Coverage of clay surfaces by soil organic matter (SOM) may limit the efficacy of the soil mineral fractions for adsorption of organic contaminants and pesticides. Two methods were scrutinized for quantitatively assessing the availability of clay surfaces in a smectitic Webster A-horizon soil for sorption of \(p\)-nitrocyanobenzene (\(p\)-NCB) and diuron. One method, described previously, involves the summation of independent contributions of SOM and swelling clays to sorption of organic solutes. For this method, several assumptions must be made and/or procedural difficulties overcome in the determination of certain terms in the equation proposed for calculating the fractional availability of mineral surfaces (\(f_a\)). To alleviate the methodological limitations, we developed an alternative approach for determining \(f_a\). Good agreement between \(f_a\) values was obtained from both methods for \(p\)-NCB but not diuron. For \(p\)-NCB sorption, \(f_a\) values varied between 0.55 and 0.71. For diuron sorption, our alternative equation estimated \(f_a\) values varied between 0.41 and 0.61; the other approach yielded negative values. The results demonstrate that SOM does reduce the availability of clay surfaces, hence, suppressing sorption by the Webster A-horizon soil. Our newly developed method provides more reasonable estimates of the availability of soil-clay surfaces for sorption than an earlier published approach.

**Introduction**

Clay minerals and soil organic matter (SOM) are generally considered the two most active components in the sorption of aqueous phase neutral organic contaminants (NOCs) by soil (1). Significant sorption of nitroaromatic compounds (NACs) from water by clays, particularly smectites, has been well documented (2–9). The extent of interaction of NOCs or other organic molecules with soil clay minerals may, however, be limited by the availability of clay sorption sites. Soil organic matter may obscure clay surfaces and thereby reduce the efficacy of the soil clay mineral fraction for adsorption of NOCs. Using scanning electron microscopy, Laird et al. (10, 11) observed that in the clay fraction of a Webster A-horizon soil, both large aggregated structures (5–20 \(\mu m\)) and discrete particles (0.5–2 \(\mu m\)) appeared to be covered with SOM. In soils, SOM and clay content are known to strongly correlate. Despite their known association, the influence of SOM on the sorptive properties of soil clay mineral fraction is still not fully understood though several studies utilizing synthetic clay-humic-acid (HA) complexes suggest, qualitatively, that HA may reduce the availability of clay surfaces for pesticide adsorption (9, 12–15).

Describing sorption of organic and inorganic species by soils as the additive product of the isolated SOM and mineral components is inadequate because it requires unrealistic assumptions, e.g., that the components act independently when it is known that they are intimately associated in soils (16, 17). Recognizing this, Karickhoff (18) proposed an equation that might allow experimental assessment of soil–clay surface availability for sorption of NOCs, though the approach was not evaluated experimentally. This equation incorporated potential SOM blockage of sorption sites on clays by summing NOC sorption to clay and SOM:

\[
Q_{\text{whole soil}} = f_a Q_{\text{min}} f_{\text{min}} + Q_{\text{om}} f_{\text{om}}
\]

where \(Q_{\text{whole soil}}\) is the total NOC mass sorbed per unit mass of whole soil, \(Q_{\text{om}}\) and \(Q_{\text{min}}\) are the SOM-sorbed and mineral-sorbed NOC per unit mass of the respective sorbent phase, and \(f_{\text{min}}\) and \(f_{\text{om}}\) are the fractional mineral and SOM contents of soil. The term \(f_a\) represents the fractional availability of sorption sites on the clay components of whole soil, i.e., the fraction of mineral sorptive surfaces available in whole soil. The term \(f_a\) is a plausible refinement of simple additivity of the individual component contributions. Fractional availability ranges from 0 (unavailable) to 1 (100% available).

Karickhoff (18) equated the mineral fraction to the clay fraction owing to the high surface area of clays in general and of smectites in particular.

