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QUANTIFICATION OF THE AVAILABILITY OF CLAY
SURFACES IN SOILS FOR SORPTION OF
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Simone Melanie Charles

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QUANTIFICATION OF THE AVAILABILITY OF CLAY SURFACES IN SOILS FOR SORPTION OF NITROAROMATICS

By

Simone Melanie Charles

A DISSERTATION

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ABSTRACT

QUANTIFICATION OF THE AVAILABILITY OF CLAY SURFACES IN SOILS FOR SORPTION OF NITROAROMATICS

By

Simone Melanie Charles

Nitroaromatics (NACs) comprise an important class of environmental contaminants that pose a potential toxic threat to ecological and human health. To improve our understanding and modeling of the fate and transport of NACs in the environment, the effect of the interaction of soil clays with SOM must be better understood.

The influence of exchangeable cation on the adsorption of p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) by Webster A and B horizon soils, which contains smectite as their most abundant clay mineral, was determined. On removal of SOM from whole soils, sorption of p-NCB and 1,4-DNB increased indicating an overall negative contribution of SOM to their sorption by whole soil. The removal of the clay-sized fraction from whole soil decreased sorption of these compounds by a factor of at least 10. This suggests that the interaction between SOM and soil clays suppresses sorption of p-NCB and 1,4-DNB by soils. We also determined, independently, the effect of exchangeable cation on sorption of 1,4-DNB by SOM and on sorption of p-NCB by whole soil, the clay-sized fraction from that soil and SOM. No effect of exchangeable cation type was found for sorption of p-NCB and 1,4-DNB by SOM. For homoionic clay-sized soil fractions, the sorption of p-NCB was generally greater by monovalent-cation-exchanged clays than divalent-cation-exchanged clays, and increased with decreasing cation hydration energy ($\mathrm{Li^+}\sim\mathrm{Na^+}<\mathrm{K^+}<\mathrm{Cs^+}$ and $\mathrm{Ca^{2+}}\sim\mathrm{Mg^{2+}}<\mathrm{Ba^{2+}}$). The same trends were observed for homoionic soils exchanged with monovalent and divalent cations.

Two methods were used to assess the availability of clay surfaces (f_a) in soils for sorption of NACs. One method offered earlier by Karickhoff (1984) involves the summation of the sorption of solutes to SOM and swelling clays. We also developed an alternative approach for determining f_a that alleviates methodological limitations of the Karickhoff approach. Using three NACs (p-nitrocyanobenzene (NCB), 2,4-dinitrotoluene (DNT) and 1,4-dinitrobenzene (DNB)) and four loam soils, sorption of each NAC by whole soil and soil from which SOM was removed was determined. For each NAC, increased sorption was observed with the removal of SOM from whole soils indicating diminished availability of mineral surfaces due to obscuration or blockage by SOM; the f_a values were less than 1. For each NAC, we found a strong correlation between the f_a values and the relative contents of SOM and smectite in the soils (> 0.60). For each soil, the f_a values decreased in the order DNT > DNB > NCB. This suggests that the nature of the NAC may also influence the mechanism driving sorption site availability. We found a strong correlation between the f_a values and the strength of sorption of each NAC to smectites ($\geq$ 0.90 in three of four cases). Our studies reveal that for organic solutes with polar functional groups (e.g., NO_2) and in soils containing smectite clays, solute uptake from water will be strongly influenced by the type of exchangeable cation(s) present, the relative contents of SOM and sorptive clays (e.g., smectites) in the whole soil as well as the nature of the solute.

ACKNOWLEDGEMENTS

"In the confrontation between the stream and the rock, the stream always wins – not necessarily through strength, but through persistence" Anonymous

The process of this study entailed character building as well as academic achievement. I am certain that I will continue to grow professionally and as an individual. My appreciation extends to all those with whom I have interacted during the course of my studies; such interactions facilitated my learning and growth.

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CHAPTER 1

EFFECTS OF EXCHANGEABLE CATION ON SORPTION OF NITROCYANOBENZENE TO SURFACE SOILS

ABSTRACT

The influence of exchangeable cation on the adsorption of p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) by Webster A and B horizon soils, which contain smectite as their most abundant clay mineral, was determined. On removal of soil organic matter (SOM), sorption of p-NCB and 1,4-DNB increased indicating an overall negative contribution of SOM to their sorption by whole soil. This suggests that SOM suppresses sorption of p-NCB and 1,4-DNB by soil mineral components. Removal of the clay-sized fraction from whole soil decreased sorption of these compounds by a factor of at least 10. We determined, independently, the effect of exchangeable cation on sorption of 1,4-DNB by SOM, and on sorption of p-NCB by whole soil, the clay-sized fraction of soil and SOM. No effect of exchangeable cation type was found for sorption of p-NCB and 1,4-DNB by SOM. For homoionic clay-sized soil fractions, the extent of p-NCB sorption was generally greater for monovalent-cation-exchanged clays than divalent-cation-exchanged clays, and increased with decreasing cation hydration energy ($Cs^+ > K^+ > Na^+ \sim Li^+$ and $Ba^{2+} > Mg^{2+} \sim Ca^{2+}$). The same trends were observed for homoionic soils exchanged with monovalent and divalent cations.

INTRODUCTION

Nitroaromatic compounds (NACs) are commonly used as pesticides, explosives, and intermediates in the synthesis of dyes, ammunition and solvents. Their uses and manufacture have resulted in contamination of soils, sediments, quarries and aquifers. In order to assess the fate of NACs in the environment, their mobility and reactivity in the soil must be understood. Sorption processes play an important role in determining mobility, translocation, and (bio)availability of these solutes in soil. Clay minerals and organic matter are generally considered the two most active soil components in the sorption of aqueous phase organic contaminants. For many nonpolar organic compounds, sorption is highly correlated with the organic carbon (OC) content of a soil or sediment and is relatively independent of other sorbent properties (Chiou et al., 1979, 1983; Karickhoff et al., 1979). This has been observed as linear relationships between the organic carbon normalized sorption coefficient (K_{oc}) and the octanol-water partition coefficient (K_{ow}) (a direct relationship) and water solubility (S_w) (an inverse relationship) of nonpolar organic compounds (Chiou, 2002). In these instances sorption has been conceptualized as solute partitioning into SOM (Chiou et al., 1979, 1983; Karickhoff, 1979). It has been further suggested that adsorption of such solutes by mineral phases in soils is suppressed by the preferential adsorption of water (Chiou, 2002). However, many pesticides and organic contaminants, e.g. NACs, contain polar functional groups that can engage in specific interactions with clays even in the presence of bulk water. In fact, compared on a unit mass basis, adsorption of NACs from water by smectite clays was greater than that by SOM (Sheng et al., 2002). Thus, clay minerals may play a dominant role in sorption of certain polar organic molecules, particularly in geosorbents with low SOM contents (Weissmahr et al., 1999).

Several studies have reported the high affinity of NACs for smectites in aqueous solution (Haderlein et al., 1996; Weissmahr et al., 1998; Boyd et al., 2001; Sheng et al., 2002; Johnston et al., 2001; Johnston et al., 2002). This has been attributed to the formation of electron donor (clay) – acceptor (NAC) complexes facilitated by the electron withdrawing properties of the nitro (NO_2) group (Weissmahr et al., 1997). Alternatively, complexation of the NO_2 groups of NACs with exchangeable cations on the clay has been suggested as a primary sorption mechanism (Boyd et al., 2001). Partial solute dehydration associated with adsorption in smectite interlayers of optimal distance (ca. 12.3 Å) also provides favorable energy for adsorption (Boyd et al., 2001; Li et al., 2004).

Several studies document the importance of the nature of the exchangeable cation on sorption of NACs by clays. Sorption of NACs by reference smectite clays was favored by weakly hydrated exchangeable cations and a low surface charge density of the clay (Haderlein et al., 1993; Weissmahr et al., 1997; Boyd et al., 2001; Sheng et al., 2002). These factors combine to manifest optimal interlayer distances, and promote NAC interactions with exchangeable cations (Boyd et al., 2001). Significant adsorption of NACs by smectite clays was observed in the presence of weakly hydrated cations (e.g. K^+, Cs^+, NH_4^+), while strongly hydrated cation-systems (e.g. Na^+, Mg^{2+}, Ca^{2+}) exhibited low adsorption of NACs (Haderlein et al., 1993). These results agree with the lower sorption observed for 2,4-dinitro-o-cresol (DNOC) sorption by smectite clays saturated with more strongly hydrated cations (Sheng et al., 2002). Johnston et al. (2002) reported shifts in the NO_2 vibrational modes of 1,3,5-trinitrobenzene (1,3,5-TNB) on its adsorption by K^+-smectite using Fourier Transformed Infrared Spectroscopy (FTIR). They attributed these shifts in NO_2 vibrational modes (ν_{asym} and ν_{sym} (-NO) bands) to complexation of K^+ by NO_2 groups. These shifts were not observed for smectites saturated with more strongly hydrated cations (i.e. Na^+, Mg^{2+}, Ca^{2+} and Ba^{2+}). Overall, cation hydration seems to be a central determinant of NAC sorption by reference smectite clays. Sorption of NACs occurs primarily in the interlayers of these clays, and cation hydration determines the interlayer distance, the effective size of adsorption domains between cations, and the ability of NO_2 groups to complex directly with exchangeable cations (Boyd et al., 2001; Johnston et al., 2001, 2002; Sheng et al., 2002; Li et al., 2004).

Although the effect of cation saturation on NAC sorption by homoionic clays is well documented, little is known about the effect of exchangeable cation type on sorption by soils with relatively high SOM contents, or on the relative contributions of soil organic and mineral components on NAC sorption and how this might be affected by the nature of the exchangeable cation. The objective of this study was to document the effect of exchangeable cation type on NAC sorption by whole soil, SOM and the soil clay-mineral fraction.

EXPERIMENTAL SECTION

A clay loam Webster soil (fine loamy, mixed, mesic Typic Haplaquoll) (Soil Survey Staff, NRCS) (A and B horizons) was fractionated by standard procedures (Kunze & Dixon, 1986). Carbonates (CO_3), SOM, iron oxides (FeO_x), and clay-sized particles were sequentially removed from each soil horizon. Carbonates were removed using 0.5N sodium acetate acidified to pH 5 at 80°C, followed by the removal of SOM using 30% H_2O_2 at 80°C, followed by the removal of free FeO_x using the citrate-bicarbonate-dithionite method. The clay-sized fraction (<2.0 µm) was obtained by wet sedimentation of the CO_3-OM-Fe-removed soil fraction (Whittig & Allardice, 1987). The fraction remaining after the removal of CO_3, SOM, FeO_x and clay-sized particles was termed the residual soil fraction. The masses of CO_3 and FeO_x removed, and the mass of residual fraction remaining were determined gravimetrically. Additional soils used were a Pahokee peat, Houghton muck and Brookston loam. The SOM content of whole soils and the amount of SOM remaining after extraction of bulk SOM using H_2O_2 were determined by the Michigan State University (MSU) Soil Testing Laboratory using dry combustion and a Leco carbon analyzer (St. Joseph, Michigan) (Nelson and Sommers, 1996). The content of clay-sized particles in the Webster soils was determined by the MSU Soil Testing Laboratory using the hydrometer method (Gee and Bauder, 1986).

To prepare homoionic sorbents, soil and soil fractions (ca. 100 g) were washed with 200 ml of a 0.1*M* solution of the cation chloride salt overnight, thereafter centrifuged and the supernatant discarded; this procedure was repeated five times. The soils were then washed with approximately 200 ml of Millipore Milli-Q (Billerica, Massachusetts) deionized H_2O, thereafter centrifuged and the supernatant tested with $AgNO_3$; the procedure was repeated until a negative Cl^- ion test with $AgNO_3$ was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1°C) until used.

Para-nitrocyanobenzene (p-NCB), 1,4-dinitrobenzene (1,4-DNB) and 1,2,4-trichlorobenzene (1,2,4-TCB) were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin) with purities of 97%, 98%, and 99% respectively, and used as received. For p-NCB, 1,4-DNB, and 1,2,4-TCB, the water solubilities (S_w) at 25°C are 1650, 69 and 49 mg L^{-1}, respectively; the log K_{ow} values are 1.19, 1.46, and 4.02, respectively (Howard and Meylan, 1997).

Sorption of solutes by K^+-saturated soil and soil fractions were measured in triplicate using a batch equilibrium technique. This involved adding aqueous solutions of p-NCB, 1,4-DNB, or 1,2,4-TCB over a range of initial concentrations (C_i, 1-42 mg L^{-1} for p-NCB and 1,4-DNB; 1-30 mg L^{-1} for 1,2,4-TCB) to a known mass of soil. Initial solutions of the compounds were prepared in 0.05M solution of the cation chloride salt. Total initial volumes of 5 ml (p-NCB, 1,4-DNB) or 7 ml (TCB) were pipetted into 7.5 ml borosilicate glass vials containing various amount of sorbent (0.1-0.4g for p-NCB and 1,4-DNB; 0.04-0.35g for 1,2,4-TCB). The vials were rotated continuously overnight (24 hours) in the dark at room temperature (23 ± 1°C); preliminary studies showed equilibrium was reached within 24 hours (data not provided). The liquid and solid phases were separated by centrifugation at 4068*g* for 40 min, and the solute's equilibrium aqueous concentration (C_e) measured using a Perkin-Elmer high performance liquid chromatograph (HPLC)

(Perkin-Elmer, Norwalk, Connecticut). This instrument consisted of a binary liquid chromatography pump 250 with a series 200 autosampler and a uv-visible detector set at a suitable adsorption wavelength for the respective compound (λ 254, 262, and 228nm for p-NCB, 1,4-DNB, and 1,2,4-TCB, respectively). An Alltech platinum EPS C18 column (Deerfield, Illinois) was used for p-NCB and 1,4-DNB. A Varian microsorb-MV C18 column (Palo Alto, California) was used for 1,2,4-TCB. The mobile phase was an isocratic mixture of methanol (HPLC grade) and Milli-Q deionized water (methanol: water ratios of 55:45 for p-NCB, 65:35 for 1,4-DNB, and 92:8 for 1,2,4-TCB) with a flow rate of 1.0 ml min^{-1}. The amount of solute sorbed by each sorbent was calculated as the difference between C_i and C_e. Compound recoveries in control vials without sorbent were above 95%. Because of the high solute recoveries, the data were not adjusted.

The effect of exchangeable cation type on sorption by SOM was evaluated using either organic soils relatively devoid of mineral matter or a mineral soil devoid of swelling clays (i.e. smectites) implicated in the sorption of NACs (Boyd et al., 2001; Haderlein et al., 1993). The sorbents used were the Pahokee peat (euic, hyperthermic Lithic Medisaprist), Brookston loam (fine-loamy, mixed, superactive, mesic Typic Argiaquoll) and Houghton muck (euic, mesic Typic Haplosaprist) (Soil Survey Staff, NRCS). The peat was purchased from the International Humic Substances Society (BS103P) (Denver, Colorado). The Brookston loam was obtained from Ionia, Michigan, and the Houghton muck from Bath, Michigan. Sorption isotherms for p-NCB and 1,4-DNB, and 1,2,4-TCB by these soils were obtained using the batch equilibrium technique described above.

These soils were saturated with K^+ or Mg^{2+} to evaluate the effect of cation type on sorption of NOCs.

The unfractionated Webster soil (A horizon) and its isolated clay-sized fraction were saturated with different exchangeable cations (Cs^+, K^+, Na^+, Li^+, Mg^{2+}, Ca^{2+}) to determine the effect of exchangeable cation on sorption of p-NCB. Batch equilibrium experiments were conducted using the M^{n+}-saturated soil clay fractions and whole soils with p-NCB as the sorbate. Sorption of p-NCB by K^+-saturated reference clays which are representative of the identified clay types in the soil clay fraction (see below) were also measured using batch equilibrium experiments as described above. The clays used were: Wyoming montmorillonite (SWy-2), illite (IMt-2) and kaolinite (KGa-2) obtained from the Clay Minerals Society Source Clay Repository (Columbia, MO) and beidellite from Ward's Natural Science (Rochester, NY).

X-ray diffraction (XRD) was used to identify the clay mineralogy of the clay-sized fractions (Whittig and Allardice, 1987). Oriented samples of Mg^{2+}- and K^+-saturated soil clay-sized fractions were prepared by dropping suspensions of the clay-sized materials on glass slides, then air-drying, heating at 500°C, and treatment with ethylene glycol. Samples were analyzed using CuKα radiation and a Philips APD 3720 X-ray diffractometer (Philips Electronic Instruments, NJ).

Semi-quantitative estimates for the amount of smectite in the unfractionated Webster soils was attempted using the measured cation exchange capacity (CEC) of the unfractionated soils ((Michigan State University (MSU) Soil Testing Laboratory using the ammonium acetate method (Sumner and Miller, 1996)), and an average CEC of a soil smectite and SOM of 80 and 160 cmol kg^{-1}, respectively, using the equation:- CEC = $(160 \text{ cmol kg}^{-1})(f_{om}) + (80 \text{ cmol kg}^{-1})(f_{cm})$ (1)

where f_{om} and f_{cm} are the fractional SOM and smectite clay contents of the soil. The calculation assumed that the CEC of the soil originated solely from SOM and soil smectites. By comparing the X-ray diffraction peak areas associated with the non-smectite minerals to the smectite peak, we estimated the relative fractional amounts of each non-smectite non-quartz mineral present in the clay-sized fraction as a fraction of the smectite peak (illite/mica, 0.125; kaolinite, 0.125). Multiplying the percent smectite in the soil obtained using equation (1) (e.g., 24%) by the relative fractional amount of each non-smectite mineral determined from the relative peak areas in the X-ray diffraction graph, we calculated the amount of non-smectite minerals (e.g. illite/mica, 3%; kaolinite, 3%). We subtracted the estimated smectite content (e.g. 24%) from the total clay content (e.g. 31%) to obtain the amount of non-smectite minerals (e.g. 7%) and compared this value to the sum of the non-smectite minerals estimated using the peak areas (3% + 3%).

Statistical Analysis

The sorption coefficient (K_f) and the constant related to the sorption isotherm curvature (n) were estimated using the Freundlich equation, $Q=K_fC_e^n$, where Q is the sorbed solute concentration per unit mass of the sorbent (mg g^{-1}), K_f is the sorption coefficient, n is a constant related to the isotherm curvature (concave or convex). Comparisons of sorption isotherms were made by comparing the K_f and n values for each soil-solute system using nonlinear regression in SAS (SAS Institute, 1999). A significant difference between isotherms was assigned when there was a significant difference ($\alpha = 0.05$) between K_f and n or K_f values of compared isotherms (Laboski and Lamb, 2004).

RESULTS AND DISCUSSION

The Webster soils (fine loamy, mixed, mesic Typic Haplaquoll) contain smectites (Figure 1.1). Nitroaromatics are known to be sorbed significantly by smectite clays (Haderlein et al., 1996; Weissmahr et al., 1998; Boyd et al., 2001; Sheng et al., 2002; Johnston et al., 2001; Johnston et al., 2002). The smectite contents of the Webster A and B soils, calculated using the CECs of the soils, are 24 and 16% smectite, respectively (Table 1.1) and were therefore chosen as the study soils.

Removal of SOM from the Webster A and B horizons increased sorption of p-NCB and 1,4-DNB, with K^+ as the saturating exchangeable cation (Figure 1.2, 1.3). In whole soil it appeared that the overall effect of SOM was to suppress sorption of NCB and 1,4-DNB, though SOM itself is undoubtedly a sorptive sink for these compounds. Karickhoff (1984) proposed that, if SOM blocked clay sorption sites, then SOM removal could result in increased sorption by clays, although this effect had not been demonstrated experimentally until now. Removal of the clay-sized fraction decreased sorption by a factor of at least 10 in all soils for both p-NCB and 1,4-DNB compared to unfractionated soil, with K^+ as the saturating cation (Figure 1.2, 1.3). Given the very low sorption of NACs by free FeO_x (data not reported) and the established high affinity of smectites for NACs (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1997; Haderlein et al., 1993 Boyd et al., 2001; Johnston et al., 2002; Johnston et al., 2001; Sheng et al., 2002; Li et al., 2003), our data supports the premise that SOM and soil clays are the two components that significantly influence NAC sorption. The contribution by soil clays to sorption of p-NCB and 1,4-DNB was greater than the contribution by

SOM. The contribution of CO_3 and the residual fraction to sorption of the solutes was minimal for all soils (Figure 1.2, 1.3). We found low levels of CO_3 present in the unfractionated soils (data not shown) consistent with the findings of Laird et al. (1994) for a Webster soil.

The influence of exchangeable cation on sorption of organic solutes by soil will depend on its influence on the dominant soil components responsible for solute sorption, i.e. SOM and clay. Trichlorobenzene (TCB) is a nonpolar organic compound whose sorption by soil results predominated (if not exclusively) from partitioning into SOM (Chiou, 2002).

