 7 times larger than those for the two Luscar AHPs, L-155 and L-160.

For HCB and heptachlor, the $K_{oc}$ values for binding to L-155 and L-160 are close to those predicted by equation 3 (Fig. 1), typically varying from the predicted values by factors of 0.65 to 1.1. Equation 3 (Burkhard 2000) summarizes the binding behaviour of naturally occurring aqueous humic substances. Thus, our data suggest that the binding of these contaminants by the Luscar AHPs was similar in strength to the binding that occurs by typical humic substances that occur in natural aquatic environments. However, the $K_{oc}$ values for TCB, HCA and n-hexane to L-155 were less closely predicted by equation 3 (Fig. 1), typically lower by factors of 0.11 to 0.37.

A similar pattern was found when our data for Aldrich HA was compared to equation 2, which is based on a compilation of previous data for the binding of a large range of contaminants to Aldrich HA (Burkhard 2000). The $K_{oc}$ values for the binding of heptachlor and HCB to Aldrich HA (Table 4) fall close to the predicted values based on equation 2 (Fig. 1), varying from them by factors of 0.56 to 1. The measured $K_{oc}$ values for the binding of TCB and HCA are smaller than those predicted by equation 2 (Fig. 1), by factors of 0.26 to 0.45.

The above results indicate that, of the five compounds tested, the binding of heptachlor and of HCB match most closely the Burkhard equations. This interpretation is dependent on the H and $K_{ow}$ values that we selected for the contaminants. The data used by Burkhard to generate equations 2 and 3 were largely based on tests with compounds dominated by aromatic C (PAHs, PCBs, pesticides such as DDT), and only a few tests for aliphatic-C dominated compounds were included. As such, it appears that the Burkhard equations should not be used to predict the binding of aliphatic compounds, such as HCA and n-hexane. Such an interpretation is consistent with the conclusions of Goss and Schwarzenbach (2001), Poerschmann and Kopinke (2001) and others, who conclude that empirical equations that relate $K_{oc}$ to $K_{ow}$ are not be widely applicable to different groups of nonionic organic compounds. Each equation developed to summarize or predict $K_{oc}$-$K_{ow}$ relationships should be based on tests with a single, defined class of organic compounds that have similar/common chemical structures and properties.
Despite its superior binding strength, Aldrich HA is an expensive product and thus it will probably not be used as a commercial remediation product in large-scale field applications. By comparison, if other commercial products, such as the humalite-derived Luscar AHPs tested, are marketed as relatively inexpensive alternatives, they may prove to be useful as commercial remediation products. As shown in Fig. 2, the potential increases in aqueous concentrations of some organic contaminants during flushing of contaminated soils or aquifers could be up to several hundred fold in the presence of concentrated Luscar AHPs added as flushing agents. Thus, these AHPs might prove to be useful flushing agents to speed the cleanup of these soils and aquifers.

Based on this study, the two Luscar AHPs, L-155 and L-160, appear to be better proxies for typical natural aqueous humic substances than...
This observation suggests that it may be possible to develop one or more Luscar products specifically for use as a laboratory standard reference material for testing the binding of organic contaminants to representative aqueous humic substances. Such a commercial product might provide a useful alternative to Aldrich HA, for which a large volume of data has already been obtained. It would be useful to conduct further studies to compare the chemical structures and/or sorbant properties of Luscar AHP to those of natural aqueous humic substances.

Our data indicate that equation 3 (Burkhard 2000) may be useful to predict the binding of strongly hydrophobic chlorinated aromatic compounds to Luscar AHPs, such as heptachlor and HCB. Further work is required to confirm this for a larger range of Luscar products, and/or to determine other suitable parameters and/or equations for the binding of various groups of organic contaminants (e.g., chlorinated and nonchlorinated, aromatics and aliphatics) to Luscar AHPs.

Conclusions

The results of this study indicate that there are minor or negligible changes in binding strength over the full range of aqueous concentrations tested for two humalite-derived humic products provided by Luscar Ltd.,
and for Aldrich humic acid (HA). This is consistent with other findings for Aldrich HA and other humic products. The data provide no support for earlier reports that, at high concentrations, aqueous humic substances form micelles, resulting in sharp increases in $K_{oc}$ values.

Aldrich HA was a stronger binder of the five hydrophobic organic compounds tested than the two Luscar humic products, by factors of approximately 3 to 7. Our data indicate that the binding of the selected hydrophobic organics to the two Luscar products is similar to the binding predicted for humic substances that occur in natural aquatic environments. It may be useful to develop one or more Luscar products specifically for use as a laboratory standard reference material for testing the binding of organic contaminants, as an alternative to Aldrich HA, for which a large volume of data has already been obtained. Pending further study, Luscar humic products might better simulate natural organic matter for many aquatic environments.

Our binding data suggest that increases in total aqueous concentrations of some organic contaminants in soils or aquifers could approach several hundred fold in the presence of concentrated Luscar humic products added as flushing agents. Thus, these products might prove to be useful as commercial flushing agents for soil and groundwater remediation.

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References