Although a few studies have shown the extent of NOC sorption to soil or HA-clay complexes does not equate to the sum of sorption of the individual mineral and SOM components (9, 12–15), there appear to be no studies that have attempted to experimentally quantify the extent to which clay surfaces are available for NOC sorption in soil. The objective of this study is to quantify the fractional availability of mineral surfaces on a smectitic soil for sorption of \(p\)-NCB and diuron using eq 1 proposed by Karickhoff (18) and a newly proposed method of data analysis presented herein.

**Experimental Section**

A-horizon Webster soil was air-dried and sieved to remove coarse fragments (\(>2.0 \, \mu m\)). The soil was fractionated by standard procedures (19). Carbonates and SOM were sequentially removed from the Webster soil; carbonates were removed by stirring the soil with 0.5 M sodium acetate (acidified to pH 5) while heating at 80 °C, followed by the removal of SOM using 30% \(\text{H}_2\text{O}_2\) at 80 °C (denoted SOM-removed fraction). Homolitic soils and soil fractions were prepared by washing the soils with 0.1 M \(\text{KCl}\) or \(\text{MgCl}_2\) overnight, thereafter centrifuging and discarding the supernatant. This procedure was repeated four times. The soils were then washed with Milli-Q deionized \(\text{H}_2\text{O}\) until a negative \(\text{Cl}^-\) ion test with \(\text{AgNO}_3\) was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1 °C) until used. The SOM contents were determined as 3.9% for the whole soil, and 0.23% for the SOM-removed soil using dry combustion (20). The gravimetric clay content of the Webster soil (31%) was determined by the hydrometer method (21). \(p\)-NCB and diuron (1,1-dimethyl-3-(3,4-dichlorophenyl)urea) were purchased from Aldrich Chemical Co. and used as received.

The clay-sized particles (\(<2.0 \, \mu m\)) were obtained from soil using wet sedimentation after removal of carbonates, SOM, and free iron oxides (\(\text{FeO}_x\)) (22), then saturated with...
K⁺ and Mg²⁺ as described above. Suspensions of Mg²⁺- and K⁺-saturated clay-sized particles were dropped onto glass slides and dried at ambient conditions to produce clay films. The clay films were also treated by heating at 500 °C, or with ethylene glycol. X-ray diffraction (XRD) patterns of the treated clay films were used to identify the clay mineralogy of the clay-sized fraction in the soil (22). The clay samples were analyzed using Cu Kα radiation and a Philips APD 3720 X-ray diffractometer. The clay-sized fraction of the Webster soil contained mica and/or illite, smectite, vermiculite, and kaolinite. This was consistent with the clay mineralogy reported for another Webster soil sample (23).

Semiquantitative estimates for the amount of smectite in the Webster A-horizon soil were attempted by combining XRD analysis with the measured SOM content and cation exchange capacity (CEC) of the soil. The CEC was determined using the ammonium acetate method (24). The measured CEC value was set equal to the average CEC values of a soil smectite and SOM of 120 and 160 cmol(+)/kg⁻¹, respectively, multiplied by their respective fractional content (fsm and fn) in the Webster soil, then solved for fsm using the following equation:

\[ \text{CEC} = (160 \text{ cmol kg}^{-1})(f_{\text{sm}}) + (120 \text{ cmol kg}^{-1})(f_{\text{n}}) \]  

For comparison, Laird et al. (25) reported that the dominant smectite in another Webster soil was beidellite with CEC of 125 cmol(+)/kg⁻¹. To validate the smectite content estimated by eq 2, we compared the XRD peak areas corresponding to each non-smectite clay mineral with the smectite peak area, then estimated the relative fractional amounts of each non-smectite clay mineral to the fraction of smectite peak (e.g., illite/mica, 0.125 and kaolinite, 0.125). Multiplying the percentage of smectite in the soil obtained using eq 2, i.e., 24%, by the relative peak areas from the XRD results, we calculated the amount of non-smectite clay minerals as illite/mica of 3% and kaolinite of 3%. We subtracted the estimated smectite content of 24% from the total clay content (31%) and obtained the amount of non-smectite clay of 7%, which is close to the sum of non-smectite clay minerals estimated using the peak areas (3 + 3%).