The amount of TCB sorbed (Q_{om}) by K^+-saturated Houghton muck, Brookston loam and Webster soils at an equilibrium concentration of 5 mg L^{-1} (Table 1.1) was calculated using the K_f and n parameters from the sorption data normalized to the amount of SOM in the soils fitted to the Freundlich equation ($Q = K_f * C_e^n$; $Q_{om} = Q / f_{om}$, where Q is the sorbed solute concentration per unit mass of the sorbent (mg g^{-1}), K_f is the sorption coefficient, n is a constant related to the isotherm curvature (concave or convex), f_{om} is the fractional SOM content of the soil). The values ranged from 2.15 to 3.60 mg g^{-1}; less than a factor of 2 (Table 1.2). The Q_{om} values for TCB sorption by Mg^{2+}-saturated Houghton muck, Brookston loam, peat and Webster soils at an equilibrium concentration of 5 mg L^{-1} ranged from 1.15 to 3.30 (Table 1.2); less than a factor of 3. The sorption isotherms for TCB sorption by K^+- and Mg^{2+}- saturated organic and mineral soils normalized to the

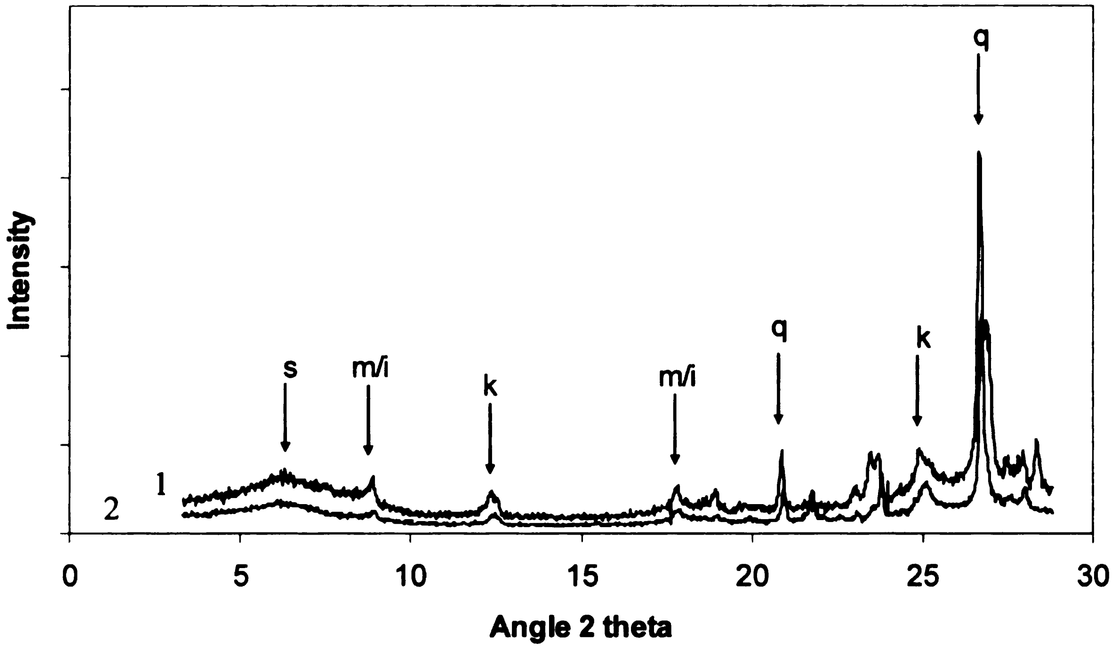


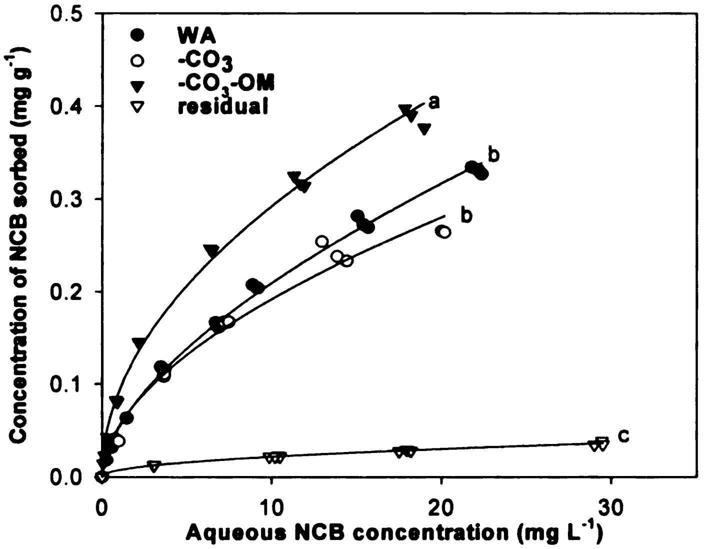
Figure 1.1. X-ray spectra of Webster A (1) and B (2) soils, Mg^{2+}-exchanged, air dried.

(s, smectite; m/i, mica and/or illite; k, kaolinite; q, quartz)

Table 1.1. Measured SOM, clay content and CEC for Webster A and B (whole soils and soils from which SOM was removed), peat, Houghton muck (HM) and Brookston loam (BL) soils. Calculated Q_{om} values derived from sorption isotherm data for trichlorobenzene (TCB), p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) sorption by K^+- and Mg^{2+}-saturated soils at an equilibrium concentration of 5 mg L^{-1}. Q_{om} = amount of solute sorbed per unit mass of sorbent (Q) / fractional SOM content of sorbent.

Soil	**Texture**	**%OM**	**%clay**	**%smectite**	**CEC cmol kg^{-1}**	**Q_{om} (mg solute g^{-1} SOM)**					
						TCB		**p-NCB**		**1,4-DNB**	
						K^+	**Mg^{2+}**	**K^+**	**Mg^{2+}**	**K^+**	**Mg^{2+}**
Peat	organic	73.2	-	-	-	3.48	3.13	1.07	0.55	1.10	0.62
HM	organic	43.7	-	-	126	3.52	3.33	0.56	0.38	0.56	0.47
BL	sandy clay loam	9.4	24	-	18	3.60	3.30	0.65	0.46	1.36	0.61
WA	Clay loam	3.2	31	24	35	3.16	2.24	na	na	na	na
WB	Clay loam	1.3	31	16	23	2.15	1.15	na	na	na	na
WAO	clay loam	0.3	31	24	-	3.22	3.51	na	na	na	na
WBO	clay loam	0.4	31	16	-	3.46	3.02	na	na	na	na

WA – Webster horizon A WAO – Webster horizon A OM-removed
WB – Webster horizon B WBO – Webster horizon B OM-removed
na - not applicable because sorption is dominated by clay minerals rather than OM



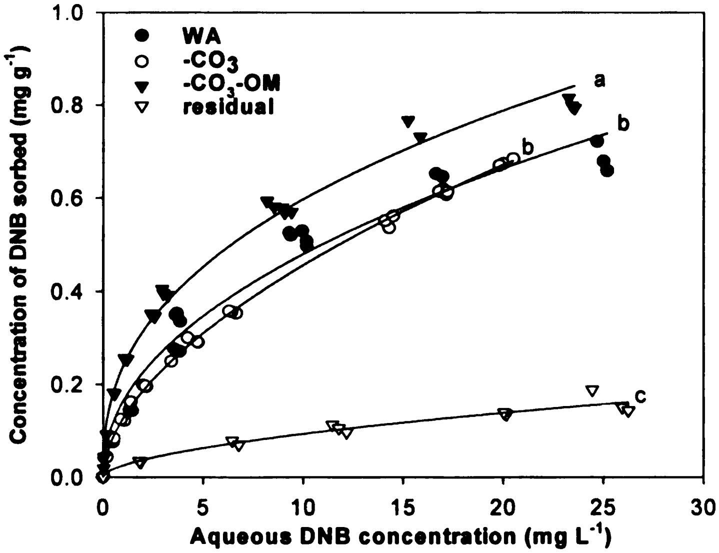


Figure 1.2. Adsorption isotherms for sorption of p-nitrocyanobenzene (NCB) and 1,4-dinitrobenzene (DNB) by Webster A (K^+-saturated) soil fractions.

(carbonates removed, -CO_3; CO_3 and SOM removed, -CO_3-OM; residual fraction, fraction remaining after removal of CO_3, OM, free FeO_x and clay-sized fraction, residual)

(isotherms with different letters are statistically different at $p < 0.05$)

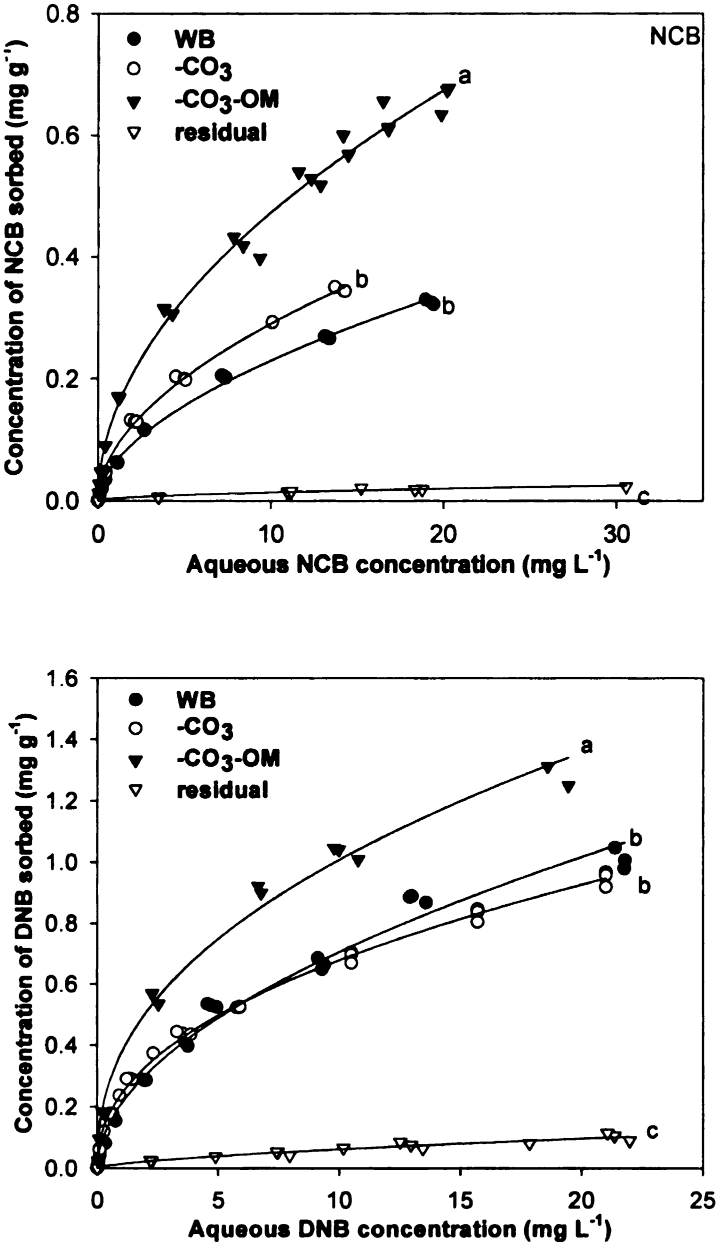


Figure 1.3. Adsorption isotherms for sorption of p-nitrocyanobenzene (NCB) and 1,4-dinitrobenzene (DNB) by Webster B (K^+-saturated) soil fractions.

(carbonates removed, -CO_3; CO_3 and SOM removed, -CO_3-OM; residual fraction, fraction remaining after removal of CO_3, OM, free FeO_x and clay-sized fraction, residual)

(isotherms with different letters are statistically different at $p < 0.05$)

Table 1.2. Freundlich sorption equation K_f and n values used to calculate Q_{om} values derived from sorption isotherm data for trichlorobenzene (TCB), p-nitrocyanobenzene (p-NCB) and 1,4-dinitrobenzene (1,4-DNB) sorption by K^+- and Mg^{2+}-saturated soils at an equilibrium concentration of 5 mg L^{-1}. Q_{om} = amount of solute sorbed per unit mass of sorbent (Q) / fractional SOM content of sorbent.

Soil	TCB				p-NCB				1,4-DNB			
	K^+		Mg^{2+}		K^+		Mg^{2+}		K^+		Mg^{2+}	
	K_f	n	K_f	N	K_f	n	K_f	N	K_f	n	K_f	N
Peat	1.09	0.72	1.15	0.62	0.58	0.37	0.21	0.59	0.59	0.39	0.22	0.63
HM	0.93	0.83	0.99	0.75	0.31	0.38	0.14	0.63	0.28	0.43	0.26	0.36
BL	0.87	0.88	1.12	0.67	0.27	0.53	0.19	0.54	0.93	0.23	0.31	0.42
WA	0.83	0.83	0.56	0.86	na	na	na	na	na	na	na	na
WB	0.35	1.12	0.09	1.62	na	na	na	na	na	na	na	na
WAO	0.38	1.33	0.96	0.81	na	na	na	na	na	na	na	na
WBO	0.42	1.31	0.58	1.02	na	na	na	na	na	na	na	na

WA – Webster horizon A WAO – Webster horizon A OM-removed

WB – Webster horizon B WBO – Webster horizon B OM-removed

na - not applicable because sorption is dominated by clay minerals rather than OM fractional SOM content of each soil overlapped (Figures 1.4, 1.5). The similarities of Q_{om} values for TCB sorption by K^+-saturated organic and mineral soils indicates that SOM was the dominant, if not singular, sorbent phase for TCB, and that SOM functioned very similarly in this regard among the soils tested.

When p-NCB and 1,4-DNB were used as the solutes, the Q_{om} values at an equilibrium concentration of 5 mg L^{-1} (Table 1.1) calculated using the Freundlich K_f and n values (Table 1.2) for their sorption by K^+-saturated peat, Houghton muck and Brookston loam fell within a relatively narrow range of 0.56 to 1.07 and 0.56 to 1.36mg g^{-1}, respectively; both being a range of less than 3. For p-NCB and 1,4-DNB sorption by Mg^{2+}-saturated peat, Houghton muck and Brookston loam the range in Q_{om} at 5mg L^{-1} was 0.38 to 0.55 and 0.47 to 0.62mg g^{-1} respectively (Table 1.1); both being a range of less than 2. The SOM-normalized sorption isotherms for NAC sorption by K^+- and Mg^{2+}- saturated soils almost overlapped (p-NCB) and overlapped (1,4-DNB) (Figure 1.6, 1.7). The Brookston loam soil is devoid of smectite clays implicated in the mineral phase sorption of NACs, so for all three sorbents, SOM is likely the dominant sorption phase. A study of dichlorobenzene and carbon tetrachloride by a much larger group of soils revealed variations in K_{om} (where $Q_{om} = K_{om} * C_e$) of a factor of ~3 among soils (Kile et al., 1995), similar to those we observed among organic and mineral soils for TCB, p-NCB, and 1,4-DNB sorption. Hence an organic soil (devoid of sorptive clays) can be reasonably used to evaluate sorption of NOCs by SOM, and importantly to evaluate the independent contribution of SOM to sorption of polar compounds by mineral soils where sorption by both SOM and mineral components is expected. In addition, the overlap between the Q_{om}

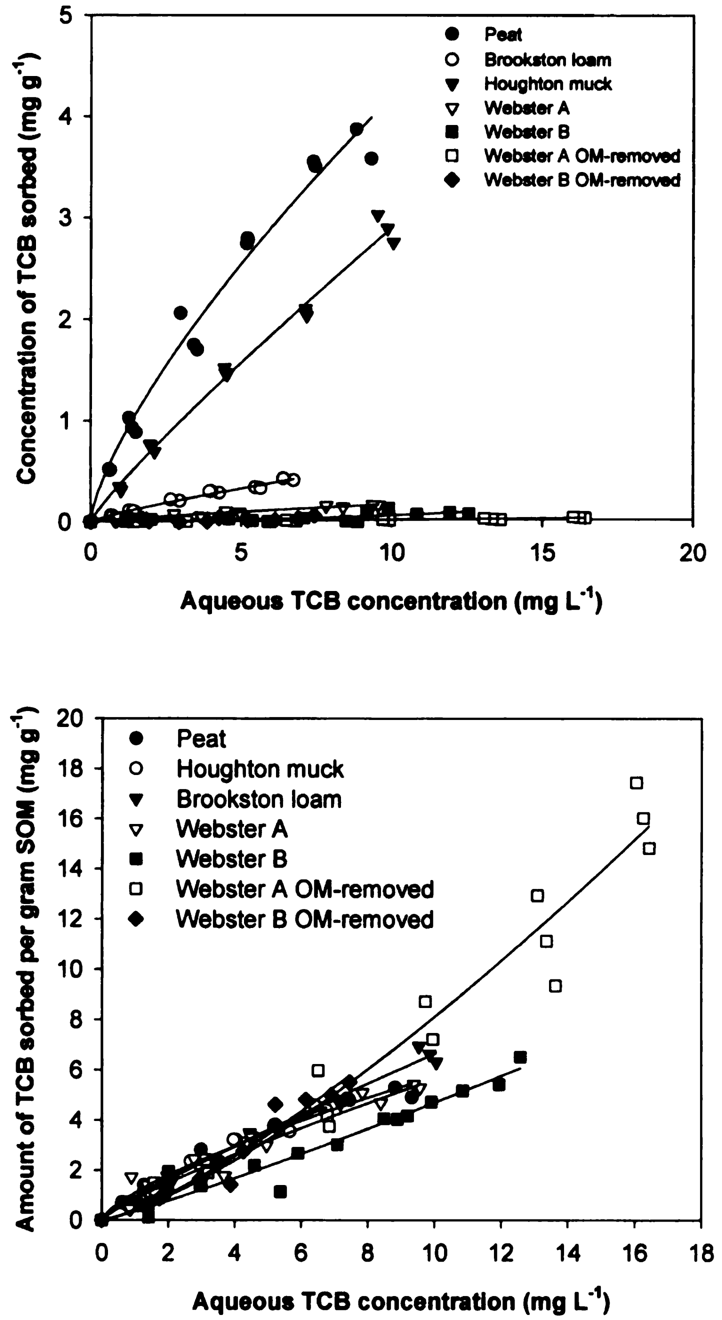


Figure 1.4. Adsorption isotherms for sorption of 1,2,4-trichlorobenzene (TCB) by (a) K^+-saturated peat, Houghton muck, Brookston loam, Webster A, Webster B, Webster A and B from which bulk SOM was removed and (b) sorption isotherms normalized to amount of SOM in soils.

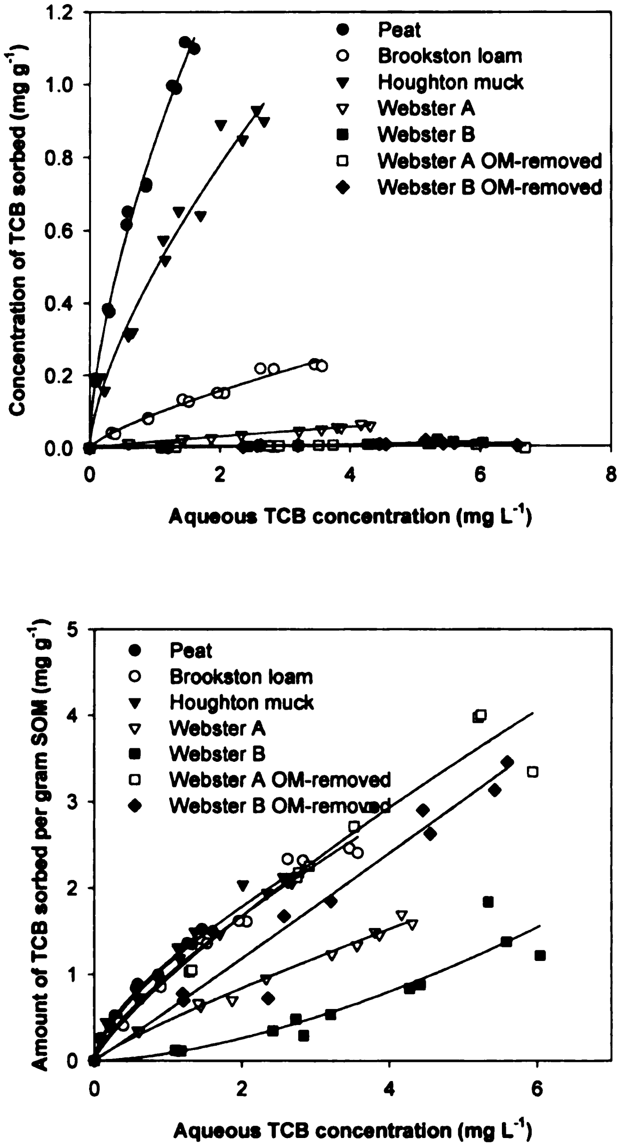


Figure 1.5. Adsorption isotherms for sorption of 1,2,4-trichlorobenzene (TCB) by (a) Mg^{2+}-saturated peat, Houghton muck, Brookston loam, Webster A, Webster B, Webster A and B from which bulk SOM was removed and (b) sorption isotherms normalized to amount of SOM in soils.