The effect of exchangeable cation type on sorption by SOM was evaluated using either organic soils relatively devoid of minerals or a mineral soil devoid of smectites. The sorbents used here were Pahokee peat, Houghton muck, and Brookston loam (26). The peat was purchased from the International Humic Substances Society (BSI03P) and the other two soils obtained locally. These soils were saturated with K⁺ or Mg²⁺ as described above.

Sorption isotherms for p-NCB and diuron sorption by K⁺- and Mg²⁺-saturated soils, and SOM-removed Webster A-horizon soil were measured in triplicate using a batch equilibrium technique. This involved adding aqueous solutions of p-NCB (0–42 mg L⁻¹) or diuron (0–30 mg L⁻¹) over a range of initial aqueous concentrations to a known mass of soil. The p-NCB and diuron solutions were prepared in 0.05 M KCl or MgCl₂ corresponding to the saturating cation. Solutions (5 mL) were pipetted into 7.5 mL borosilicate glass vials containing various amounts of sorbent (0.2–0.4 g). The vials were rotated continuously for 24 h in the dark at room temperature; preliminary studies showed equilibrium was reached within 24 h. The liquid and solid phases were separated by centrifugation at 4068 g for 30 min, and the solute aqueous equilibrium concentration was determined by high performance liquid chromatography (Perkin-Elmer). For detection, a UV−visible detector was set at λ = 254 nm for p-NCB and λ = 248 nm for diuron. A platinum EPS C18 column (Alltech Associates) was used with an isocratic mobile phase consisting of a mixture of methanol (HPLC grade) and Millipore Milli-Q deionized water (methanol: water ratio of 55:45 for p-NCB and 75:25 for diuron) at a flow rate of 1.0 mL min⁻¹. The amount of solute sorbed was calculated from the difference between the initial aqueous concentration and the final aqueous concentration.

Solute sorption was quantified by fitting the data to the Freundlich equation, \( Q = K_C C_i^n \), where \( Q \) is the sorbed solute concentration per unit mass of sorbent, \( C_i \) is the equilibrium aqueous concentration, \( K_C \) is Freundlich sorption coefficient, and \( n \) is a constant related to the isotherm curvature (concave or convex). The Freundlich \( K_C \) and \( n \) values are given in Table 1. Comparisons of sorption isotherms were made by comparing the \( K_C \) and \( n \) values for each soil-solute system using SAS (27) detailed in reference (28). Using the obtained \( K_C \) and \( n \) values, \( Q \) values were calculated at four equilibrium aqueous phase concentrations, 5, 10, 15, and 20 mg L⁻¹. Using either eq 1 or our alternative equation (presented below), four corresponding \( f_{\text{sm}} \) values were obtained for the Webster A-horizon soil. Standard deviations of each \( f_{\text{sm}} \) value associated with each concentration were calculated using error propagation procedures.

The maximum percent of smectite clay surface covered by the SOM was estimated using Lagaly’s formula area per carbon atom of 5.67 Å² (29), a percent carbon in SOM of 62% (30), an average smectite surface area of 750 m² g⁻¹ (31), the estimated percent smectite in whole soil, and the measured percent SOM in the whole and SOM-removed soils. The operating assumption underlying this exercise was that all carbon from SOM resides on smectite surfaces. The calculation, therefore, provides an estimate for the maximum extent of coverage of the sorptive mineral surface by the SOM present. So, with 3.87% SOM and 24% smectite in the Webster soil: 1 g of the Webster soil contains a surface area of organic carbon = \( (0.62 \times 0.0387/12)(6.023 \times 10^{23})(5.67)(10^{-29}) = 68 \) m², and 1 g of the Webster soil contains a smectite clay surface area = \( (750 \times 0.24) = 180 \) m². The maximum percent of smectite clay surface that could be covered by soil organic

| TABLE 1. Freundlich Equation \( K_C ((mg \text{ g}^{-1}) (mg \text{ L}^{-1})^n) \) and \( n \) Values for Sorption of p-NCB and Diuron by K⁺- and Mg²⁺-saturated Soils* |
|-----------------|-----------------|-----------------|-----------------|
|                  | p-NCB           | Mg²⁺           | Diuron          | Mg²⁺           |
|                  | \( K_C \)       | \( n \)        | \( K_C \)       | \( n \)        |
| Pahokee peat     | 0.428           | 0.374          | 0.155           | 0.591          |
| Houghton muck    | 0.134           | 0.382          | 0.060           | 0.633          |
| Brookston loam   | 0.026           | 0.534          | 0.018           | 0.539          |
| Webster A-horizon soil | 0.053       | 0.598          | 0.007           | 0.622          |
| Webster A-horizon soil with SOM removed | 0.092 | 0.501 | 0.001 | 0.903 |

* nd, not determined.
exchangeable cation (in this instance, K
the clay mineral fraction was strongly influenced by the
nature of exchangeable cations (32).

Sorption of NACs by SOM was minimally influenced by the
Results and Discussion
carbon is therefore 38% (68/180).

FIGURE 1. Adsorption isotherms for sorption of p-nitrocyanobenzene
(p-NCB) by K\(^+-\) and Mg\(^{2+}\)-saturated peat, Houghton muck, Brookston
loam, and diuron by K\(^+-\) and Mg\(^{2+}\)-saturated peat. Isotherms marked
with the same letter indicate not significantly different.

Sorption data were normalized to SOM contents of the
soil (whole soil, and soil from which SOM was removed). Isotherms
and diuron sorption by K\(^+-\) and Mg\(^{2+}\)-saturated peat were 1.9 and
for p-NCB sorption by a Brookston
layer distances of
 Å (2\(\times\)9 Å). For smectites, these
cation effects are well understood at the molecular level.
Sorption of NACs occurs primarily in the clay interlayers,
and cation hydration determines the interlayer distance, size
of adsorption domains, and ability of \(\text{NO}_2\) groups of NACs
to complex directly with exchangeable cations (6). Cations
of smaller hydrated radii (e.g., K\(^+\)) promote complexation,
and manifest larger adsorption domains and optimal inter-
layer distances of \(\approx 3\) Å, which closely matches the thickness
of planar NACs. This allows the simultaneous interaction
of sorbed NACs with the opposing planar siloxane sheets, and
in this configuration, the NACs are largely dehydrated; both
processes are energetically favorable (36). Interestingly,
K-montmorillonite with sorbed NACs does not undergo
interlayer expansion (from \(\approx 12.5\) Å when exposed to 100% relative humidity, whereas in the absence of sorbed NACs it
expands to \(\approx 15\) Å (2, 36). In contrast, smectites saturated
with cations such as Ca\(^{2+}\) or Mg\(^{2+}\) always swell to \(\geq 15\) Å
(\(d_{001}\)) in water regardless of the presence or absence of NACs.

The influence of exchangeable cations on organic solute
sorption is much more apparent when the soil-clay fraction
is the dominant sorptive phase. The K\(^+-\) saturated whole, and
SOM-removed Webster A-horizon soils sorbed p-NCB to a
much greater extent compared to the same Mg\(^{2+}\)-saturated
soils (Figure 2). The sorption results are consistent with
several previous studies that report stronger sorption of NACs
by reference smectites and soils saturated with cations having
relatively low hydration energies (e.g., K\(^+\)) compared to that
by the same sorbents saturated with cations having higher
hydration energies (e.g., Mg\(^{2+}\)) (2-9, 35). For smectites, these
cation effects are well understood at the molecular level.
In previous study (32) we observed either no statistical difference, or
only slight differences in sorption of trichlorobenzene by the
K\(^+-\) vs Mg\(^{2+}\)-saturated Webster A-horizon soil, Webster
A-horizon soil with SOM partially removed and the Brookston
loam soil. Trichlorobenzene, a solute lacking polar func-
tionality, is sorbed exclusively by partitioning into SOM (31). It
could, therefore, be used as a test solute to evaluate the
effect of exchangeable cation on sorption by SOM in the
soils containing smectite clays (i.e., the Webster soil).