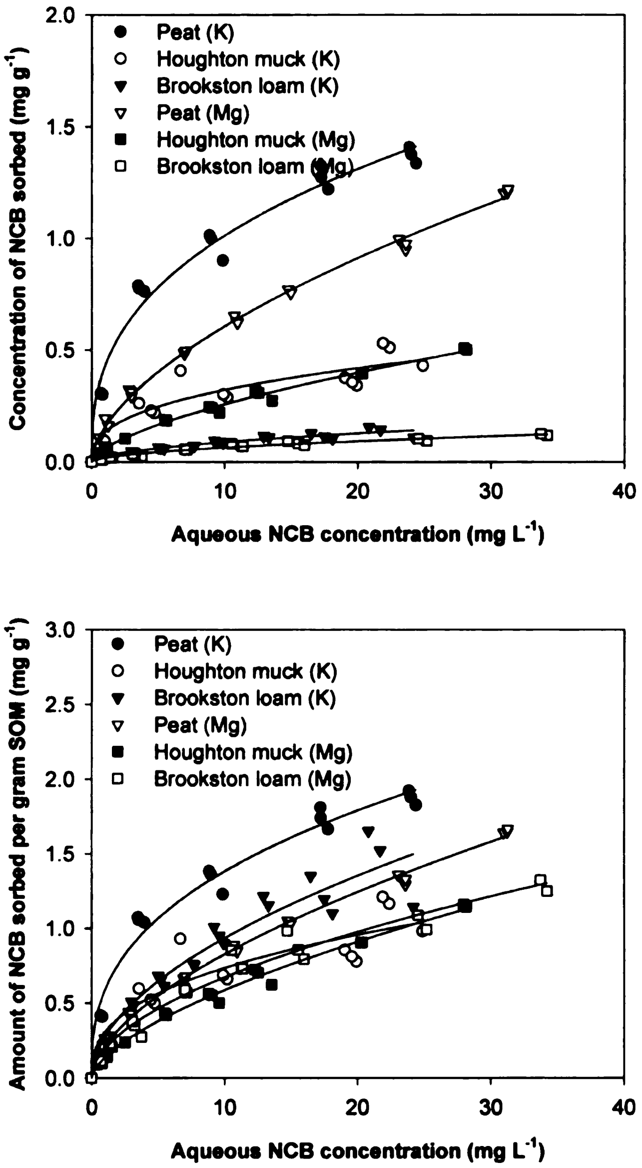
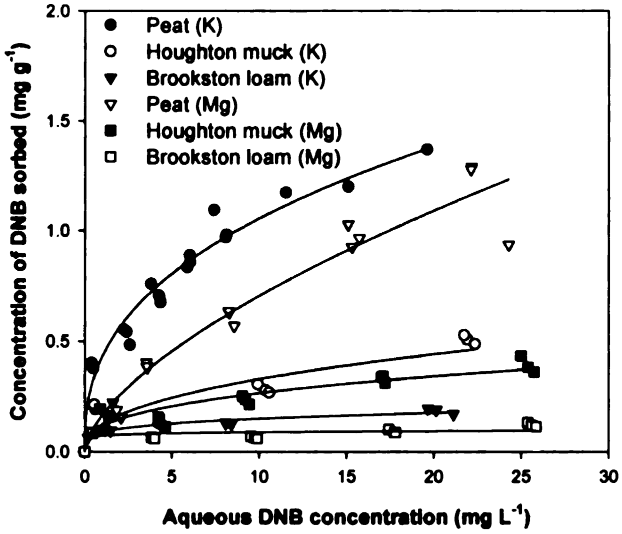


Figure 1.6. Adsorption isotherms for sorption of p-nitrocyanobenzene (p-NCB) by (a) K^+- and Mg^{2+}-saturated peat, Houghton muck, Brookston loam and (b) sorption isotherms normalized to amount of SOM in the soils.



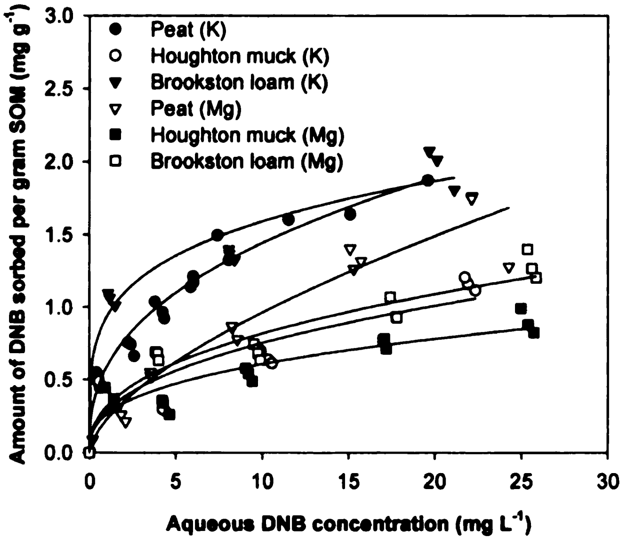


Figure 1.7. Adsorption isotherms for sorption of 1,4-dinitrobenzene (DNB) by (a) K^+- and Mg^{2+}-saturated peat, Houghton muck, Brookston loam and (b) sorption isotherms normalized to amount of SOM in the soils.

values for sorption of TCB, p-NCB and 1,4-DNB by the K^+- and Mg^{2+}-saturated soils as well as the narrow range in Q_{om} values (i.e. less than a factor of 3) indicates that the K^+- and Mg^{2+}-saturated systems function similarly for the sorption of NOCs. The residual SOM (i.e., SOM remaining after H_2O_2 extraction of bulk SOM) sorbed TCB similarly to bulk SOM in the mineral and organic soils. This is evidenced by the similarity in the calculated Q_{om} values at an equilibrium concentration of 5 mg L^{-1} (Table 1.1) for TCB sorption by K^+- and Mg^{2+}-saturated peat, Houghton muck, Brookston loam, Webster soils and SOM-removed soils. Our results therefore provide evidence that, in systems where sorption is dominated by SOM, sorption is not strongly influenced by the saturating cation. Among the group of solutes and soils characterized in this study it appears that differences in sorption induced by different cations saturating the CEC would result from their effect on the sorptive characteristics of the clay-sized mineral fraction and not the SOM.

XRD analysis indicated that the minerals present in the clay fractions of the Webster A and B horizons included kaolinite (ca. 2-3%), quartz (ca. 1-11%), smectite (ca.16-24%) and mica and/or illite (ca. 2-3%) (Figure 1.1). For the Webster A sorption experiments for p-NCB sorption by K^+-saturated kaolinite, illite, montmorillonite (SWy-2) and beidellite showed that the smectite clays (i.e., SWy-2 and beidellite) were by far the most effective sorbents for p-NCB, with the montmorillonite (SWy-2) at least 2x more effective than beidellite (Figure 1.8). These results agree with previous studies that report the affinity and the adsorption capacity of clays for NACs increased in the order kaolinite < illite << montmorillonite (Haderlein et al., 1996). Thus, among the soil minerals

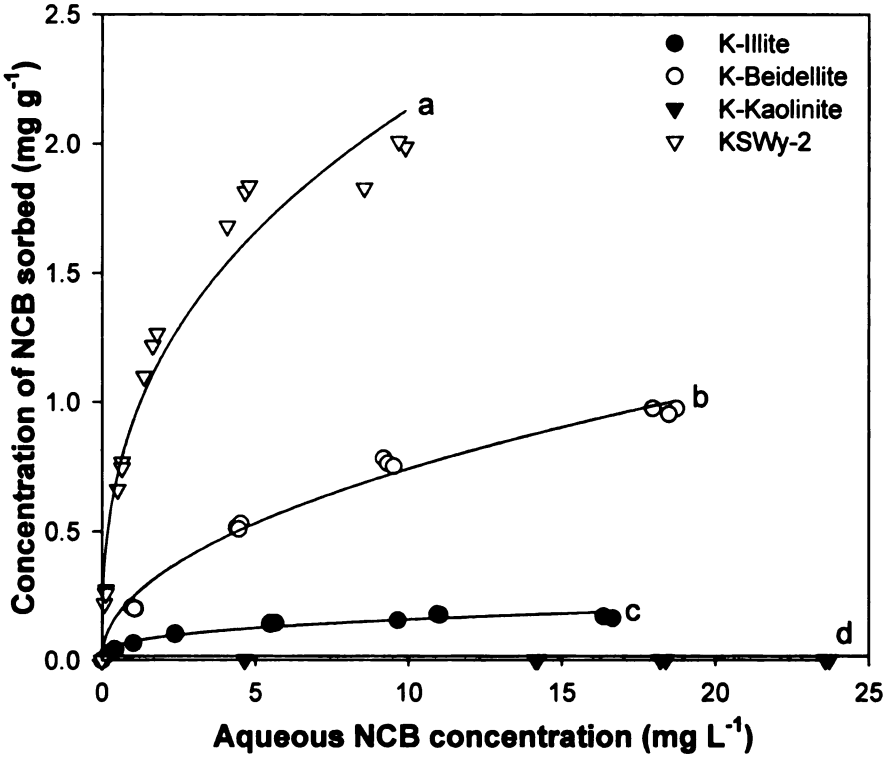


Figure 1.8. Adsorption isotherms for sorption of p-nitrocyanobenzene by K^+-saturated reference clays (illite IMt-2; beidellite; montmorillonite SWy-2).

(isotherms with different letters are statistically different at $p < 0.05$)

present in the soils studied, smectites appear to be the dominant sorptive phase. Previous studies have demonstrated that, for pure smectite samples, NAC sorption is affected strongly by the type of exchangeable cation (Li et al., 2003; Boyd et al., 2001; Sheng et al., 2001, 2002; Johnston et al., 2001, 2002; Weissmahr et al., 1997; Haderlein et al., 1996).

Isotherms for NAC sorption by soil clay-sized fraction were nonlinear and generally exhibited saturation-type curvature approaching a maximum surface concentration (Figure 1.9). The concentration of p-NCB at an equilibrium concentration of 5 mg L^{-1} sorbed by homoionic clay-sized fractions of Webster A (Table 1.3) was calculated by fitting the sorption isotherm data to the Freundlich equation (K_f and n values in Table 1.4). Sorption of p-NCB increased in accordance with decreasing hydration energy, i.e., Li^{+}~Na^{+}<<K^{+}<Cs^{+} and Ca^{2+}~Mg^{2+}<Ba^{2+} (Table 1.3; Figure 1.9). Overall, Cs^{+} and K^{+}-exchanged soil clays were much more effective sorbents than Na^{+}, Li^{+}, Ca^{2+}, Mg^{2+}, or Ba^{2+}-exchanged soil clays. These results are consistent with results reported using reference clays showing higher NAC sorption by smectites saturated with more weakly hydrated cations. Haderlein et al. (1993; 1996) found the extent of sorption of NACs was greater for K^{+} and NH_4^{+}-clays compared to Al^{3+}, Ca^{2+}, Mg^{2+}, and Na^{+}-clays (Arizona montmorillonite and kaolinite). Similar results were obtained by Weissmahr et al. (1997, 1999) for NAC sorption to various reference minerals (illite, kaolinite and SAz-1). Sheng et al (2002) measured 4,6-dinitro-o-cresol (DNOC) sorption to SWy-2 smectites and observed that K^{+} and Cs^{+}-exchanged SWy-2 clays sorbed DNOC more effectively than Al^{3+}, Ba^{2+}, Ca^{2+}, or Na^{+}-exchanged SWy-2 reference clays.

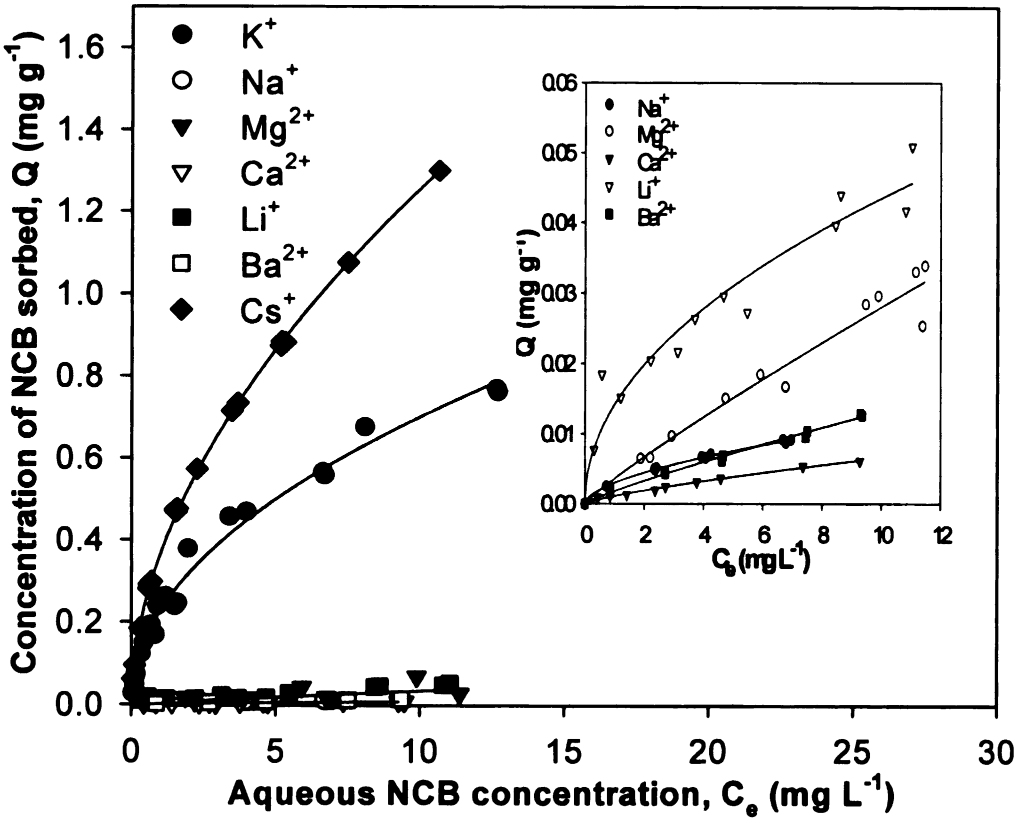


Figure 1.9. Adsorption isotherms for sorption of p-nitrocyanobenzene (p-NCB) by clay-sized fraction of Webster A soil exchanged with various cations (Cs$^+$, K$^+$, Na$^+$, Li$^+$, Ba^{2+}, Mg^{2+}, and Ca^{2+}). Insert is a magnification of adsorption isotherms for sorption of p-NCB by clay-sized fraction of Webster A soil exchanged with Na$^+$, Li$^+$, Ba^{2+}, Mg^{2+}, and Ca^{2+}.

Table 1.3. Comparison of amount of solute sorbed per unit mass of sorbent (Q) at an equilibrium concentration of 5mgL^{-1} for p-nitrocyanobenzene sorption by homoionic Webster A clay-sized fraction and Webster A unfractionated soil. Q values are also normalized to lowest Q value.

			Clay-sized fraction		**Unfractionated soil**	
Cation	**Free Energy of Hydration (kJ mol^{-1})**[†]	**Smectite surface area available for sorption**[‡] **%**	**Q (mg Kg^{-1})**	**Q normalized to lowest Q**	**Q (mg Kg^{-1})**	**Q normalized to lowest Q**
Cs	-258	83	863.94	114.1	203.13	13.0
K	-304	64	498.40	65.8	138.25	8.9
Na	-375	21	7.57	**1.0**	15.57	**1.0**
Li	-481	-27	31.04	4.1	21.27	1.4
Ba	-1258	51	7.26	3.9	19.46	1.1
Mg	-1838	42	15.12	**1.0**	18.27	**1.0**
Ca	-1515	26	3.86	1.9	20.83	1.1

[†] Y. Marcus. 1985. Ion Solvation. John Wiley and Sons, pp. 107-109.

[‡] Based on hydrated radii of cations, an average smectite surface area of 750 m^2 g^{-1}, an average CEC of 100 cmol(+) kg^{-1}

Table 1.4. Freundlich sorption equation K_f and n values used to calculate the amount of solute sorbed per unit mass of sorbent (Q) at an equilibrium concentration of 5 mg L^{-1} for p-nitrocyanobenzene sorption by homoionic Webster A clay-sized fraction and Webster A unfractionated soil.

Cation	**Clay-sized fraction**		**Unfractionated soil**	
	K_f	N	K_f	N
Cs	0.3628	0.5391	0.0958	0.4673
K	0.2264	0.4903	0.0528	0.5983
Na	0.0030	0.5773	0.0059	0.5990
Li	0.0142	0.4877	0.0077	0.6339
Ba	0.0018	0.8631	0.0059	0.7365
Mg	0.0036	0.8915	0.0067	0.6219
Ca	0.0011	0.7731	0.0071	0.6694

Sorption of NACs by smecties occurs largely on the clay interlayers, and cation hydration determines the interlayer distance, the size of adsorption domains (i.e. regions of siloxane surface unobscured by water), and the ability of NO_2 groups to complex directly with exchangeable cations (Boyd et al., 2001). Considering the hydrated radii of Cs^+, K^+, Na^+, Li^+, Ba^{2+}, Ca^{2+}, and Mg^{2+} (3.6, 5.3, 7.9, 10.0, 8.8, 9.6 and 10.8 Å respectively) (Evangelou, 1998), it is apparent that lower cation hydration manifests larger adsorption domains between cations. Large hydration spheres and strongly held waters of hydration would act to inhibit the direct interaction of NO_2 groups with the interlayer cation, as proposed by Boyd et al. (2001), Johnston et al. (2001, 2002) and Li et al. (2004). The hydration sphere water molecules are less strongly held (lower enthalpy of hydration) by ions with larger ionic radii (e.g. K^+) compared to ions with smaller ionic radii (e.g., Na^+) and lower valence. These factors would account for the greater p-NCB sorption occurring by Cs^+- and K^+-exchanged soil clay fraction (ionic radii 0.169 and 0.133 nm; ΔH_{hyd} -258 and -304 kJ mol^{-1}, respectively) compared to that by soil clay fractions exchanged with Na^+, Li^+, Ca^{2+}, Mg^{2+} or Ba^{2+} (ionic radii, 0.095, 0.060, 0.099, 0.065 or 0.135 nm; ΔH_{hyd}, -375, -481, -1515, -1258, or -1258 kJ mol^{-1}, respectively).

The effect of enthalphy of hydration can be illustrated by comparing K^+ and Ba^{2+}. Although these ions have similar ionic radii, at an equilibrium concentration of 5mg L^{-1}, our K^+-exchanged soil clay fraction sorbed p-NCB to a greater extent (69 times greater) than the Ba^{2+}-exchanged soil clay fraction (Table 1.3). The greater hydration sphere and hydration energy (-1290 kJ mol^{-1}) of the Ba^{2+} ion compared to the K^+ ion (-314 kJ mol^{-1})

suggests that ion-dipole interactions between the exchangeable cation and polar functional groups on the NAC would require the displacement of more strongly held water molecules in the case of Ba^{2+}-exchanged system. The removal of water requires energy and so, for direct cation-solute interactions, the Ba^{2+}-exchanged system would require a larger energy input than the K^+ system. Supporting FTIR studies observed -NO vibrational band shifts for 1,3,5-trinitrobenzene sorption on K^+-smectite but not for Ba^{2+}-smectite (Boyd et al., 2001; Johnston et al., 2001, 2002).

Li et al. (2004) calculated an enthalpy of interaction involved in complex formation between the solute and the exchangeable cation. Their analyses considered other energy yielding or consuming processes including water removal from the clay and partial dehydration of the solute in the interlayer. The interaction energies between K^+-SWy-2 and 1,3,5-TNB, 1,3-dinitrobenzene (1,3-DNB) and 1,4-DNB at 80% dehydration of the solute were -99, -69, and -73 kJ mol^{-1}, respectively. The calculated enthalpies of interaction between Ca^{2+}-exchanged SWy-2 for these compounds were lower ranging from -30 to -38 kJ mol^{-1}. The calculated interaction enthalpies help explain the observation of greater NAC sorption by the less strongly hydrated system (e.g. K^+) than by the more strongly hydrated system (e.g., Ca^{2+}). Finally, Cs^+ and K^+-saturated smectites manifest interlayer distances of ~ 3 Å (d_{001} ~ 12.3 Å) in the presence of sorbed NACs, and this distance appears optimal for sorption of planar NACs (Li et al., 2004; Sheng et al., 2002; Sheng et al., 2001). These spacings closely match the width of p-NCB and through simultaneous interactions with the opposing siloxane sheets the adsorbed molecules are largely dehydrated (assuming 80% dehydrated in the above calculation of interaction enthalpy), an energetically favorable process (Li et al., 2004). Smectites saturated with the other cations (e.g. Na^+, Ba^{2+}, Ca^{2+}) always swell to > 15 Å in the presence of bulk water. The energy requirement for compressing the interlayers, and dehydrating the solute, may be larger than the energy gain from solute dehydration thereby making the overall process energetically less favorable.

The effects of saturating cation on sorption of p-NCB by whole soils were similar to those by the isolated soil clay fractions (Table 1.3; Figure 1.10). Cs^+ and K^+-soil were approximately 14 and 9 times more effective than Na^+ or Li^+-soil for p-NCB sorption at an equilibrium concentration of 5 mg L^{-1} (Table 1.3); sorption by Cs^+- and K^+-saturated soils was also much higher than by the divalent-cation-exchanged soils (Table 1.3; Figure 1.10). Among the divalent cations, the extent of p-NCB sorption at an equilibrium concentration of 5 mg L^{-1} also increased with decreasing hydration energy ($Mg^{2+}<Ca^{2+}=Ba^{2+}$) (Table 1.3).