The influence of exchangeable cations on organic solute
sorption is much more apparent when the soil-clay fraction
of several previous studies that report stronger sorption of NACs
by reference smectites and soils saturated with cations having
relatively low hydration energies (e.g., K\(^+\)) compared to that
by the same sorbents saturated with cations having higher
hydration energies (e.g., Mg\(^{2+}\)) (2-9, 35). For smectites, these
cation effects are well understood at the molecular level.
Sorption of NACs occurs primarily in the clay interlayers,
and cation hydration determines the interlayer distance, size
of adsorption domains, and ability of \(\text{NO}_2\) groups of NACs
to complex directly with exchangeable cations (6). Cations
of smaller hydrated radii (e.g., K\(^+\)) promote complexation,
and manifest larger adsorption domains and optimal inter-
layer distances of \(\approx 3\) Å, which closely matches the thickness
of planar NACs. This allows the simultaneous interaction
of sorbed NACs with the opposing planar siloxane sheets, and
in this configuration, the NACs are largely dehydrated; both
processes are energetically favorable (36). Interestingly,
K-montmorillonite with sorbed NACs does not undergo
interlayer expansion (from \(\approx 12.5\) Å when exposed to 100% relative humidity, whereas in the absence of sorbed NACs it
expands to \(\approx 15\) Å (2, 36). In contrast, smectites saturated
with cations such as Ca\(^{2+}\) or Mg\(^{2+}\) always swell to \(\geq 15\) Å
(\(d_{001}\)) in water regardless of the presence or absence of NACs.

FIGURE 2. Adsorption isotherms for p-nitrocyanobenzene (p-NCB)
diuron sorption by K\(^+-\) and Mg\(^{2+}\)-saturated Webster A-horizon
soil (whole soil, and soil from which SOM was removed). Isotherms
with the different letters (a, b, c, d) are statistically different at p < 0.05.
appear representative and unaltered. Laird et al. (11, 23) have shown that biedellite and montmorillonite are the pre-
dominate smectites in the Webster soil. We previously
measured p-NCB sorption by K-biedellite and K-montmo-
rollonite (32). Compared with that result, the p-NCB sorption
isotherms measured in this study normalized to the smectic
content of the Webster soil (24%) is intermediate between
K+-saturated biedellite and K-montmorillonite.

Sorption of p-NCB by the Mg2+-saturated Webster A-
horizon soil was greater than that by the Mg2+-saturated SOM-
removed soil (Figure 2). Removal of SOM may liberate some
clay surface sites, but, as discussed above, Mg2+-exchanged clays have low affinities for aqueous phase NACs. Hence, in
the Mg2+-saturated OM-removed soil, clays are relatively
inefficient as sorbents for sorption of p-NCB. Rather, SOM is
the principal sorbent phase; hence, its removal decreased
p-NCB sorption.

With K+ as the dominant exchangeable cation, SOM
removal resulted in greater p-NCB sorption compared to the
whole soil (Figure 2). This indicates that the presence of SOM in
the Webster soil reduced p-NCB sorption overall. Although SOM undoubtedly acts as a sorptive phase for p-NCB, its
removal apparently liberates clay surfaces which can then serve as additional sites for p-NCB adsorption. Additional adsorption of p-NCB by these (now) unobscured sites apparently exceeds that afforded by SOM so that the net result of SOM removal is to increase p-NCB sorption. Suppressed sorption by SOM indicates f\text{s} values less than 1.