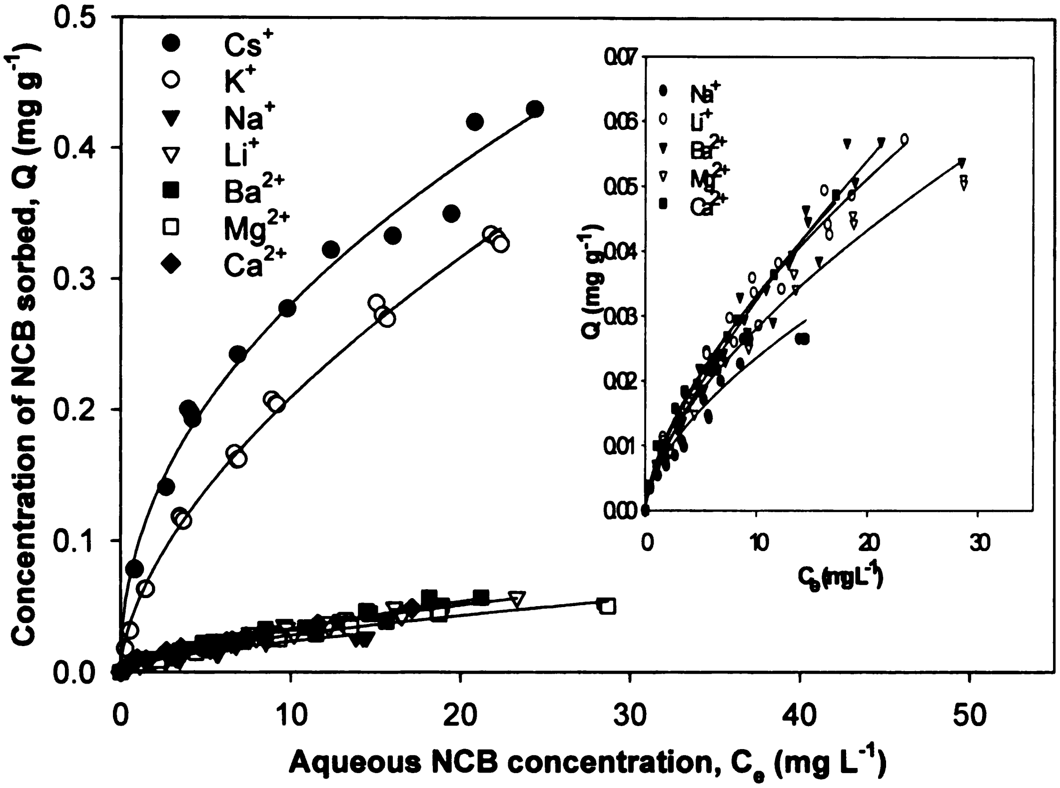


Figure 1.10. Adsorption isotherms for sorption of p-nitrocyanobenzene by Webster A soils exchanged with various cations (Cs^+, K^+, Na^+, Li^+, Ba^{2+}, Mg^{2+}, and Ca^{2+}). Insert is a magnification of adsorption isotherms for sorption of p-nitrocyanobenzene by Webster A soils exchanged with Na^+, Li^+, Ba^{2+}, Mg^{2+}, and Ca^{2+}.

CONCLUSION

Adsorption of NACs by Webster soil was strongly influenced by the nature of the dominant exchangeable cation due to their effects on the sorptive characteristics of smectite clays present in this soil. The observed order of sorptivity of p-NCB as related to the saturating exchangeable cation could be explained by the hydration energy of exchangeable cations and its effect on the molecular-scale environment of the clay interlayers. Increasing the hydration energy of the exchanged cation decreases the extent of sorption of p-NCB by the clay-sized soil fraction and whole soil due to diminished effective size of adsorption domains between exchangeable cations, less favorable interactions between the exchange cation and NO_2 groups of sorbed NACs, and to greater interlayer separations which disallows solute dehydration. Exchangeable cation type did not strongly influence sorption of organic solutes by SOM. Thus in soils lacking smectite clays, sorption of nonionic organic solutes will probably not be strongly influenced by the type of exchangeable cation. Conversely, for organic solutes with polar functional groups (e.g., NO_2), and in soils containing smectite clays, solute uptake from water will be strongly influenced by the type of exchangeable cation(s) present.

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CHAPTER 2

AVAILABILITY OF CLAY SURFACES IN SOILS FOR ADSORPTION OF ORGANIC CONTAMINANTS

ABSTRACT

In soil, clay and soil organic matter (SOM) are usually intimately associated with each other. Clay surface coverage by SOM may limit the efficacy of the clay mineral fraction for the sorption of organic contaminants and pesticides in soil. Accordingly, one would predict that the sorption of such solutes by soil might differ from the summation of their sorption to the soil's isolated components. Two methods were used to assess the availability of clay surfaces in a Webster soil for sorption of p-nitrocyanobenzene (p-NCB), a solute known to be strongly sorbed by smectite clays. One method offered earlier by Karickhoff (1984) involves the summation of the sorption of p-NCB to SOM and swelling clays. In order to determine the fractional availability of the clay surfaces (i.e., the fraction of the clay mineral surface available for sorption within soil, f_a) for p-NCB sorption utilizing Karickhoff's equation, several assumptions must be made and/or procedural difficulties overcome in the determination of each term of the equation. We developed an alternative approach for determining f_a that alleviates these methodological limitations. Preliminary results reveal good agreement between f_a values obtained from both methods of analysis for p-NCB but not diuron sorption. Generally, for p-NCB sorption, f_a values varied between 0.55 and 0.71. For diuron sorption, using our alternative equation for data analysis, f_a values varied between 0.28 and 0.47. This

suggests that organic matter does suppress sorption of p-NCB and diuron by Webster A soil by 29 to 45% and 53 to 72%, respectively.

INTRODUCTION

Nitroaromatic compounds (NACs) are commonly used as pesticides, explosives, intermediates in the synthesis of dyes, ammunition, and solvents. Their uses have resulted in contamination of soils, sediments, surface waters, and aquifers. Understanding NAC mobility and reactivity in the environment is needed to accurately predict their environmental fate. Clay minerals and soil organic matter (SOM) are generally considered the two most active soil components in the sorption of aqueous phase organic contaminants such as NACs. For compounds with functional groups (e.g. NO_2) capable of engaging in specific interaction with clays, adsorption to soil clays may occur to a greater extent than to SOM (Sheng et al., 2001; Sheng et al., 2002).

Significant sorption of NACs from water by clays, particularly smectites, is well documented. The high affinity of NACs for smectites has been attributed to electron withdrawing properties of the NO_2 group which may promote formation of electron donor-acceptor complexes (Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1997), and/or complexation of the NAC with the exchangeable cations on the clay (Boyd et al., 2001; Johnston et al., 2001, 2002; Sheng et al., 2002; Li et al., 2003). Sorption of NACs by smectites is strongly influenced by the nature of the exchangeable cation. Monovalent cations with comparatively low hydration energies (e.g., K^+) manifest much higher NAC sorption than more strongly hydrated mono- or divalent cations (e.g. Na^+, Mg^{2+}, Ca^{2+}). In addition, the increasing number of NO_2 groups, a planar molecular structure, and the absence of "bulky" substituents (Haderlein et al., 1996; Haderlein and Schwarzenbach, 1993; Sheng et al., 2002; Johnston et al., 2001; Li et al., 2003) promote NAC-clay interactions.

The extent of interaction of NACs with clay minerals may, however, be limited by the availability of the clay sorption sites within soil. Soil organic matter may obscure clay surfaces hence reducing the efficacy of the clay mineral fraction for the adsorption of NACs. Organic matter associated with clays is known to facilitate aggregate formation through cohesion of clay and/or clay-humus complexes into larger particles through H-bonding, coordination with polyvalent cations, and/or cementation or encapsulation (Stevenson, 1994). The extent to which the clay surfaces in any soil are coated by organic substances depends on the nature and amount of clay and SOM (Stevenson, 1994). Using scanning electron microscopy Laird et al. (2001a) observed, in the clay fraction of a Webster Ap soil from which SOM was not removed (i.e., whole clay fraction), both large aggregated structures (5-20 μm) and discrete particles (0.5-2 μm). They described the surfaces as having a diffuse-porous appearance and suggested that the surfaces were covered with humic materials. Scanning electron micrographs of the clay fraction treated with H_2O_2 to remove humic materials showed the presence of numerous individual mineral grains, only a few small aggregates and no large aggregates (Laird et al., 2001b). This suggested the involvement of humic substances in aggregate formation and the destruction of aggregates through H_2O_2-treatment. Laird et al. (1994; 2001b) found that the SOM associated with the clay fraction of a Webster Ap soil was dependent on the particle size of the soil clay fractionate. The fine clay fraction (<0.02 μm) was relatively enriched with aliphatic carbon, bound hydroxyls, and amines and was more humified based on the C/N ratio of the associated SOM (Laird et al., 2001a), as compared to the coarse (0.2-2.0 μm) and medium (0.02-0.2 μm) clay fractions.

The influence of organic components on the sorptive properties of the soil clay mineral fraction is still not fully understood despite numerous studies on organic compound sorption by synthetic clay-organic complexes. Li et al (2003) did not find any measurable impact of humic acid (HA) on NAC sorption by K^+-saturated HA-smectite complexes. However for Ca^{2+}-saturated HA-smectite complexes, HA appeared to obscure some mineral surfaces resulting in reduced sorption of 4,6-dinitro-o-cresol. Pusino et al. (1992) compared experimentally measured sorption coefficients of metolachlor by a HA-clay complex with those estimated assuming an independent adsorptive behavior by the clay and humic components. They found that the estimated K_d values were higher than the experimental values indicating that the humics reduced the availability of the clay surfaces for sorption. Pusino et al. (1994) found reduced sorption of triclopyr by HA-clay complexes compared to pure clay systems. Celis et al. (1999) found that HA coating on clay-ferrihydrite binary complexes reduced the sorption of 2,4-dichlorophenoxyacetic acid. Celis et al. (1997) found reduced sorption of thiazafluron by Ca^{2+}-Wyoming montmorillonite when coated with HA. Removal of the HA from the clay surface resulted in increased sorption of thiazafluron. Celis et al. (1999), Celis et al. (1998) observed decreased specific N_2 BET surface areas of synthetic HA-clay complexes compared to corresponding clays devoid of HAs. They proposed that the HAs were associated with the external surfaces of the clay.

Karickhoff (1984) presented an equation that could be used to experimentally assess the availability of soil clay surfaces for sorption of nonionic organic contaminants (NOCs). This equation summed NOC sorption to clay and SOM at a specific relative concentration, which incorporated the potentially reduced availability of sorption sites on clays in whole soil:

$$Q_{\text{whole soil}} = Q_{min} + Q_{som} = (f_a * K_{min} * C_e * f_{min}) + (K_{om} * C_e * f_{om}) \qquad [1]$$

where $Q_{\text{whole soil}}$ is the total solute mass sorbed per unit mass of whole soil (mg g^{-1}), Q_{min} and Q_{som} are the mineral fraction (i.e., soil without SOM)-sorbed and SOM-sorbed solute per unit mass of sorbent, respectively, C_e is the aqueous solute equilibrium concentration, and K_{min} and K_{om} represent the sorption coefficients of the solute by the soil fraction from which SOM was removed (mineral fraction) and SOM, respectively, f_{min} and f_{om} are the fractional mineral fraction and SOM contents of soil, and f_a represents the fractional availability of sorption sites on the clay in whole soil (i.e. the fraction of the sorptive surfaces that are available in unfractionated soil). Fractional availability can range from 0 (unavailable) to 1 (100% available). Karickhoff (1984) equates the mineral fraction with the clay fraction owing to the high surface area of smectites in the clay fraction. Note that equation 1 assumes that the clays and SOM are the only sorptive materials in soil. This is probably a good assumption for NACs, which exhibit insignificant sorption to Al or Fe (hydr)oxides, carbonates, or quartz (Haderlein and Schwarzenbach, 1993).

A few studies have shown how the extent of sorption of NOCs to soil or HA-clay complexes does not equate to the sum of its individual components (Pusino et al., 1992; Celis et al., 1997; Liu et al., 2002). However, there appear to be no studies that have attempted to experimentally quantify the extent to which clay surfaces are available for sorption in soil. The objective of this study was to quantify the fractional availability of mineral surfaces for sorption of NACs by whole soil using the Karickhoff equation and our newly proposed method of data analysis (described below).

EXPERIMENTAL SECTION

The A horizon of a Webster clay loam (fine loamy, mixed, mesic Typic Haplaquoll) was air-dried and sieved to remove coarse fragments (>2 mm). The soil was fractionated by standard procedures (Kunze & Dixon, 1986). Carbonates (CO_3) and SOM were sequentially removed from each soil horizon. Carbonates were removed by stirring the soil with 0.5*N* sodium acetate acidified to pH 5 while heating at 80°C, followed by the removal of SOM with 30% H_2O_2 at 80°C (denoted OM-removed soil). Homoionic soils and soil fractions were prepared by washing the soils with 200 ml aliquots of 0.1*M* solution of KCl or $MgCl_2$ overnight, thereafter centrifuging and discarding the supernatant. This procedure was repeated four times. The soils were then washed with 200 ml aliquots of Milli-Q deionized H_2O, thereafter centrifuged and the supernatant tested with $AgNO_3$. The procedure was repeated until a negative Cl^- ion test with $AgNO_3$ was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1°C) until used. Para-nitrocyanobenzene (p-NCB) was purchased from Aldrich Chemical Company (Milwaukee, Wisconsin) with a purity of 97% and used as received. Its water solubility (S_w) at 25°C is 1650 mg L^{-1} and its log K_{ow} value is 1.19 (Howard and Meylan, 1997). Diuron (1,1-dimethyl-3-(3,4-dichlorophenyl)urea was purchased from Aldrich Chemical Company (Milwaukee, Wisconsin) with a purity of 98% and used as received. Its S_w at 25°C is 42 mg L^{-1} and its log K_{ow} value is 2.75 (Howard and Meylan, 1997).

The clay-sized particles (<2.0 μm) were obtained from soil using wet sedimentation after removal of CO_3, SOM and free iron oxides (FeO_x) (Whittig & Allardice, 1987), then saturated with K^+ and Mg^{2+} as described above. Dispersed suspensions of Mg^{2+}- and K^+-

saturated clay-sized particles were dropped on to glass slides to produce clay films. The clay films were then treated by air-drying, heating at 500°C, and ethylene glycol. X-ray diffraction patterns of the treated clay films were used to identify the clay mineralogy of the clay-sized fraction of the soil (Whittig & Allardice, 1987). The clay samples were analyzed using CuKα radiation and a Philips APD 3720 X-ray diffractometer (Philips Electronic Instruments, NJ).

Semi-quantitative estimates for the amount of smectite in the unfractionated Webster A soil was attempted using the measured cation exchange capacity (CEC) of the unfractionated soils using the ammonium acetate method (Sumner and Miller, 1996) (Michigan State University (MSU) Soil Testing Laboratory), and an average CEC of a soil smectite and SOM of 80 and 160 cmol kg^{-1}, respectively, using the equation:

$$CEC = (160 \text{ cmol kg}^{-1})(f_{om}) + (80 \text{ cmol kg}^{-1})(f_{cm}) \quad [2]$$

where f_{om} and f_{cm} are the fractional SOM and smectite clay contents of the soil. The calculation assumed that the CEC of the soil originated solely from SOM and soil smectites. By comparing the X-ray diffraction peak areas associated with the non-smectite minerals to the smectite peak, we estimated the relative fractional amounts of each non-smectite non-quartz mineral present in the clay-sized fraction as a fraction of the smectite peak (illite/mica, 0.125; kaolinite, 0.125). Multiplying the percent smectite in the soil obtained using equation (2) (e.g., 24%) by the relative fractional amount of each non-smectite mineral determined from the relative peak areas in the X-ray diffraction graph, we calculated the amount of non-smectite minerals (e.g. illite/mica, 3%; kaolinite, 3%). We subtracted the estimated smectite content (e.g. 24%) from the total clay content (e.g. 31%) to obtain the amount of non-smectite minerals (e.g. 7%) and compared this value to the sum of the non-smectite minerals estimated using the peak areas (3% + 3%).

Removal of SOM with H_2O_2 may result in the liberation and/or oxidation of metals previously bound to SOM which could result in the formation of sesquioxides. The potential contribution of sesquioxides to p-NCB sorption was assessed. For this purpose ferric hydroxide was prepared by mixing $FeCl_3$ with KOH; KOH was present in excess of stoichiometric quantities needed to react with all of the ferric ions in the system. The $Fe(OH)_3$ suspension was centrifuged for 30 min at 4068*g*, the supernatant discarded and the pellet washed five times with 200 ml portions of 0.1*M* KCl. The $Fe(OH)_3$ was then washed with deionized H_2O to a negative Cl^- ion test with $AgNO_3$, freeze-dried and stored at room temperature (23 ± 1°C). X-ray diffraction analysis was performed on an air-dried film of $Fe(OH)_3$ prepared by using a disposable pipette to drop a dispersed suspension of $Fe(OH)_3$ on to a glass slide.

The effect of exchangeable cation type on sorption by SOM was evaluated using either organic soils relatively devoid of mineral matter or a mineral soil devoid of swelling clays (i.e. smectites) implicated in the sorption of NACs (Boyd et al., 2001; Haderlein and Schwarzenbach, 1993). The sorbent used was the Pahokee peat (euic, hyperthermic Lithic Medisaprist) (Soil Survey Staff, NRCS). The peat was purchased from the International Humic Substances Society (BS103P) (Denver, Colorado). Sorption isotherms for diuron by these soils were obtained using the batch equilibrium technique described above. These soils were saturated with K^+ or Mg^{2+} to evaluate the effect of cation type on sorption of diuron.

Sorption isotherms for p-NCB sorption by K^+- and Mg^{2+}-saturated unfractionated soils and SOM-removed soils as well by $Fe(OH)_3$ were obtained, in triplicate, using a batch equilibrium technique. This involved adding aqueous solutions of p-NCB (1-42 mg L^{-1}) or diuron (1-30 mg L^{-1}) over a range of initial aqueous concentrations (C_i) to a known mass of soil. The p-NCB and diuron solutions were prepared in 0.05*M* KCl or $MgCl_2$ corresponding to the saturating cation. Five ml of the solute solutions were pipetted into 7.5 ml borosilicate glass vials containing various amounts of sorbent (between 0.2 and 0.4 g for soil). The vials were rotated continuously for 24 hours in the dark at room temperature (23 ± 1°C); preliminary studies showed equilibrium was reached within 24 hours. The liquid and solid phases were separated by centrifugation at 4068*g* for 30 min, and the solute's equilibrium concentration in water (C_e) was determined using a Perkin-Elmer high performance liquid chromatograph (HPLC) (Perkin-Elmer, Norwalk, CT) consisting of a binary LC pump 250 with a series 200 autosampler and a uv-visible detector set at λ 254 nm for p-NCB and λ 248 nm for diuron. A platinum EPS C18 column from Alltech Associates was used (Deerfield, IL). The mobile phase was an isocratic mixture of methanol (HPLC grade) and Millipore Milli-Q (Billerica, Massachusetts) deionized water (methanol: water ratio of 55:45 for p-NCB and 75:25 for diuron) with a flow rate of 1.0 ml min^{-1}. The amount of solute sorbed was calculated as the difference between the initial aqueous concentration (C_i) and the final aqueous concentration (C_e). Compound recoveries in control vials without sorbent were above

95% and not used to adjust the data. The extent of solute sorption was quantitated by fitting the data to the Freundlich equation, $Q=K_fC_e^n$, where Q is the sorbed solute concentration per unit mass of the sorbent (mg g^{-1}), K_f is the sorption coefficient, n is a constant related to the isotherm curvature (concave or convex). The Michigan State University (MSU) Soil Testing Laboratory determined the SOM content of the unfractionated (3.87% OM) and OM-removed soil (0.23% OM) using dry combustion and a Leco carbon analyzer (St. Joseph, Michigan) (Nelson and Sommers, 1996), and the gravimetric clay content (31%) of the Webster soil by the hydrometer method (Gee and Bauder, 1986).

Data Analysis

Calculation of f_a values

Each sorption isotherm data set was fitted to the Freundlich equation, with an $r^2 > 0.9$ in all cases. Using the K_f and n values obtained, the Q value was calculated for four equilibrium aqueous phase concentrations, 5, 10, 15, 20 mg L^{-1}. Using either the Karickhoff [1] or our alternative equation (presented below), four corresponding f_a values were obtained for each soil (i.e., one for each concentration). Standard deviations of each f_a value associated with each concentration were calculated using error propagation procedures. For the Karickhoff equation, only the K^+-saturated system was used because preliminary results indicated that this system provides sufficient difference in sorption between the unfractionated and OM-removed soils to facilitate accurate determination of f_a values. The independently obtained K_{om} values utilized when analyzing f_a by equation [1] were previously measured as discussed in Chapter 1.