To quantitatively assess f\text{s}, we used two methods of data
analysis: eq 1 proposed by Karickhoff (18) and an alternative
equation introduced herein. One potential difficulty with the
determination of f\text{s} using eq 1 is variation in Q\text{om} (or K\text{om})
values for the test solute and its potential influence on the
calculated f\text{s} value. For solutes that sorb preferentially to
SOM the effect of the variation in Q\text{om} values on f\text{s} will be
large compared to that for solutes that preferentially sorb to
smectites (e.g., NACs). In addition, to determine the isolated
SOM contribution to sorption by a specific soil as required
by eq 1, a surrogate for that SOM must be used as a sorbent
since the SOM cannot be isolated in total or without alteration
from the test soil. This difficulty introduces error into eq 1
since Q\text{om} is not obtained by direct measurement on the
system being analyzed. The experimental determination of
f\text{om} may also present error in certain instances, for example
when f\text{om} < 1%. An assumption inherent in eq 1 is that the
SOM is fully accessible for sorption. The assumption was
viewed as acceptable by Karickhoff (18), but recently, Celis et al. (17) suggested the possibility of SOM domain blockage
arising from its interaction with minerals. However, Kile et al. (34) found very little (~2%) variation in K\text{om} values for
sorption of dichlorobenzene and CCl4 on a large number of soils
from widely different geographical regions. This suggests
that either the degree of SOM blockage was similar among
soils, or more plausibly, that SOM is fully accessible.

We propose an alternative to eq 1 that eliminates reliance
on Q\text{om} to determine f\text{s}. It involves measuring the difference
in NAC sorption between sorbent systems whose CEC is
saturated with different cations. This method is predicated on
the observation that NAC sorption by SOM whose CEC
sites are exchanged with K+ vs Mg2+ was nearly identical
(Figure 1) (32), and on the observation that NAC sorption by
smectite clay is strongly dependent on the cation saturating
the clay exchange sites; K+-smectites have higher affinities for
NACs while Mg2+-smectites do not (2–4, 6–9), even though
the f\text{s} value would remain the same in both systems. We therefore propose, if two experiments are done in which NAC sorption is measured for a soil saturated with K+ vs Mg2+cations, then

\[ Q_{\text{whole soil, K-sat}} - Q_{\text{whole soil, Mg-sat}} = f_s \left( Q_{\text{min, K-sat}} f_{\text{min}} - Q_{\text{min, Mg-sat}} f_{\text{min}} \right) + (Q_{\text{om, K-sat}} f_{\text{om}} - Q_{\text{om, Mg-sat}} f_{\text{om}}) \]  \hspace{1cm} (3)

where the terms of eq 3 are the same as those in eq 1 except that
subscripts K-sat and Mg-sat are added to differentiate the
K+- and Mg2+-saturated soils.

Since Q\text{om, K-sat} \approx Q\text{om, Mg-sat} then

\[ Q_{\text{whole soil, K-sat}} - Q_{\text{whole soil, Mg-sat}} \approx f_s \left( Q_{\text{min, K-sat}} f_{\text{min}} - Q_{\text{min, Mg-sat}} f_{\text{min}} \right) \]  \hspace{1cm} (4)

Equation 4 eliminates the Q\text{om} and f\text{om} terms, which are needed in eq 1.

For p-NCB, extraction of SOM caused an increase in overall
sorption by the K+-saturated soil (Figure 2), suggesting
qualitatively that SOM contribution to p-NCB sorption was
less than its negative effect on sorption due to obscuration
of p-NCB binding sites on soil clays. For this system, estimates
of f\text{s} using either eq 1 or eq 4 ranged from about 0.6 to 0.7
(Table 2). When K+-saturated peat, Houghton muck or
Brookston loam were used as the surrogate sorbent for
determining the SOM contribution in eq 1, or when Mg2+-
vs K+-saturated sorbents were used as the SOM surrogate,
f\text{s} values from eq 1 did not differ greatly (Table 2). This is
consistent with our observation that, on a unit SOM basis,
the sorption isotherms for p-NCB sorption by K+- and Mg2+-
saturated peat, Houghton muck and Brookston loam were
very similar. That f\text{s} values for p-NCB sorption derived using
eq 1 versus eq 4 did not differ greatly (Table 2) is a
manifestation of the fact that the SOM term in eq 1, and the
error associated with it, is small (for example, only ~20% of
whole soil at C\text{o} = 10 mg L\text{–1}) compared to the mineral fraction
term.