Estimation of degree of OM mineral surface coverage

The maximum percent of the smectite clay surface covered by the SOM was estimated using Lagaly's formula area per carbon atom of 5.67 $Å^2$ (Lagaly, 1981), a percent carbon in SOM of 62% (Stevenson and Cole, 1999), an average smectite surface area of 750 $m^2 g^{-1}$ (Sposito, 1984), the estimated percent smectite in unfractionated soil, and the measured percent SOM in the unfractionated and OM-removed soil. 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 Webster A (WA) soil:

1g of WA has a surface area of OC = $((0.62 \times 0.0387)/12)(6.023 \times 10^{23})(5.67)(10^{-20})$ = 68.27 m^2,

1g of WA has a smectite clay surface area = (750×0.24) = 180 m^2, therefore

The maximum percent of smectite clay surface covered by OC = (68.27/180) = 38%.

Statistical Analysis

The sorption coefficient (K_f) and the constant related to the sorption isotherm curvature (n) were estimated using the Freundlich equation, $Q=K_fC_e^n$. Comparisons of sorption isotherms were made by comparing the K_f and n values for each soil-solute system using nonlinear regression in SAS (SAS Institute, 1999). A significant difference between isotherms was assigned when there was a significant difference between K_f and n or K_f values of compared isotherms (Laboski and Lamb, 2004).

RESULTS AND DISCUSSION

Sorption of p-NCB and diuron by $Fe(OH)_3$ was negligible (data not shown) and therefore sesquioxides are not expected to act as sorbents for p-NCB or diuron in whole soils. This is consistent with studies by Haderlein and Schwarzenbach (1993) who reported that NACs did not adsorb significantly to aluminum and iron (hydr)oxides, carbonates or quartz. In addition, Laird et al. (1994) found no indication of surface coatings of particles in the fine clay fraction of a Webster soil by free FeO_x.

Considering the two soil components responsible for NAC sorption by soils, SOM and swelling clays, sorption of NACs by SOM is not influenced by the nature of the saturating cation. We observed no statistically significant effect of exchangeable cation (K^+ and Mg^{2+}) on p-NCB sorption by peat, Houghton muck and Brookston loam soils or diuron sorption by peat. This was reflected in the observed proximity of the sorption isotherms for p-NCB sorption by K^+- and Mg^{2+}-saturated peat, Brookston loam and Houghton muck each normalized to the SOM content in each soil (Figure 2.1). These soils are composed of either predominantly SOM (peat and muck) or are devoid of clays known to sorb NACs (i.e. swelling clays) and therefore sorption in these systems is dominated by SOM. We also observed no statistically significant effect of exchangeable cation (K^+ and Mg^{2+}) on diuron sorption by K^+- and Mg^{2+}-saturated peat (Figure 2.2). These results provide evidence that sorption of p-NCB and diuron by SOM, in systems where sorption is dominated by SOM, is not strongly influenced by the saturating cation. This can be explained by sorption to SOM being a partition process (Chiou, 2002) and such a dissolution mechanism is not expected to be influenced by the

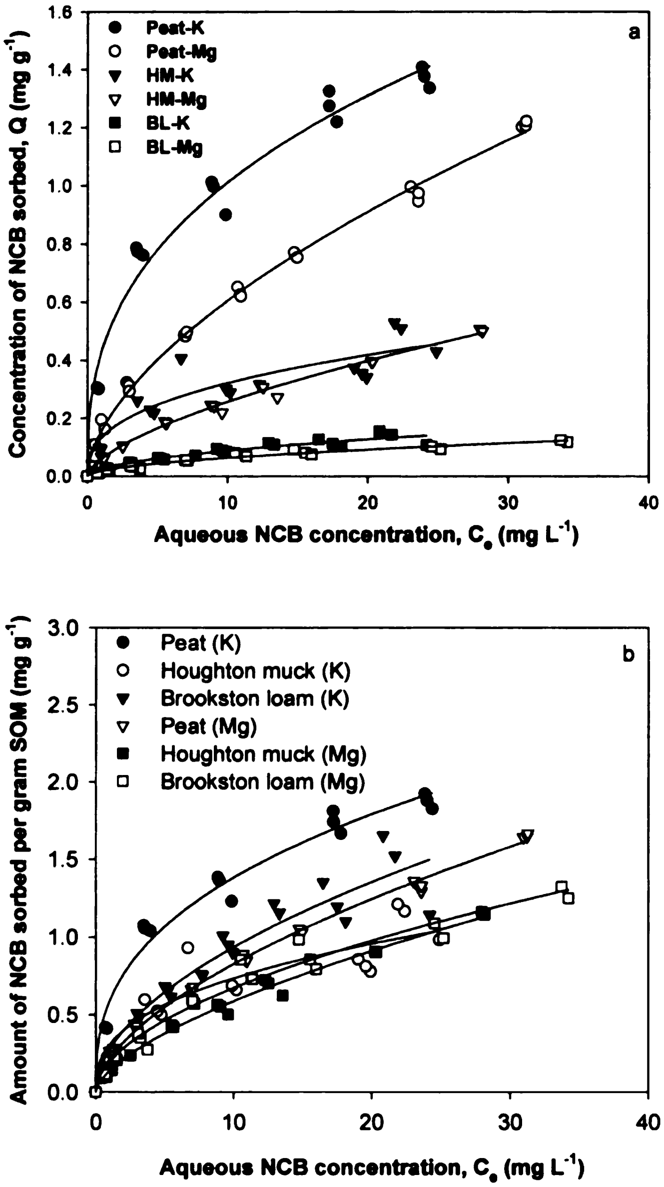

Figure 2.1. Adsorption isotherms for sorption of p-nitrocyanobenzene (p-NCB) by (a) K^+- and Mg^{2+}-saturated peat, Houghton muck, Brookston loam and (b) sorption isotherms normalized to amount of SOM in the soils.

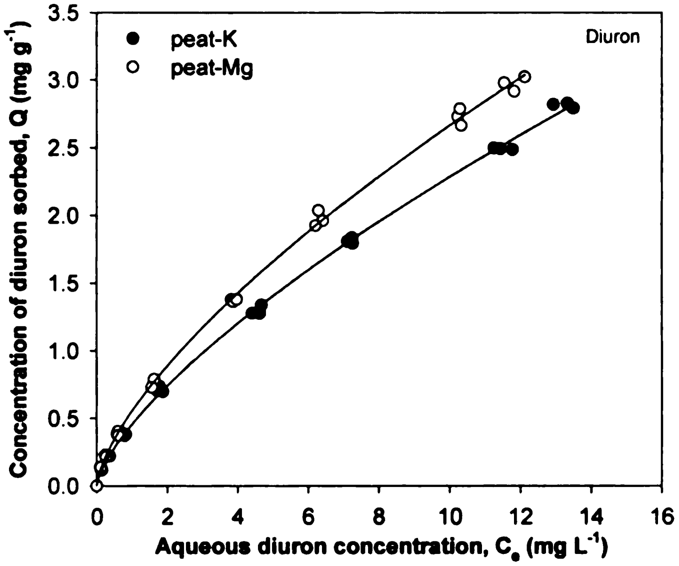

Figure 2.2. Adsorption isotherms for sorption of diuron by K^+- and Mg^{2+}-saturated peat, Houghton muck, Brookston loam.

saturating cation. It appears that any significant effects of cation saturation observed for p-NCB or diuron sorption to soil and soil fractions would result from the effect of cation saturation on the sorptive characteristics of the clay-sized mineral fraction and not the SOM. The clay types in the soil clay-sized fraction were identified as mica and/or illite, smectite, vermiculite, and kaolinite. This was consistent with the clay mineralogy reported by Laird et al. (1991) for a Webster soil.

Unfractionated and SOM-removed soils saturated with K^+ (K_f 0.0528 and 0.0922 L kg^{-1}; n 0.5983 and 0.5012, respectively) sorbed p-NCB to a much greater extent compared to Mg^{2+}-saturated soils (K_f = 0.0067 and 0.0007 L kg^{-1}; n = 0.6219 and 0.9033, respectively) (Figure 2.3). These results are consistent with several studies that report stronger sorption of NACs by reference clays and soils saturated with cations of relatively low hydration energies (e.g. K^+, Cs^+) compared to that by sorbents saturated with cations of relatively higher hydration energies (e.g. Na^+, Ca^{2+}, Mg^{2+}) (Li et al., 2003; Sheng et al., 2002; Haderlein et al., 1996; Haderlein and Schwarzenbach, 1993; Weissmahr et al., 1997, 1999; Johnston et al., 2002). Cations of larger hydrated radii (e.g., Mg^{2+}) occupy a larger surface area of the clay interlayer thereby diminishing the effective size of adsorption domains between cations and facilitating less NAC sorption compared to clays saturated with cations of smaller hydrated radii (e.g., K^+). In addition, hydration water associated with cations having smaller enthalpies of hydration (e.g., K^+, ΔH_{hyd} -314 kJ mol^{-1}) are less strongly held compared to water molecules hydrating cations with larger enthalpies of hydration (e.g., Mg^{2+}, ΔH_{hyd} -1258 kJ mol^{-1}). Large hydration spheres and strongly held waters of hydration would act to inhibit the direct

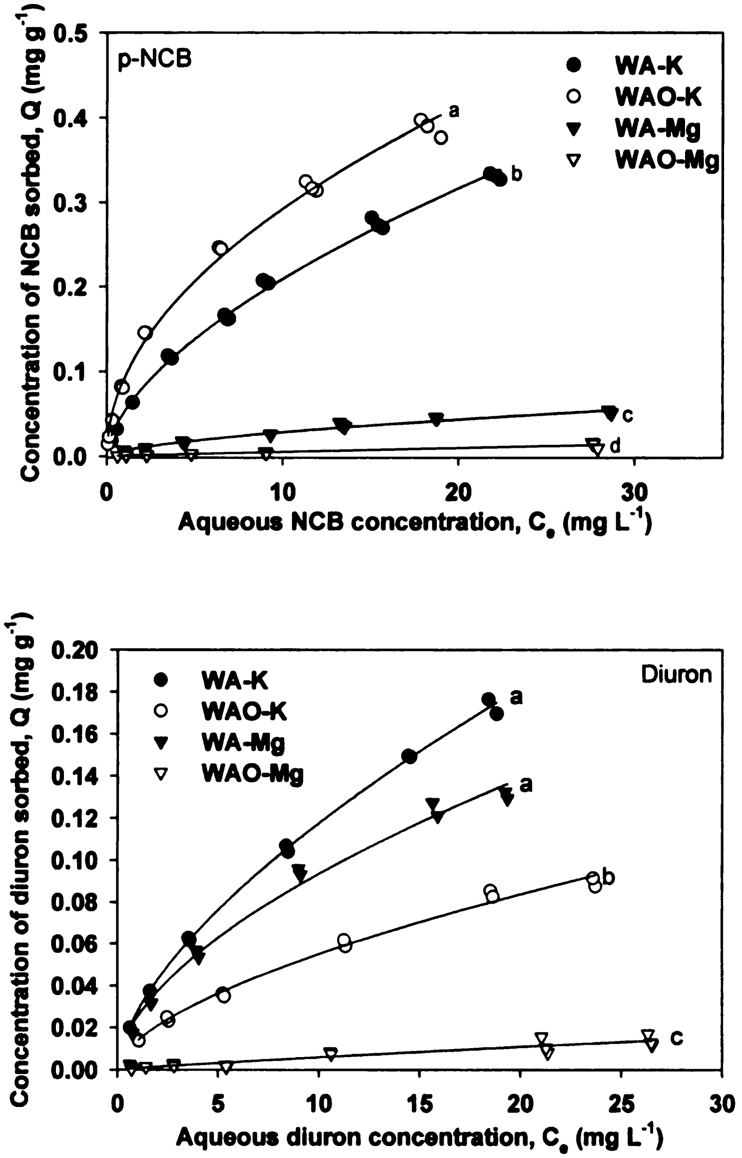

Figure 2.3. Adsorption isotherms for p-nitrocyanobenzene (p-NCB) and diuron sorption by K^+- and Mg^{2+}-saturated by Webster A soil (whole soil, WA, and soil from which SOM was removed, WAO).

Isotherms with the different letters are statistically different at $p < 0.05$.

interaction of NO_2 groups with the interlayer cation (Boyd et al., 2001; Johnston et al., 2001, 2002; Li et al., 2004). Li et al. (2004) calculated an enthalpy of interaction between the NAC and the exchangeable cation. This calculation accounted for the associated processes of water removal required (an energy consuming process) for direct interaction between the cation and the NAC, and partial (80%) dehydration of the solute in the clay interlayers (see below). The interaction energies between K^+-SWy-2 and 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3-dinitrobenzene (1,3-DNB) and 1,4-DNB were -99, -69, and -73 kJ mol^{-1}, respectively (Li et al., 2004). The calculated enthalpies of interaction between Ca^{2+}-exchanged SWy-2 for these compounds ranged from -30 to -38 kJ mol^{-1} (Li et al., 2004). These interaction enthalpies reflect greater NAC sorption by the less strongly hydrated system (e.g. K^+) than by the more strongly hydrated system (e.g., Ca^{2+}). Previously, K^+-saturated smectites were reported to manifest interlayer distances of ~ 3 Å (d_{001} ~ 12.3 Å) in the presence of sorbed NACs (Li et al., 2004; Sheng et al., 2002; Sheng et al., 2001); a distance which closely matches the width of p-NCB and appears optimal for sorption of planar NACs. That is, through simultaneous interactions with the opposing siloxane sheets the adsorbed molecules are largely dehydrated, an energetically favorable process (Li et al., 2004). Smectites saturated with cations such as Na^+, Ca^{2+}, or Mg^{2+} always swell to $\geq$ 15 Å in the presence of bulk water. The energy requirement for compressing the interlayers, and dehydrating the solute, may be larger than the energy gain from solute dehydration thereby making the overall process energetically less favorable. Therefore Mg^{2+}-saturated systems exhibit lower NAC sorption than K^+-saturated systems (Figure 2.3).

Sorption of p-NCB by the Mg^{2+}-saturated soil was greater than that by the Mg^{2+}-saturated SOM-removed soil (Figure 2.3). Removal of SOM may liberate some clay surface sites, but, as discussed above, Mg^{2+}-exchanged clays have low affinities for aqueous phase NACs. Hence, in the Mg^{2+}-saturated SOM-removed soil, clays are relatively inactive as sorbents for sorption of p-NCB. Rather, SOM is the principal sorbent phase hence with its removal p-NCB sorption decreases (Figure 2.3).

The K^{+}-saturated OM-removed soils statistically sorbed more p-NCB than the K^{+}-unfractionated soils (Figure 2.3). This indicates that the presence of SOM in whole soil reduces p-NCB sorption. Although SOM acts as a sink for p-NCB, its removal may liberate clay sorptive surfaces which could serve as additional sites for p-NCB sorption. Additional sorption of p-NCB by these unobscured sites apparently exceeds that afforded by SOM so that the net result of SOM removal is to increase p-NCB sorption compared to that by whole soil. Suppressed sorption by OM suggests f_a values (i.e. the fraction of the sorptive surfaces that are available in unfractionated soil) less than 1. To quantitatively assess f_a, we used two approaches; the Karickhoff equation [1] and an alternative equation introduced herein. One potential difficulty with the determination of f_a using Karickhoff's equation [1] is the variation in the K_{om} values for the test solute and its potential influence on the calculated f_a value. Kile et al. (1995) reported a variation of a factor of 2 to 3 for K_{oc} (organic carbon normalized partition coefficient) values for dichlorobenzene and carbon tetrachloride for a series of soils and sediments. For solutes that sorb preferentially to SOM the effect of the variation in K_{om} values may be large compared to that for solutes that preferentially sorb to smectites (e.g., NACs). In addition, in order to determine the isolated SOM contribution to NAC sorption by a specific soil, a surrogate for that SOM must be used as a sorbent since the SOM cannot be isolated in total or without alteration. This difficulty introduces error into the equation since K_{om} is not obtained by direct measurement on the system being analyzed.

An alternative equation to the Karickhoff equation [1] is proposed that eliminates reliance on K_{om} to determine clay surface fractional availability, f_a, in whole soils. It involves measuring the difference in NAC sorption between sorbent systems whose cation exchange capacity (CEC) was saturated with different cations. This method is based, in part, on the observation that NAC sorption by SOM whose CEC is exchanged with various cations was unaffected by the nature of the saturating cation (Figure 2.1 as determined in Chapter 1). Using peat, Brookston loam and Houghton muck, each saturated with K^+ or Mg^{2+} ions, as the sorbents for p-NCB, we determined that p-NCB sorption by the corresponding K^+- and Mg^{2+}-saturated sorbent did not differ (Figure 2.1). The method is also based on the observation that NAC sorption by clay *is* strongly dependent on the cation saturating the clay exchange sites (Sheng et al., 2002; Johnston et al., 2001, 2002; Li et al., 2003; Haderlien et al., 1996; Haderlein and Schwarzenbach, 1993; Boyd et al., 2001). For example, K^+-smectites have high affinities for NACs while Mg^{2+}-smectites do not (Haderlein et al., 1996; Haderlein and Schwarzenbach, 1993; Johnston et al., 2001; Boyd et al., 2001; Sheng et al., 2002). We therefore propose if two experiments are done in which NAC sorption is measured for a soil saturated with K^+ versus Mg^{2+} cations, then from equation 1:

$$Q_{\text{whole soil, K sat}} - Q_{\text{whole soil, Mg sat}} = \{f_a * \{(K_{\text{min, K sat}} * C_e * f_{\text{min}}) - (K_{\text{min, Mg sat}} * C_e * f_{\text{min}})\}\} + \{(K_{\text{om, K sat}} * C_e * f_{\text{om}}) - (K_{\text{om, Mg sat}} * C_e * f_{\text{om}})\} \quad [2]$$

where $Q_{\text{whole soil, K sat}}$ and $Q_{\text{whole soil, Mg sat}}$ are the total contaminant masses sorbed by whole soil whose CEC is saturated with either K^+ and Mg^{2+}, respectively; $K_{\text{min, K sat}}$ and $K_{\text{min, Mg sat}}$ represent the partition coefficients normalized to soil fraction from which SOM was removed (mineral) for sorbent systems saturated with either K^+ and Mg^{2+}, respectively; $K_{\text{om, K sat}}$ and $K_{\text{om, Mg sat}}$ represent the partition coefficients normalized to SOM for sorbent systems saturated with either K^+ and Mg^{2+}, respectively; f_{min} is the fration of the whole soil remaining after removal of bulk SOM; f_{om} is the fractional SOM contents of soil; f_a represents the fractional availability of clay surfaces in whole soil.

Since $K_{\text{om, K sat}} = K_{\text{om, Mg sat}}$ then:

$$Q_{\text{whole soil, K saturated}} - Q_{\text{whole soil, Mg saturated}} = \{f_a * \{(K_{\text{min, K sat}} * C_e * f_{\text{min}}) - (K_{\text{min, Mg sat}} * C_e * f_{\text{min}})\}\} \quad [3]$$

Equation [3] eliminates the K_{om} and f_{om} terms, which are needed in the Karickhoff [1] equation. Within both the Karickhoff [1] and alternative [3] equations, we accounted for the extent of p-NCB sorption by the residual SOM associated with the SOM-removed fraction. We determined that SOM remaining after removal of bulk SOM sorbs p-NCB similarly to that of bulk SOM. However, in the alternative equation, the effect of K^+-saturated residual SOM on p-NCB sorption cancels out that of Mg^{2+}-saturated residual SOM. When K^+-saturated peat, Houghton muck or Brookston loam were used as the surrogate sorbent for determining the organic contribution in equation [1], the f_a values did not differ greatly (Table 2.1). When Mg^{2+}-saturated sorbents were used as the SOM

Table 2.1. Calculated f_a values for p-nitrocyanobenzene (p-NCB) sorption by Webster A soil using Karickhoff's equation [1] (using p-NCB sorption by K^+- and Mg^{2+}-saturated peat, Houghton muck and Brookston loam to determine the K_{om} term), average f_a values for K^+- and Mg^{2+}-saturated sorbents and our alternative equation [2].

Equation	**Concentration ($mg\ L^{-1}$)**	**f_a values (K^+-saturated)**	**f_a values (Mg^{2+}-saturated)**	**Average f_a values**
Karickhoff (peat)	5	0.55 (0.02)	0.59 (0.02)	0.57 (0.02)
	10	0.60 (0.02)	0.63 (0.02)	0.62 (0.02)
	15	0.63 (0.03)	0.66 (0.03)	0.65 (0.03)
	20	0.65 (0.03)	0.68 (0.03)	0.67 (0.03)
Karickhoff (Houghton muck)	5	0.60 (0.02)	0.62 (0.02)	0.61 (0.02)
	10	0.65 (0.02)	0.66 (0.02)	0.66 (0.02)
	15	0.69 (0.03)	0.69 (0.03)	0.69 (0.03)
	20	0.71 (0.03)	0.71 (0.03)	0.71 (0.03)
Karickhoff (Brookston loam)	5	0.58 (0.02)	0.61 (0.02)	0.60 (0.02)
	10	0.62 (0.02)	0.65 (0.02)	0.64 (0.02)
	15	0.64 (0.03)	0.68 (0.03)	0.66 (0.03)
	20	0.66 (0.03)	0.70 (0.03)	0.68 (0.03)
Alternative	5	0.61 (0.02)	0.61 (0.02)	0.61 (0.02)
	10	0.65 (0.02)	0.65 (0.02)	0.65 (0.02)
	15	0.68 (0.03)	0.68 (0.03)	0.68 (0.03)
	20	0.70 (0.03)	0.70 (0.03)	0.70 (0.03)

Across each concentrations, f_a values calculated using K^+-saturated Karickhoff-peat < Karickhoff-BL < Karickhoff-HM = Alternative ($p \leq 0.05$). The f_a values at each concentration were statistically different (5ppm < 10ppm< 15ppm < 20ppm) ($p < 0.05$). Standard deviations in parentheses.

surrogate, f_a values did not differ greatly from those determined using the K^+-saturated sorbents (Table 2.1). This is a direct manifestation of our determination that, on a unit SOM basis, the sorption isotherms for p-NCB sorption by K^+- and Mg^{2+}-saturated peat, Houghton muck and Brookston loam were similar (Figure 2.1). The assumption is that these soils could be used to determine the isolated SOM contribution of Webster soil for sorption of p-NCB. Comparing the f_a values for p-NCB sorption derived using the Karickhoff [1] and alternative [3] equation, the values did not differ greatly (Table 2.1). This is because the SOM term in the Karickhoff equation is very small (only ~20% of whole soil p-NCB sorption at $C_e = 10$ mg L^{-1}) compared to the mineral fraction term. As noted earlier, NACs sorb to a greater extent to clays than to SOM (Sheng et al., 2001) and therefore the organic contribution and, by extension the error associated with the term, is small, when using NACs as the probe solute to estimate f_a values.

For diuron, the K^+-saturated OM-removed soil (K_f, 0.0137 L kg^{-1}; n, 0.6043) sorbed less than K^+-saturated unfractionated soil (K_f, 0.0277 L kg^{-1}; n, 0.6274) for Webster A soil (Figure 2.2). This demonstrates that SOM enhanced sorption of diuron by unfractionated soil and that removal of SOM diminished sorption in excess of any enhanced sorption that might result from increasing mineral surface availability. Sheng et al. (2001) observed greater sorption of diuron to Houghton muck soil (representing SOM) compared to K^+-SWy-2 smectite. Parker and Rate (1998) 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. Murphy et al. (1990) found increased sorption of hydrophobic compounds (e.g., anthracene (log K_{ow} 4.45)) by hematite and kaolinite coated with natural humic substances compared to the pure minerals. Sanchez-Martin and Sanchez-Camazano (1991) observed that the removal of organic matter from soils resulted in less chloridazon (log K_{ow} 1.14) sorption compared to whole soil. Cox et al. (1998) reported similar findings for imidacloprid (log K_{ow} 0.57) sorption by soil clay fractions and model sorbents. Li et al. (2003) observed enhanced dichlobenil (log K_{ow} 2.74) sorption by humic acid (HA)-modified Ca^{2+}-smectites (SWy-2 and SAz-1) compared to that by unmodified clays. Celis et al. (1998) observed a similar trend for atrazine (log K_{ow} 2.51) sorption by Ca-SWy-HA complexes. Pusino et al. (1992) observed decreased sorption of metolachlor (log K_{ow} 3.13) sorption by a sandy loam and a loamy sand soil after removal of SOM. Hence, the sorption of diuron by the liberated sorption sites may not exceed that by the removed SOM and thus overall sorption decreases (Rebhun et al., 1992).

For diuron, using equation [1], negative f_a values were calculated using K^+- and Mg^{2+}-saturated peat to determine the SOM contribution to solute sorption (Table 2.2). In contrast, positive f_a values were obtained when calculated using our alternative equation [2] (Table 2.2). The negative f_a values obtained using equation [1] point out an inherent weakness in the data analysis suggested by Karickhoff (1984) especially for compounds/soils where SOM is the dominant sorptive component. We suggest that because of the sensitivity of the Karickhoff equation to the accurate determination of SOM content and K_{om}, the alternative equation [2] is more reliable for f_a determinations. This is particularly true for compounds that sorb to SOM to a greater extent than to

Table 2.2. Calculated f_a values for diuron sorption by Webster A soil using Karickhoff's equation [1] (using diuron sorption by K^+- and Mg^{2+}-saturated peat to determine the K_{om} term), average f_a values for K^+- and Mg^{2+}-saturated sorbents and our alternative equation [2].

Equation	**Concentration (mg L^{-1})**	**f_a values (K^+-saturated)**	**f_a values (Mg^{2+}-saturated)**	**Average f_a values**
Karickhoff (peat)	5	-0.06 (-0.05)	-0.46 (-0.04)	-0.26 (-0.05)
	10	-0.20 (-0.03)	-0.64 (-0.04)	-0.42 (-0.04)
	15	-0.30 (-0.04)	-0.77 (-0.06)	-0.53 (-0.05)
	20	-0.38 (-0.06)	-0.86 (-0.08)	-0.62 (-0.07)
Alternative	5	0.47 (0.07)	0.47 (0.07)	0.47 (0.07)
	10	0.40 (0.05)	0.40 (0.05)	0.40 (0.05)
	15	0.34 (0.04)	0.34 (0.04)	0.34 (0.04)
	20	0.28 (0.05)	0.28 (0.05)	0.28 (0.05)

smectite clays, such as diuron (log K_{ow} 2.68*)* (Sheng et al., 2001; Nkedi-Kizza et al., 1983). Our results indicate that 29% to 45% (i.e., ca. 37%) of clay surfaces are obscured from p-NCB sorption by SOM in Webster A soil. The estimate for the clay basal surface coverage by the 3.87% SOM in the Webster A soil, which included the swelling clay interlayer surface area and hence incorporates the SOM coverage of interlayer basal surfaces, was 38%. The similarity of the surface coverage estimate (38%) to the complement of the average f_a value suggests that SOM covers the basal surfaces of the soil clays. We know that p-NCB and other NACs (Sheng et al., 2001, 2002; Li et al., 2003), as well as organic cations such as hexadecyltrimethylammonium (Jaynes and Boyd, 1991a), tetramethylammonium (Lee et al., 1989, 1990), and trimethylphenylammonium (Jaynes and Boyd, 1991b), intercalate between clay layers when they sorb to smectites so SOM may be occupying those interlayer sites. Obscuration of clay surfaces may also result from aggregate formation facilitated by SOM through the bridging of clay particles or reduction of repulsive forces between clay particles (Stevenson, 1994; Walker and Crawford, 1968). When diuron sorption data were analyzed using equation [2], the f_a values ranged from 0.28-0.47 (i.e. ca. 0.38) indicating that, for diuron sorption, 53% to 72% of clay surfaces are obscured by SOM in Webster A soil.

CONCLUSION

Our study reveals that the association of SOM with clay suppressed sorption of p-NCB and diuron by whole soil by at least 29 to 45% and at least 53 to 72%, respectively. In addition, the method of sorption data analysis proposed by Karickhoff (1984) for determining clay surface availability in whole soil may not be applicable for analyzing diuron sorption. Fate and transport models that utilize sorption parameters based on the additive effect of reference clay and humic material sorption may deviate from reality and may overestimate the amount of NAC sorbed.

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CHAPTER 3

SORPTION OF P-NITROCYANOBENZENE TO SOILS: THE RELATIONSHIP BETWEEN SOIL PROPERTIES AND AVAILABILITY OF CLAY SURFACES

ABSTRACT

The swelling clay and soil organic matter (SOM) contents of soils tend to correlate, yet they are typically considered to be independent sorbent phases. The inter-association of SOM with soil clays (particularly swelling clays) modified the efficacy of the soil clays for the sorption of p-nitrocyanobenzene (p-NCB). Removal of SOM from the whole soils increased sorption of p-NCB by the remaining soil fraction. The SOM thereby suppressed sorption of p-NCB by whole soil. We quantified the suppression of p-NCB by the whole soil as 17 to 53% (i.e. the fraction of the soil sorptive surfaces unavailable for p-NCB sorption was between 47 and 83%). The extent of suppression of p-NCB sorption was strongly related to the relative contents of SOM and smectite in the soils tested.

INTRODUCTION

Soil organic matter (SOM) and soil clays are intimately associated with each other in whole soil, through mechanisms including cation exchange, Van der Waals interactions, water bridging, cation bridging and ligand exchange (Parker and Rate, 1998). Using a Webster A soil, Laird (2001) identified two types of clay-associated humic substances, (1) a diffuse filamentous film covering basal 2:1 phyllosilicate surfaces in the medium (0.02-0.2 μm) and fine clay (< 0.02 μm) fractions and (2) discrete particles of high-density metal-humic complexes in the coarse clay (0.2-2.0 μm) fraction. Nkedi-Kizza et al. (1983) found that SOM was primarily associated with the < 2 μm clay-sized fraction of Webster soil. A major role played by SOM might be to neutralize repulsive forces that might otherwise keep clay particles apart thereby facilitating cohesion of the clay particles (Walker and Crawford, 1968).

The association of SOM with clays may influence the ability of either soil clays or SOM to sorb nonionic organic compounds (NOCs) such as nitroaromatics (NACs). For example, the interaction of pesticides with clay minerals may be limited by the availability of the clay sorption sites within soil. Our previous study (Chapter 2) revealed that availability of clay surfaces for NAC sorption by Webster soil was limited by the association of SOM with soil clays. Despite the long-standing notion that SOM obscures some of the clay surface area in soils, there is a paucity of evidence that quantitates this effect. Karickhoff (1984) proposed an equation to account for the individual contributions of SOM and soil clays to NOC sorption, and for reduced availability of clay surfaces for sorption due to coverage by SOM:

$$Q_{\text{whole soil}} = (f_a * K_{min} * C_e * f_{min}) + (K_{om} * C_e * f_{om}) \qquad [1]$$

where $Q_{\text{whole soil}}$ is the total solute mass sorbed per unit mass of whole soil (mg g^{-1}), C_e is the aqueous solute equilibrium concentration, and K_{min} and K_{om} represent the sorption coefficients of the solute to soil fraction from which SOM was removed (mineral) fraction and SOM, respectively, f_{min} and f_{om} are the fractional mineral and SOM contents of soil, and f_a represents the fractional availability of sorption sites on the clay (i.e. the fraction of sorptive surfaces available for NOC sorption in whole soil). An inherent assumption in this equation is that the sorptive capacity of the SOM is unaffected by the presence of mineral matter. An alternative method of determining f_a as previously outlined involved measuring the difference in NAC sorption between sorbent systems whose cation exchange capacity (CEC) is saturated with different cations. This method is based on the premise that NAC sorption by clay is strongly dependent on the cation saturating the clay exchange sites (Li et al., 2003; Boyd et al., 2001; Sheng et al., 2001, 2002; Johnston et al., 2001, 2002; Weissmahr et al., 1997; Haderlein et al., 1996) whereas NAC sorption by SOM is unaffected by the nature of the saturating cation (Chapter 1). Both the Karickhoff approach and our alternative method revealed similar results, i.e., ~ 30-45% of p-NCB sorptive surfaces in a Webster A soil were rendered unavailable in the presence of SOM (Chapter 2). The objective of this study was to determine the availability of mineral sorptive surfaces for NAC sorption among a larger group of soils, and to relate availability to soil properties.

EXPERIMENTAL SECTION

Both the A and B horizons of two soils, a Webster clay loam (fine loamy, mixed, mesic Typic Endoaquoll) and a Clarion sandy clay loam (fine loamy, mixed, mesic Typic Hapludoll) (Soil Survey Staff, NRCS), were air-dried and sieved to remove coarse fragments (>2mm). The soils were fractionated by standard procedures (Kunze & Dixon, 1986). Carbonates (CO_3) and SOM were sequentially removed from each soil horizon. Carbonates were removed by stirring the soil with 0.5*N* sodium acetate acidified to pH 5 while heating at 80°C, followed by the removal of SOM with 30% H_2O_2 at 80°C (denoted OM-removed soil). Homoionic soil fractions and whole (unfractioned) soils were prepared by washing the soils with 200 ml aliquots of 0.1*M* solution of KCl or $MgCl_2$ overnight, thereafter centrifuging and discarding the supernatant. This procedure was repeated four times. The soils were then washed with 200 ml aliquots of Millipore Milli-Q (Billerica, Massachusetts) deionized H_2O, thereafter centrifuged and the supernatant tested with $AgNO_3$. The procedure was repeated until a negative Cl^- ion test with $AgNO_3$ was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1°C) until used. Para-nitrocyanobenzene (p-NCB) was purchased from Aldrich Chemical Company (Milwaukee, Wisconsin) with a purity of 97% and used as received. Its water solubility (S_w) at 25°C is 1650 mg L^{-1} and its log K_{ow} value is 1.19 (Howard and Meylan, 1997).

Sorption of p-NCB by unfractionated soils and OM-removed soils (K^+- and Mg^{2+}-saturated) were measured in triplicate using a batch equilibrium technique over a range of initial aqueous phase concentrations (C_i) (1-42 mg L^{-1}) to a known mass of soil. Initial solutions of p-NCB were prepared in 0.05*M* KCl or $MgCl_2$ electrolyte solutions to correspond to the saturating cation of the study soils. Total volumes of 5 ml were pipetted into 7.5 ml borosilicate glass vials containing various amounts of sorbent (between 0.2 and 0.4 g). The vials were rotated continuously overnight (24 hours) in the dark at room temperature (23 ± 1°C) to ensure complete sorption; preliminary studies showed equilibrium was reached within 24 hours. The liquid and solid phases were separated by centrifugation at 4068*g* for 30 min, and the solute's equilibrium concentration in water (C_e) measured. The concentrations of p-NCB in the supernatants were determined by a Perkin-Elmer high performance liquid chromatograph (Perkin-Elmer, Norwalk, Connecticut) consisting of a binary LC pump 250 with a series 200 autosampler and a uv-visible detector set at λ 254 nm. A platinum EPS C18 column from Alltech Associates was used (Deerfield, Illinois). The mobile phase was an isocratic mixture of methanol (HPLC grade) and Milli-Q deionized water (methanol: water ratio of 55:45) with a flow rate of 1.0 ml min^{-1}. The amount of p-NCB sorbed was calculated as the difference between the initial aqueous concentration (C_i) and the final aqueous concentration (C_e). Compound recoveries in control vials without sorbent were above 95% and not used to adjust the data.

The extent of sorption of p-NCB by each soil was described by fitting the data to the Freundlich equation, $Q = K_fCe^n$, where Q is the sorbed concentration of p-NCB per unit mass of soil (mg g^{-1}), K_f is the Freundlich constant, and n is an exponent related to isotherm shape (Chiou, 2002). The n and K_f sorption parameters were used to determine the sorption per gram of soil or clay at specific equilibrium concentrations within the data range (i.e., @ 5, 10, 15 and 20 mg L^{-1}). The SOM content of the unfractionated and OM-removed soils was determined by the Michigan State University (MSU) Soil Testing Laboratory using dry combustion and a Leco carbon analyzer (St. Joseph, Michigan) (Nelson and Sommers, 1996). Soil cation exchange capacity (CEC) and gravimetric clay content was determined by the MSU Soil Testing Laboratory using the ammonium acetate method (Sumner and Miller, 1996) and the hydrometer method (Gee and Bauder, 1986), respectively. Soil pH was determined using a pH meter and 1:1 water to soil ratio (Sparks et al., 1996).

X-ray diffraction (XRD) was used to identify the clay mineralogy of the clay-sized fractions (Whittig & Allardice, 1987). Oriented samples of Mg^{2+}- and K^{+}-saturated clay-sized particles were prepared by dropping suspensions of the clay-sized materials, isolated from the OM-removed soils on glass slides, air-drying, heating at 500°C, then treatment with ethylene glycol. Samples were analyzed using CuKα radiation and a Philips APD 3720 X-ray diffractometer (Philips Electronic Instruments, NJ). Semi-quantitative estimates for the amount of smectite in each unfractionated soil were determined assuming an average CEC for a soil smectite and SOM of 80 and 160 cmol kg^{-1}, respectively, as described in Chapter 1.

Data Analysis

Calculation of f_a values

The chief goal of this work was to estimate the availability (f_a) of smectite surfaces in the study soils for p-NCB sorption. Two independent equations were used for the calculation of f_a. First, a modified equation from Karickhoff (1984) [1]:

$$Q_{\text{whole soil}} = (f_a * K_{min} * C_e * f_{min}) + (K_{om} * C_e * f_{om}) \qquad [1]$$

where $Q_{\text{whole soil}}$ is the total solute mass sorbed per unit mass of soil (mg g^{-1}), C_e is the solute aqueous equilibrium concentration, and K_{min} and K_{om} represent the sorption coefficients of the solute by soil fraction from which SOM was removed (mineral) and SOM, respectively, f_{min} and f_{om} are the fractional mineral and SOM contents of soil, respectively, and f_a represents the fractional availability of sorption sites on the clay (i.e. the fraction of sorptive surfaces available for NOC sorption in whole soil).

Second, an alternative equation [2] developed by us in Chapter 2:

$$Q_{\text{whole soil}, K^+} - Q_{\text{whole soil}, Mg^{2+}} = \{f_a * \{(K_{min, K^+} * C_e * f_{min}) - (K_{min, Mg^{2+}\,sat} * C_e * f_{min})\}\} [2]$$

where $Q_{\text{whole soil}, K^+}$ and $Q_{\text{whole soil}, Mg^{2+}}$ is the total solute mass sorbed per unit mass of soil (mg g^{-1}) whose CEC is saturated with either K^+ and Mg^{2+}, respectively, C_e is the solute aqueous equilibrium concentration, f_a represents the fractional availability of sorption sites on the clay, f_{min} is the fractional mineral content of the soil, and K_{min, K^+} and $K_{min, Mg^{2+}}$ represent the partition coefficients normalized to soil mineral fraction saturated with either K^+ and Mg^{2+}, respectively.

Within both the Karickhoff [1] and alternative [2] equations, the extent of p-NCB sorption by the residual SOM associated with the OM-removed soil must be accounted for. However, in equation [2], the sorptive contribution of K^+-saturated residual SOM cancels out that of Mg^{2+}-saturated residual SOM, thus obviating the need to estimate K_{om} (Chapter 2). Sorption data were fitted to the Freundlich equation with $r^2 > 0.9$ in all cases. Using the K_f and n values obtained, the Q value (amount p-NCB sorbed per mass of soil) was calculated for four concentrations that were within the data range (@ 5, 10, 15, and 20 mg L^{-1}). Using either equation [1] or [2], four f_a values were obtained for each soil (i.e., one for each concentration). Standard deviations around each f_a value were calculated using error propagation procedures. For the Karickhoff equation, only the K^+-saturated system was used.

Estimation of degree of OM mineral surface coverage

The hypothetical percentage of the mineral surface covered by a specified amount of SOM present was estimated using Lagaly's formula area per C of 5.67 $Å^2$ (Lagaly, 1981), a percent carbon in SOM of 62% (Stevenson and Cole, 1999), an average smectite surface area of 750 m^2 g^{-1} (Sposito, 1984), the estimated percent smectite in unfractionated soil, and the measured percent SOM in each unfractionated and OM-removed soil as described in Chapter 2. The operating assumption underlying this estimate was that all C from SOM resides on smectite surfaces.

Sensitivity Analysis and Validation of f_a values

Validation of the f_a values was determined by manipulating equation [1] to give the equation: $f_a = -[(K_{om}/K_{min}) * (f_{om}/f_{min})] + (K/K_{min}*f_{min})$ [3]

where plotting f_a versus f_{om}/f_{min} for each soil should give an intercept of 1 when the SOM content is zero (i.e., 100% availability of sorptive surfaces). Linear regression equations describing the relationship between f_a values and the ratio of SOM to smectite content ($f_{om}/f_{smectite}$ or %OM/%smectite), to SOM content and to smectite content in unfractionated soils were obtained. If the calculated f_a values are reasonable, the intercept of the regression equations should tend to unity (i.e., no mineral blockage by SOM) when SOM content tends to zero.

Statistical Analysis

The sorption coefficient (K_f) and the constant related to the sorption isotherm curvature (n) were estimated using the Freundlich equation, $Q=K_fC_e^n$. Comparisons of sorption isotherms were made by comparing the K_f and n values for each soil-solute system using nonlinear regression in SAS (SAS Institute, 1999). A significant difference between isotherms was assigned when there was a significant difference between K_f and n or K_f values of compared isotherms ($\alpha = 0.05$) (Laboski and Lamb, 2004).