For diuron, the K+-saturated SOM-removed soil sorbed
less than K+-saturated whole soil (Figure 2). This demon-
strates that SOM contributes to sorption of diuron by soil,
and that SOM removal diminished sorption in excess of any
enhancement resulting from increasing mineral surface
availability. Sheng et al. (1) observed somewhat greater
sorption of diuron to Houghton muck soil (representing SOM)
compared to K-smectite. Parker and Rate (37) suggest that
surface coatings of SOM may promote sorption of the solute
to soil if the SOM surface coating is a more effective sorbent
than the clay particles they obscure. Sanchez-Martin and
Sanchez-Camazano (38) observed that the removal of organic
matter from soils resulted in less sorption of chloridazon
compared to that by whole soil. Cox et al. (39) reported similar
findings for imidacloprid sorption by soil clay fractions and
model sorbents. Celis et al. (15) observed a similar trend for
atrazine sorption by HA-smectite complexes. Pusino et al.
(12) observed decreased sorption of metolachlor sorption by
a sandy loam and a loamy sand soil after removal of SOM.
Li et al. (9) observed that for synthetic K-smectite-HA
complexes, HA had no discernible effect on sorption of NACs,
whereas it could enhance or suppress sorption by Ca-clays.

For diuron, using eq 1, negative f\text{s} values (theoretically
impossible) were calculated using either K+- or Mg2+-
saturated peat to determine the SOM (K\text{om}) contribution
to solute sorption (Table 3). In contrast, positive f\text{s} values were
obtained using eq 4 (Table 3). The negative f\text{s} values obtained
using eq 1 point out an inherent weakness in the data analysis
suggested by Karickhoff (18), especially for combinations of
compounds/soils where SOM is an equal or dominant
sorptive component. We suggest that because of the sen-
sitivity of eq 1 to the determination of SOM content and Q\text{om},
where a value would remain the same in both systems. We
suggest that because of the sensitivity of eq 1 to the
determination of SOM content and Q\text{om}, where a value would
remain the same in both systems. We
TABLE 2. Calculated Fractional Availability of Mineral Surfaces \( (f_a) \) for \( p \)-nitrocyanobenzene (\( p \)-NCB) Sorption by \( K^+ \) - or \( Mg^{2+} \)-exchanged Webster A-horizon soils

<table>
<thead>
<tr>
<th>data analysis (SOM surrogate)</th>
<th>concentration (mg L(^{-1}))</th>
<th>( f_a ) values (K(^+-)saturated)</th>
<th>( f_a ) values (Mg(^{2+})-saturated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>equation 1 (peat)</td>
<td>5</td>
<td>0.55 (0.02)</td>
<td>0.59 (0.02)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.60 (0.02)</td>
<td>0.62 (0.02)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.63 (0.03)</td>
<td>0.66 (0.03)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.65 (0.03)</td>
<td>0.68 (0.03)</td>
</tr>
<tr>
<td>equation 1 (Houghton muck)</td>
<td>5</td>
<td>0.60 (0.02)</td>
<td>0.62 (0.02)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.65 (0.02)</td>
<td>0.66 (0.02)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.69 (0.03)</td>
<td>0.69 (0.03)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.71 (0.03)</td>
<td>0.71 (0.03)</td>
</tr>
<tr>
<td>equation 1 (Brookston loam)</td>
<td>5</td>
<td>0.58 (0.02)</td>
<td>0.61 (0.02)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.62 (0.02)</td>
<td>0.65 (0.02)</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.64 (0.03)</td>
<td>0.68 (0.03)</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.66 (0.03)</td>
<td>0.70 (0.03)</td>
</tr>
</tbody>
</table>

\( f_a \) values

- Using Karickhoff's eq 1 (using diuron sorption by \( K^+ \) - and \( Mg^{2+} \)-saturated Pahokee peat, Houghton muck and Brookston loam to determine the \( K_{am} \) term), and our alternative eq 4 which integrates sorption data from both \( K^+ \) - and \( Mg^{2+} \)-exchanged soils.