RESULTS AND DISCUSSION

Nitroaromatics are known to be sorbed significantly by smectite clays (Haderlein et al., 1996; Weissmahr et al., 1997; Boyd et al., 2001; Sheng et al., 2002; Johnston et al., 2001, 2002). The Webster and Clarion soils contain significant amounts of smectite clays (13-24% smectite) (Table 3.1, Figure 3.1) and were therefore chosen as the study soils. The extent of NAC sorption by smectites is cation-dependent. Reference clays exchanged with cations of relatively lower hydration energies (e.g., K^+) sorb NACs to a greater extent than those exchanged with cations of relatively higher hydration energies (e.g., Mg^{2+}) (Boyd et al., 2001; Johnston et al., 2001, 2002; Sheng et al., 2002; Haderlein and Schwarzenbach, 1993; Weissmahr et al., 1997). We found that K^+-exchanged soils sorbed more NACs than Mg^{2+}-exchanged soils (Chapters 1 and 2). In this study we also found that the K^+-saturated unfractionated and OM-removed soils sorbed more p-NCB compared to Mg^{2+}-saturated soils (Table 3.2, Figure 3.2). This can be attributed to the lower hydration energy of the K^+ ion which facilitates greater interaction between the saturating cation and the solute and larger sorption domains on clay interlayer surfaces (Li et al., 2003; Sheng et al., 2002; Haderlein et al., 1996; Haderlein and Schwarzenbach, 1993; Weissmahr et al., 1997, 1999; Boyd et al., 2001; Johnston et al., 2001, 2002).

For each soil, with K^+ as the saturating cation, OM-removed soil sorbed more p-NCB than unfractionated soil (Figure 3.2). Sorption of p-NCB by the Webster B and Clarion A horizons doubled after SOM was removed, while sorption increased by about 30% when SOM was removed from the Webster A and Clarion B horizons (Figure 3.2). These data

Table 3.1. Physicochemical characteristics of Webster and Clarion soils (whole soil and soils from which SOM was removed).

WA, Webster A; WAO, Webster A OM-removed; WB, Webster B; WBO, Webster B OM-removed; CLA, Clarion A; CAO, Clarion A OM-removed; CLB, Clarion B; CBO, Clarion B OM-removed.

Soil	Texture	pH	%OM	% clay-sized fraction	%smectite	Clay mineralogy[†]	% clay surface coverage[‡]
WA	Clay loam	6.38	3.870	31	24	S,M/I,K,Q	38
WAO			0.225	-	-		2
WB	Clay loam	7.90	2.100	31	16	S,M/I,K,Q	31
WBO			1.210	-	-		17
CLA	Sandy clay loam	6.16	2.690	25	13	S,M/I,K,Q	49
CAO			0.380	-	-		7
CLB	Sandy clay loam	6.37	0.593	27	14	S,M/I,K,Q	10
CBO			0.075	-	-		1

[†] S, smectite; M/I, mica and/or illite; K, kaolinite; Q, quartz

[‡] Estimated basal smectite surfaces (see text)

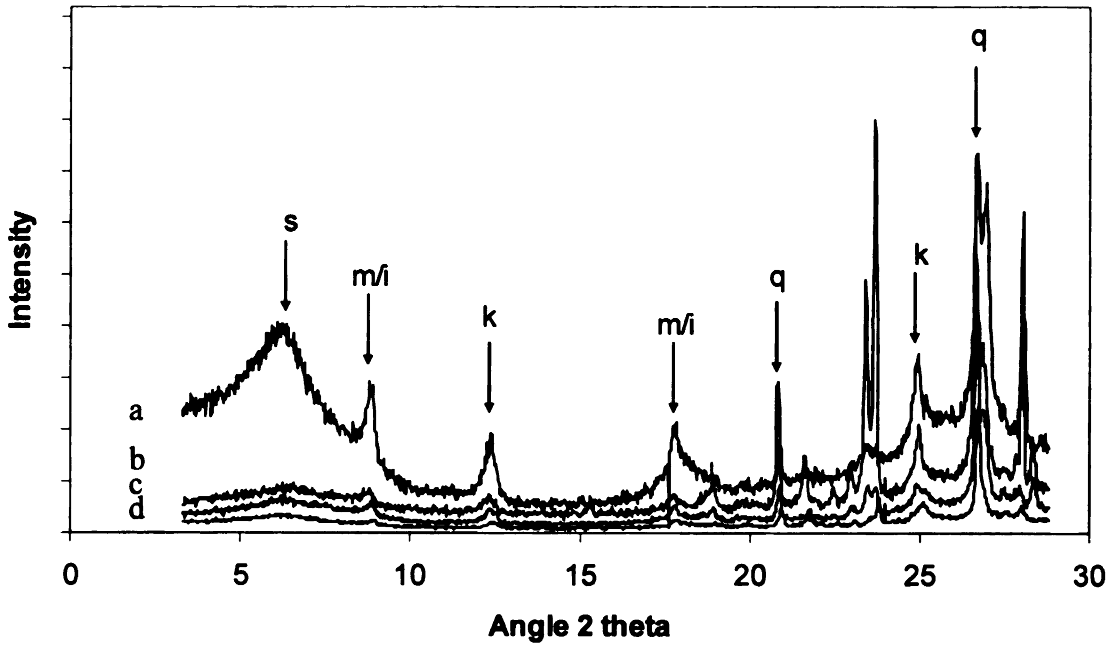

Figure 3.1. X-ray diffraction spectra for Mg^{2+}-saturated clay-sized fraction isolated by Webster and Clarion (A and B horizons) soils.

Graphs represented are (a) Clarion B, (b) Clarion A, (c) Webster B, and (d) Webster A.

s-smectite; m/i, mica and/or illite; k, kaolinite; q, quartz.

Table 3.2. Freundlich equation K_f and n values for p-nitrocyanobenzene sorption by K^+- and Mg^{2+}-exchanged Webster and Clarion (A and B horizons) whole soils and soils from which SOM was removed.

Soil		K_f	n
Webster A	K^+-whole	0.0528	0.5983
	K^+-OM removed	0.0922	0.5012
	Mg^{2+}-whole	0.0067	0.6219
	Mg^{2+}-OM removed	0.0007	0.9033
Webster B	K^+-whole	0.0634	0.5587
	K^+-OM removed	0.1452	0.5106
	Mg^{2+}-whole	0.0018	0.8151
	Mg^{2+}-OM removed	0.0009	0.9736
Clarion A	K^+-whole	0.0222	0.6427
	K^+-OM removed	0.0736	0.4821
	Mg^{2+}-whole	0.0031	0.6434
	Mg^{2+}-OM removed	0.0010	0.7079
Clarion B	K^+-whole	0.0912	0.5326
	K^+-OM removed	0.1280	0.4661
	Mg^{2+}-whole	0.0007	0.9304
	Mg^{2+}-OM removed	0.0009	0.8185

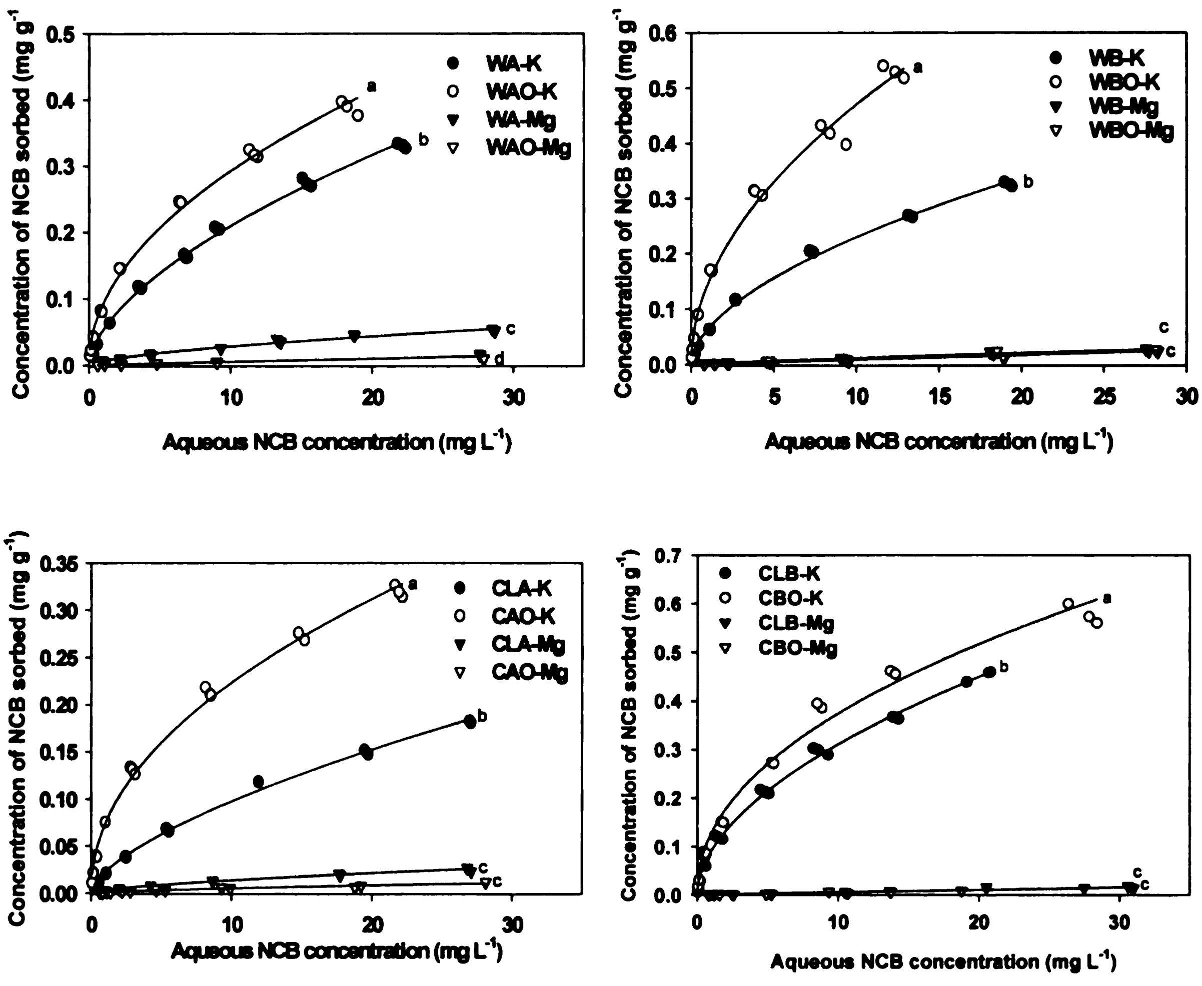

Figure 3.2. Adsorption isotherms for sorption of p-nitrocyanobenzene by K^+- and Mg^{2+}-saturated Webster and Clarion (A and B horizon) soils.

(isotherms marked with different letters are significantly different at $p < 0.05$)

WA/WB – Webster A/ Webster B horizon

CLA/CLB – Clarion A/ Clarion B horizon

WAO/WBO – Webster A/B horizon, OM removed

CLA/CLB – Clarion A/B horizon, OM removed indicate that SOM suppresses sorption of p-NCB by the soil mineral fraction despite SOM also acting simultaneously as an independent sorptive sink. Literature reports decreased sorption of organic solutes to reference minerals when associated with SOM. Liu et al. (2002) observed the sorption of four herbicides (metolachlor, acetochlor, alachlor, and propachlor) by Wyoming montmorillonite (SWy-2), humic acid (HA) extracted from a Webster clay loam, and clay-HA complexes containing various ratios of clay and SOM. They found that the measured sorption of the herbicides by the clay-HA complexes were less than the sum of sorption by clay and by HA in the same ratios as the complexes. Celis et al. (1997) found that coating Ca-montomorillonite (Ca-SWy-1) with commercial HA and soil-extracted HA decreased the sorption of thiazafluron by the clay-HA complex compared to clay alone. Subsequent removal of the HA coating on the clay-HA complex increased thiazafluron sorption compared to the clay-HA complex. Pusino et al. (1992; 1994) compared the experimental sorption coefficients (K_d values) obtained for the sorption of metolachlor (1992) and triclopyr (1994) by bentonite montmorillonite-HA complexes with the K_d values calculated assuming independent sorption of metolachlor by HA and clay. The experimental K_d values were lower than the calculated K_d values. Although these studies indicated that the presence of SOM associated with clays results in decreased sorption of NOCs by the clays, these studies utilized synthetic clay-SOM complexes. Our data indicates that in natural soils, removal of SOM from soil increases sorption of NOCs indicating that in natural soils, as in synthetic systems, SOM obscures clay surfaces for sorption of NOCs.

The phenomenon of reduced sorption in the presence of SOM is exemplified by f_a values less than 1. We used our sorption data for the K^+-saturated soils and applied the Karickhoff equation [1] to calculate f_a values (i.e. the fraction of the sorptive surfaces that is available in whole soil) for the four soil horizons. We used K^+- and Mg^{2+}-saturated peat, Houghton muck and Brookston loam to determine the SOM contribution to overall solute sorption. This approach requires an estimate of K_{om} for sorption of p-NCB, which we derived previously using three SOM surrogates (Chapter 2). The similarity in f_a values calculated using K^+- and Mg^{2+}-saturated SOM surrogates (Table 3.3, Table 3.4) indicates that the influence of cation on p-NCB sorption by SOM is minimal. We also applied our alternative equation [2] to estimate f_a; this approach utilizes sorption data from K^+- and Mg^{2+}-saturated soils and eliminates the need for an independently estimated K_{om} values. These f_a values (Table 3.3, Table 3.4) obtained for a particular soil using equation [1] did not differ significantly from those obtained using equation [2]. That is, two independent methods for estimating f_a (equations [1] and [2]) yielded similar results. Also, the f_a values were relatively independent of sorbent material (muck, peat or loam) used as a surrogate for pure SOM (Table 3.3, Table 3.4) when using equation [1]. However, f_a values varied across soils and soil horizons (i.e., f_a values for Clarion A < Webster B < Wester A < Clarion B) ($p < 0.05$). The f_a values, averaged across both equations and all K^+-saturated SOM surrogates, for Clarion B (ca. 0.83 ± 0.03) were greater than for Clarion A (ca. 0.36 ± 0.05) and those for Webster A (ca. 0.64 ± 0.04) were higher than for Webster B (ca. 0.47 ± 0.01) ($p < 0.05$). Despite various amounts of SOM initially present in the soils and different amounts being removed from the soils, f_a

Table 3.3. The f_a values for p-nitrocyanobenzene (NCB) sorption by Webster (A and B horizons) and Clarion (A and B horizons) estimated using Karickhoff's equation [1] (using solute sorption by K^+-saturated peat, Houghton muck, or Brookston loam to determine the K_{om} term).

Equation and OM surrogate used	Concentration (mg L^{-1})	Webster A	Webster B	Clarion A	Clarion B
Karickhoff (peat)	5	0.55 (0.02)	0.44 (0.02)	0.27 (0.01)	0.78 (0.04)
	10	0.60 (0.02)	0.46 (0.02)	0.32 (0.01)	0.82 (0.02)
	15	0.63 (0.03)	0.47 (0.02)	0.35 (0.01)	0.84 (0.02)
	20	0.65 (0.03)	0.47 (0.02)	0.37 (0.01)	0.86 (0.03)
Karickhoff (Houghton muck)	5	0.60 (0.02)	0.45 (0.02)	0.32 (0.01)	0.78 (0.04)
	10	0.65 (0.02)	0.47 (0.02)	0.37 (0.01)	0.82 (0.02)
	15	0.69 (0.03)	0.48 (0.02)	0.40 (0.01)	0.85 (0.02)
	20	0.71 (0.03)	0.49 (0.02)	0.42 (0.02)	0.87 (0.03)
Karickhoff (Brookston loam)	5	0.58 (0.02)	0.45 (0.02)	0.30 (0.01)	0.78 (0.04)
	10	0.62 (0.02)	0.46 (0.02)	0.34 (0.01)	0.82 (0.02)
	15	0.64 (0.03)	0.47 (0.02)	0.36 (0.01)	0.84 (0.02)
	20	0.66 (0.03)	0.48 (0.02)	0.38 (0.02)	0.86 (0.03)
Alternative	5	0.61 (0.02)	0.46 (0.02)	0.35 (0.01)	0.79 (0.05)
	10	0.65 (0.02)	0.48 (0.02)	0.39 (0.01)	0.83 (0.02)
	15	0.68 (0.03)	0.48 (0.02)	0.42 (0.01)	0.85 (0.02)
	20	0.70 (0.03)	0.49 (0.03)	0.44 (0.01)	0.87 (0.03)

For Webster B and Clarion B, across all concentrations, f_a values calculated using Karickhoff-peat = Karickhoff-HM = Karickhoff-BL= Alternative ($p < 0.05$). For Webster A and Clarion A, across all concentrations, f_a values calculated using Karickhoff-peat < Karickhoff-BL < Karickhoff-HM $\leq$ Alternative ($p < 0.05$). For all soils except Webster B, f_a values were statistically different across concentration (5ppm < 10ppm< 15ppm < 20ppm) ($p < 0.05$). For Webster B, f_a values were not statistically different across concentration ($p < 0.05$). For each equation, f_a values for Clarion A < Webster B < Webster A < Clarion B ($p < 0.05$). Standard deviations in parentheses.

Table 3.4. The f_a values for p-nitrocyanobenzene (NCB) sorption by Webster (A and B horizons) and Clarion (A and B horizons) estimated using Karickhoff's equation [1] (using solute sorption by Mg^{2+}-saturated peat, Houghton muck, or Brookston loam to determine the K_{om} term).

Equation and OM surrogate used	**Concentration ($mg\ L^{-1}$)**	**Webster A**	**Webster B**	**Clarion A**	**Clarion B**
Karickhoff (peat)	5	0.59 (0.02)	0.45 (0.02)	0.31 (0.01)	0.78 (0.04)
	10	0.63 (0.02)	0.46 (0.02)	0.35 (0.01)	0.82 (0.02)
	15	0.66 (0.03)	0.47 (0.02)	0.38 (0.01)	0.85 (0.02)
	20	0.68 (0.03)	0.48 (0.02)	0.40 (0.01)	0.86 (0.03)
Karickhoff (Houghton muck)	5	0.62 (0.02)	0.46 (0.02)	0.34 (0.01)	0.78 (0.04)
	10	0.66 (0.02)	0.47 (0.02)	0.38 (0.01)	0.82 (0.02)
	15	0.69 (0.03)	0.48 (0.02)	0.40 (0.01)	0.85 (0.02)
	20	0.71 (0.03)	0.49 (0.02)	0.42 (0.01)	0.87 (0.03)
Karickhoff (Brookston loam)	5	0.61 (0.02)	0.45 (0.02)	0.32 (0.01)	0.78 (0.04)
	10	0.65 (0.02)	0.47 (0.02)	0.37 (0.01)	0.82 (0.02)
	15	0.68 (0.03)	0.48 (0.02)	0.40 (0.01)	0.85 (0.02)
	20	0.70 (0.03)	0.49 (0.02)	0.42 (0.01)	0.87 (0.03)
Alternative	5	0.61 (0.02)	0.46 (0.02)	0.35 (0.01)	0.79 (0.05)
	10	0.65 (0.02)	0.48 (0.02)	0.39 (0.01)	0.83 (0.02)
	15	0.68 (0.03)	0.48 (0.02)	0.42 (0.01)	0.85 (0.02)
	20	0.70 (0.03)	0.49 (0.03)	0.44 (0.01)	0.87 (0.03)

For Webster B and Clarion B, across all concentrations, f_a values calculated using Karickhoff-peat = Karickhoff-HM = Karickhoff-BL= Alternative ($p < 0.05$). For Webster A and Clarion A, across all concentrations, f_a values calculated using Karickhoff-peat < Karickhoff-BL < Karickhoff-HM ≤ Alternative ($p < 0.05$). For all soils except Webster B, f_a values were statistically different across concentration (5ppm < 10ppm< 15ppm < 20ppm) ($p < 0.05$). For Webster B, f_a values were not statistically different across concentration ($p < 0.05$). For each equation, f_a values for Clarion A < Webster B < Webster A < Clarion B ($p < 0.05$). Standard deviations in parentheses.

relates to the available sites in the context of whole soil. We accounted for the sorption of p-NCB by residual SOM (i.e., SOM remaining after removal of bulk SOM) in each OM-removed soil. Thus, by our analysis, an average of 36 to 83% of the sorptive surfaces are 'available' for p-NCB sorption in the unfractionated soil horizons, with more clay surface becoming available for sorption after SOM is removed.

Data analysis revealed that f_a values are strongly negatively correlated to ratios of SOM and smectite content of soil. From 83-88% of the difference in f_a values among soil horizons could be attributed to differences in ratios of SOM and smectite in the soils (Table 3.5). This is reasonable, given that the SOM and clay are the active sorbents of p-NCB and that, of the minerals present in each soil, smectites have the highest affinities for p-NCB (Chapter 1). The availability of sorptive clay sites does not correlate particularly well with either SOM content, or smectite content alone (Table 3.5). The f_a values and %OM were moderately, negatively correlated with 40-50% of the difference in f_a values among soil horizons attributed to differences in SOM content. This suggests that the availability of sorptive surfaces in whole soil decreases with an increase in SOM content. This may only operate to a certain extent as Murphy et al. (1990) and Rebhun et al. (1992) suggested that at high concentrations of HA, multiple layering of HA on the mineral surface occurs. The f_a values and %smectite were weakly correlated with only about 20% of the difference in f_a values attributed to differences in smectite content in the soil horizons (Table 3.5). The positive correlation suggests that increasing the smectite content of a soil should increase the overall availability of clay mineral sorptive surfaces

Table 3.5. Correlation (r value) between f_a values for sorption of p-nitrocyanobenzene estimated using Karickhoff equation [1] (using solute sorption by K^+-saturated peat, Houghton muck or Brookston loam to determine the K_{om} term) and the alternative equation [2] with percent organic matter (%OM), percent smectite (%smectite) and ratio of organic matter to smectite (%OM/%smectite). Correlations were performed across the Webster and Clarion (A and B horizons) soils ($\alpha = 0.05$).