\( f_a \) values

- Using eq 1 (using \( p \)-NCB sorption by \( K^+ \) - and \( Mg^{2+} \)-saturated Pahokee peat, Houghton muck and Brookston loam to determine the \( K_{am} \) term), and our alternative eq 4 which integrates sorption data from both \( K^+ \) - and \( Mg^{2+} \)-exchanged soils.

\( f_a \) values

- Using Karickhoff's eq 1 (using \( K^+ \) - and \( Mg^{2+} \)-saturated Pahokee peat, Houghton muck and Brookston loam to determine the \( K_{am} \) term), and our alternative eq 4 which integrates sorption data from both \( K^+ \) - and \( Mg^{2+} \)-exchanged soils.

A-horizon soil. Differences in sorption mechanism and/or the nature of mineral adsorptive sites between \( p \)-NCB and diuron may account for differences in the \( f_a \) values determined for these two compounds. We have unequivocal evidence \((2, 6, 9, 36)\) that NACs, including \( p \)-NCB, are intercalated by smectites, but it is unknown whether or to what extent diuron sorption occurs in the interlayer regions of smectites \((1)\).

This study is the first to quantitatively evaluate the availability of soil clay surfaces for the adsorption of organic contaminants and pesticides. Our results indicate that 29 to 45% \((av = 37%)\) of clay surfaces are unavailable for \( p \)-NCB sorption due to obscuration by SOM in Webster A-horizon soil. The calculated theoretical clay surface coverage, including the clay interlayer surface area, by the 3.9% SOM in the Webster A-horizon soil was 38%. The similarity of the theoretical maximum clay surface coverage by SOM \((38%)\) to the complement of the average \( f_a \) value would seem to suggest that essentially all the SOM present covers the basal surfaces of the soil clays; however, it may also be coincidental. Evidence of soil humics occupying the interlayer surfaces of smectites in soils is lacking. Adsorbed organic matter in the form of basic amino acids such as arginine in smectite interlayers could plausibly be responsible for blockage of interlayer sites against sorption of NOCs \((11)\). Obscuration of clay surfaces may also result from aggregate formation facilitated by SOM through the bridging of clay particles \((40)\) or reduction of repulsive forces between clay particles \((41, 42)\). Soil organic matter associated with the edges of clay tactoids in soils could also block access of solutes such as \( p \)-NCB to clay interlayers. In this study \( f_a \) values less than 1 are unlikely related to carbonate minerals which are known to play a role in soil particle aggregation. In a previous study \((11)\), no carbonates were detected in the Webster soil.

Since this study is the first to quantify the availability of clay surfaces in whole soils, it naturally raises many questions for further study. For example, it is interesting that soil clay surfaces in the Webster A-horizon soil seem more available to a stronger-sorbing compound \((p \)-NCB\) and less available to a weaker-sorbing compound (diuron). The methods presented here look promising for probing the effects of SOM-clay associations in soils on the availability of clay surfaces for sorption of organic molecules, and they should be extended to additional adsorbates and soils. Application of this method to ionizable compounds is inadvisable since changes in pH may affect the conformation of SOM and its association with clays. Caution is also advised when mineral phases other than clays are involved in sorption.

**Acknowledgments**

This project was supported by USDA National Research Initiative Competitive grant nos. 2003-35107-12899 and 2005-35107-15237.

**Literature Cited**

14. Celis, B.; Hermosin, M. C.; Cox, L.; Cornejo, J. Sorption of 2,4-dichlorophenoxyacetic acid by model particles simulating...