Equation used and SOM surrogate	**%OM**	**%smectite**	**%OM/%smectite**
Karickhoff – peat	-0.51	0.17	-0.88
Karickhoff – Houghton muck	-0.42	0.24	-0.82
Karickhoff – Brookston loam	-0.48	0.20	-0.87
Alternative	-0.45	0.21	-0.83

for a given SOM content. This is because the amount of surface that a given amount of SOM can obscure theoretically would decrease with increasing smectite content. Plotting f_a values against %OM/%smectite indicates that the f_a values calculated are reasonable since, for each equation and each SOM-surrogate used, the intercepts are approximately equal and all approach unity at 0% SOM (Table 3.6; Figure 3.3). That is, in the absence of SOM the smectite surfaces should be fully available for sorption of p-NCB. The near-unity intercepts also suggest that other types of coatings on smectites that might be envisioned do not significantly reduce availability.

While this research clearly indicates that natural SOM renders soil clay surfaces unavailable for sorption of organic solutes, one can only postulate possible mechanisms. First, SOM could cover soil clay basal surfaces and render them unavailable. We know that p-NCB and other NACs (Sheng et al., 2001, 2002; Li et al., 2003), as well as organic cations such as hexadecyltrimethylammonium (Jaynes and Boyd, 1991a), tetramethylammonium (Lee et al., 1989, 1990), and trimethylphenylammonium (Jaynes and Boyd, 1991b), intercalate between the clay layers when sorbed by smectites so SOM may be occupying those interlayer sites. Stevenson (1994) points out that although lab studies have reported organic compound sorption in the interlamellar surfaces of clays, it has not been unequivocally established that such complexes occur in natural soils. However, recovery of amino acids from clay-rich subsoils by acid hydrolysis is incomplete unless preceded by HF pretreatment (Stevenson, 1994) suggesting that small molecules from SOM are able to intercalate clays. If all carbon (C) in SOM were assumed to cover the basal surfaces of soil smectites, then the formula for surface

Table 3.6. Linear regression describing the relationship between f_a values and ratio of SOM and smectite soil contents.

Regressions were performed across the Webster and Clarion (A and B horizons) soils. Intercept is the f_a value at which %OM is zero.

Equation used	**Slope**	**Average Intercept**	**Intercept Range**	**r^2**
Karickhoff (peat)	-2.73 (0.40)	0.92 (0.06)	0.86-0.98	0.77
Karickhoff (Houghton muck)	-2.43 (0.45)	0.91 (0.07)	0.84-0.98	0.68
Karickhoff (Brookston loam)	-2.63 (0.41)	0.92 (0.06)	0.86-0.98	0.75
Alternative	-2.36 (0.43)	0.91 (0.06)	0.85-0.97	0.69

Standard deviations in parentheses.

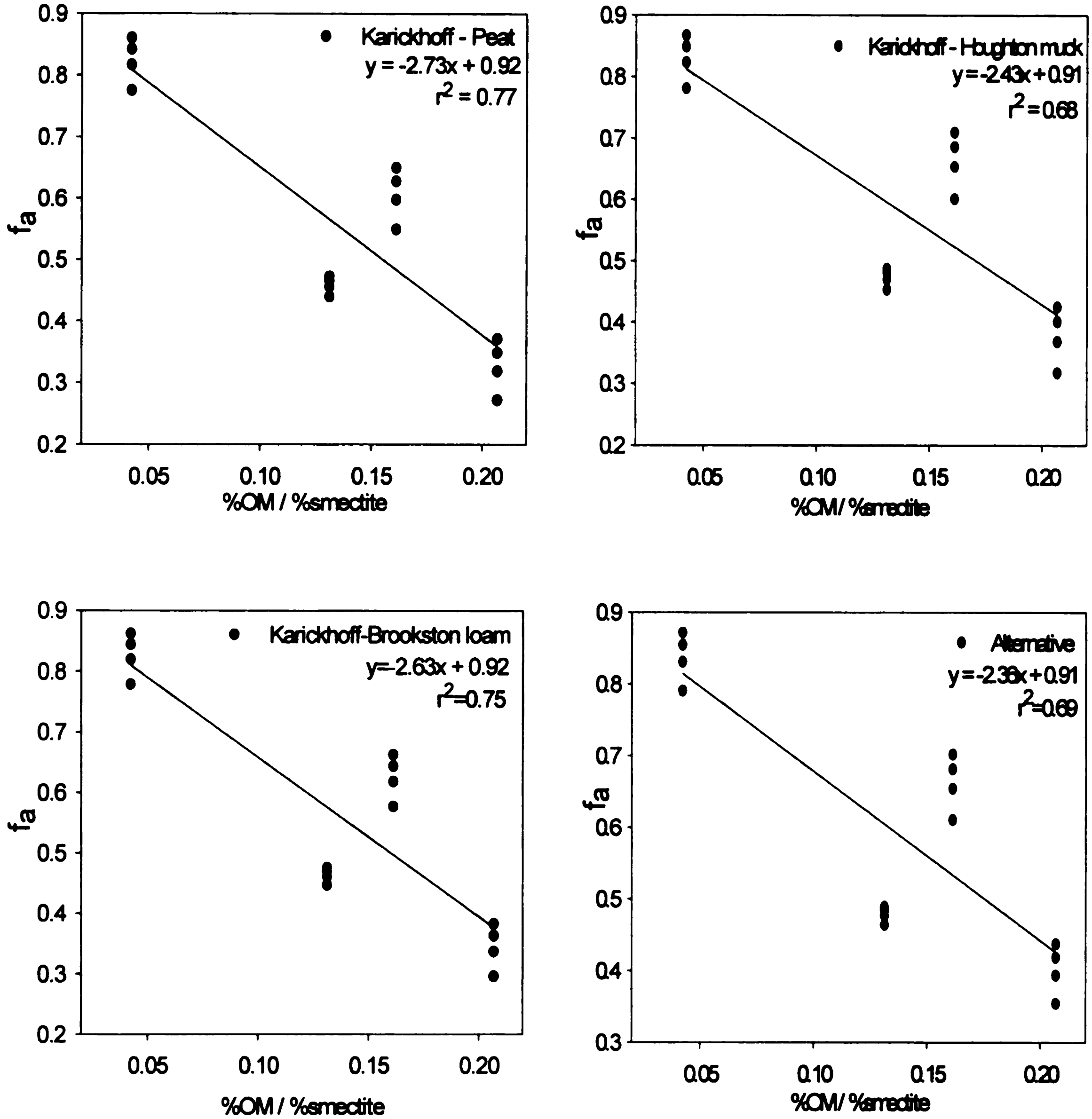

Figure 3.3. Linear regressions of f_a values obtained from data analysis of p-nitrocyanobenzene (p-NCB) sorption data using Karickhoff equation [1] and our alternative equation [2] across 4 specified concentrations (5, 10, 15, 20mg L^{-1}) versus ratio of SOM to smectite content (%OM/%smectite) across 4 soils (Webster A, Webster B, Clarion A, Clarion B). Sorption of p-NCB to K^+-peat, Houghton muck, or Brookston loam was used to obtain the Kom term in Karickhoff equation [1].

coverage used in the alkylammonium method (Lagaly, 1981) predicts that this C would cover 49, 38, 31 and 10% of the smectite surface area in the Clarion A, Webster A, Webster B, and Clarion B horizons, respectively. Note that these values are in modest agreement with the complements of the average f_a values (i.e., 1- f_a; the fraction of clay surface obscured by SOM) for each horizon (Table 3.3) which are 0.64, 0.36, 0.53, and 0.17, respectively. This agreement may be stricly fortuitous, but would provide a good explanation for the strong correlation between f_a and the %OM / %smectite ratios (Table 3.5). However, some authors (Ahlrich, 1972; Celis et al., 1997, 1999) argue that intercalation of natural SOM (at least large SOM molecules) does not occur, in opposition to the aforementioned suggestions. Celis et al. (1998) measured the specific surface area (SSA) (N_2 adsorption) of a reference smectite before and after the sorption of humic substances by the smectite. They found that the SSA decreased indicating that the external surfaces were obscured by the humic acid coating. Their X-ray diffraction d_{001} spacings did not change with humic acid coating suggesting that intercalation of humic acids did not occur. Celis et al. (1997), Celis et al. (1999), and Li et al. (2003) found similar results.

Alternatively, SOM may bind to edge sites of clay minerals and thereby facilitate aggregate formation, and/or inhibit shrinking and swelling of the smectite interlayers or may partially block the entrance of sorbates into the interlayer region. This is quite reasonable, as edge sites would typically carry positive charges and readily form complexes with carboxylate groups of SOM, thereby creating bridges between clay particles. We propose that not all of the smectite surfaces are obscured by SOM bridges, coatings or aggregation because (a) cation exchange appears to happen readily, which implies that interlayers are accessible to soil solution, and (b) strong sorption of p-NCB occurs even before removal of SOM, and we are confident that most of this sorption occurs on smectite basal surfaces. Further studies would be needed to elucidate the mechanisms behind the obscuration of sorptive surfaces in soil smectites.

CONCLUSION

Individual effects of SOM and clay are not easily ascertained because in soils, SOM is intimately associated with clay. Accordingly, clay and SOM in soils undoubtedly function in concert more than as separate entities. Our study reveals that the association of SOM with clay obscures sorptive surfaces of soil clays, with availability being dependent on the relative contents of SOM and sorptive clays (e.g., smectites) in the whole soil.

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CHAPTER 4

SORPTION OF NONIONIC ORGANIC COMPOUNDS TO SOILS: THE COMPOUND SPECIFICITY OF AN AVAILABILITY INDEX

ABSTRACT

Efficacy of the clay mineral fraction of soil for the sorption of nonionic organic compounds (NOCs) may be reduced by its association with soil organic matter (SOM). An understanding of the influence of the clay and SOM association on the fate and transport of NOCs would provide important information that would enhance quantitative predictions of sorption of NOCs by soil compositions. Previously we quantitatively assessed the fractional availability (f_a) of soil clay surfaces for sorption of p-nitrocyanobenzene (p-NCB). For p-NCB that sorbs preferably to smectite clays the relative contents of SOM and smectite was the primary determinant of the availability of smectite surfaces in soil. In this study we used three nitroaromatic (NAC) compounds (p-NCB, 2,4-dinitrotoluene (DNT) and 1,4-dinitrobenzene (DNT)) and four loam soils to further evaluate the availability of soil smectite surfaces for sorption. Sorption of each NAC by whole soil and soil from which SOM was removed was determined. Increased NAC sorption was observed with the removal of SOM from whole soils indicating diminished availability of mineral surfaces due to obscuration or blockage by SOM. The f_a values differed with NAC suggesting the nature of the NAC may also influence the mechanism driving sorption site availability. We found a strong correlation between the strength of sorption of each NAC to smectites (and the relative sorption capacity of each

NAC to SOM and smectites) and the efficacy of SOM to obscure sorption sites in whole soil.

INTRODUCTION

The ever increasing manufacture and use of synthetic organic chemicals has amplified the need for the development and improvement of models to predict their fate in the environment. Fate and transport models utilize factors representing processes that affect the fate of these chemicals in the environment. A significant fate process for nonionic organic compounds (NOCs) in soils is their sorption by clay minerals and soil organic matter (SOM), the two most important components in soil for NOC sorption. Fate and transport models for fate of NOCs in soils often include terms representing sorption of the NOC to SOM (e.g., K_{om}, f_{om}) but usually ignore the potential contribution of soil clays to sorption. Soil clays may play an equal or dominant role, compared to SOM, in the immobilization of certain important classes of NOCs, for example, nitroaromatic compounds (NACs) (Sheng et al., 2001). However, the sorptive contributions of SOM and clay components may be interrelated since these materials are often associated in soils.

Several studies investigating the sorption of NACs by synthetic humic acid (HA)-clay complexes have shown that the extent of sorption of NOCs to the complex does not equate to the sum of sorption to the individual components assuming independent and additive adsorption behavior (Pusino et al., 1992, 1994; Celis et al., 1997; Liu et al., 2002). It is suggested that SOM may adhere to clay surfaces and form bridges between clay packets, resulting in aggregate formation (Celis et al., 1999; Pusino et al., 1992, 1994; Onken and Traina, 1997), inhibit shrinking and swelling of the smectite interlayers, and/or may partially block the entrance of sorbates into the interlayer regions (Walker and Crawford, 1968).

We determined that the association of SOM with clays in soils modifies the efficacy of the clay mineral fraction for the sorption of NOCs in soil (Chapter 2 and 3). Our previous studies revealed that p-nitrocyanobenzene (p-NCB) sorption by Webster and Clarion soils from which SOM was removed was greater than that by whole soil (Chapter 2 and 3) suggesting that the association of SOM with clay minerals obscures sorptive surfaces. In the case of p-NCB, 55 to 71% of the soil clay surfaces were available for sorption by a Webster A soil whose SOM and smectite contents were ca. 4% and 24%, respectively (Chapter 2). The efficacy of SOM to obscure sorptive surfaces (i.e., the fractional availability (f_a) of sorptive surfaces) was strongly related to the ratio of SOM to smectite content in soil (Chapter 3). However, the effect of solute characteristics on availability of soil clay surfaces has not been studied. Liu et al. (2002) calculated a parameter 'a' that represented the relative change in adsorption capacity of HA-clay complexes, that is, the fraction of the complex that is potentially hindered from sorption by SOM. The 'a' values obtained for metolachlor, acetochlor, alachlor and propachlor were –0.73, -0.79, -0.62 and –0.53, respectively suggesting that the presence of HA on the complex differentially decreases sorption depending on the solute used. However, their study used synthetic HA and clay complexes so that translation to whole soil is uncertain. Our objective was to quantify the fractional availability of mineral sorption sites within whole soils for three solutes.

EXPERIMENTAL SECTION

Two mineral soils, Webster (fine loamy, mixed, mesic Typic Endoaquoll) and Clarion (fine loamy, mixed, mesic Typic Hapludoll) (A and B horizons) (Soil Survey Staff, NRCS), and an organic soil (Pahokee peat; a Euic, hyperthermic Lithic Medisaprist) were air-dried and sieved to remove coarse fragments (>2mm). The mineral soils were fractionated by standard procedures (Kunze & Dixon, 1986). Carbonates (CO_3) and soil organic matter (SOM) were sequentially removed from each soil horizon. Carbonates were removed using 0.5*M* sodium acetate buffer acidified to pH 5 at 80°C, followed by the removal of SOM using 30% H_2O_2 at 80°C (denoted OM-removed soil). Homoionic soils and soil fractions were prepared by washing the soils with approximately 200 ml portions of 0.1*M* solution of KCl or $MgCl_2$ overnight, thereafter centrifuging at 4068*g* for 30 min and discarding the supernatant. This procedure was repeated four times. The soils were then washed with 200 ml portions of Millipore Milli-Q (Billerica, Massachusetts) deionized H_2O, thereafter centrifuged and the supernatant tested with $AgNO_3$; the procedure was repeated until a negative Cl^- ion test with $AgNO_3$ was obtained. The soils were then freeze-dried and stored at room temperature (23 ± 1°C) until used. A K^+-saturated reference clay, a montmorillonite, beidellite obtained from Ward's Natural Science (Rochester, NY), was prepared as outlined above, freeze-dried and stored at room temperature until used. Clay minerals present in the soils, both A and B horizons, were previously identified as mica and/or illite, smectite, and kaolinite (Chapter 1). The Michigan State University (MSU) Soil Testing Laboratory (East Lansing, Michigan) determined the soil gravimetric clay content by the hydrometer method (Gee and Bauder, 1986), and the SOM content using dry combustion and a Leco carbon analyzer (St. Joseph, Michigan) (Nelson and Sommers, 1996).

Dinitrobenzene (1,4-DNB) was purchased from Sigma Chemical Company (St. Louis, Missouri) with a purity of 98%. Nitrocyanobenzene (p-NCB) and 2,4-dinitrotoluene (2,4-DNT) were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin) with purities of 97% and 97%, respectively. Trinitrobenzene (1,3,5-TNB) was purchased from ChemService Inc. (West Chestnut, PA) with a purity of 99%. All NOCs were used as received.

Sorption of NACs by soils, soil fractions and K^+-saturated beidellite was measured, in triplicate, using a batch equilibrium technique. This involved adding aqueous solutions of p-NCB (1 to 42 mg L^{-1}), 1,4-DNB (1-42 mg L^{-1}), and 2,4-DNT (1-34 mg L^{-1}) over a range of initial aqueous concentrations (C_i) to a known mass of soil. Solutions of the compounds were prepared in 0.05*M* KCl or $MgCl_2$ corresponding to the sorbent saturating cation. Total volumes of 5 ml were pipetted into 7.5 ml borosilicate glass vials containing between 0.2 and 0.4 g of sorbent. The vials were rotated continuously overnight (24 hours) in the dark at room temperature (23 ± 1°C) to ensure complete sorption; preliminary studies showed that sorption equilibrium for each solute was reached within 24 hours (data not reported). The liquid and solid phases were separated by centrifugation at 4068*g* for 30 min. The concentration of NAC in the supernatants (C_e) were determined by a Perkin-Elmer high performance liquid chromatograph (HPLC) (Perkin-Elmer, Norwalk, Connecticut) consisting of a binary LC pump 250 with a series

200 autosampler and a uv-visible detector set at the following wavelengths: p-NCB, 254 nm; 1,4-DNB, and 2,4-DNT, 265 nm. A platinum EPS C18 column (Alltech, Illinois) was eluted with an isocratic mixture of methanol (HPLC grade) and Milli-Q deionized water (methanol: water ratio of 55:45 for p-NCB; 65:35 for 1,4-DNB, and 2,4-DNT) with a flow rate of 1.0 ml min^{-1}. The amount of solute sorbed was calculated as the difference between the initial (C_i) and final (C_e) concentration in the supernatant. Compound recoveries in control vials without sorbent were above 95% and not used to adjust the data. Sorption data were described using the Freundlich equation, $Q = K_f C_e^n$, where Q is the solute sorbed per unit mass of sorbent (mg g^{-1}), K_f is the Freundlich constant, and n is an exponent describing the shape of the sorption isotherm (Chiou, 2002).

Removal of organic matter with H_2O_2 may result in the liberation and oxidation of heavy metals. The potential contribution of sesquioxide presence and/or formation after H_2O_2 treatment to solute sorption was determined. K^+-saturated ferric hydroxide, $Fe(OH)_3$, was prepared as previously outlined (Chapter 1) using $FeCl_3$ and KOH. Sorption of p-NCB, 1,4-DNB, and 2,4-DNT by $Fe(OH)_3$ was measured, in duplicate, using a batch equilibrium technique as described earlier.

Data Analysis

Calculation of fractional availability (f_a) of mineral surfaces

The f_a values were calculated using the equations presented by Karickhoff (1984) and in Chapter 2. The two equations are given below:

$$Q_{whole\ soil} = Q_{min} + Q_{som} = (f_a * K_{min} * C_e * f_{min}) + (K_{om} * C_e * f_{om}) \qquad [1]$$

where $Q_{whole\ soil}$ is the total solute mass sorbed by unit mass of whole soil (mg g^{-1}), Q_{min} and Q_{som} are the solute mass sorbed by unit mass of SOM-removed soil and SOM (mg g^{-1}), respectively, C_e is the aqueous solute equilibrium concentration, and K_{min} and K_{om} represent the sorption coefficients of the solute by the soil fraction from which SOM was removed (mineral) and SOM, respectively, f_{min} and f_{om} are the fractional mineral fraction and SOM contents of soil, and f_a represents the fractional availability of sorption sites on the clays in whole soil (i.e. the fraction of the sorptive surfaces that are available in unfractionated soil).

Using the Freundlich parameters, K_f and n, the Q value (amount NOC sorbed per unit mass of sorbent) was calculated for four selected concentrations that were within the data range (i.e., @ 5, 10, 15, 20 mg L^{-1}). Standard deviations for each f_a value associated with each concentration were calculated using error propagation procedures (Skoog and West, 1986). For the Karickhoff equation, the K^+-saturated system was used and peat was used as the SOM to estimate K_{om} values for p-NCB, 1,4-DNB, and 2,4-DNT. Within both the Karickhoff and alternative equations, we accounted for the extent of solute sorption by the residual SOM associated with the OM-removed fraction; the residual SOM being the OM remaining after extraction of bulk SOM using H_2O_2.

Sensitivity Analysis of f_a values

Manipulating a modified form of Karickhoff's equation (Chapter 3) we derived a linear equation relating f_a and the SOM and smectite contents:

$$f_a = (-K_{om} / K_{min}) \text{ x } (f_{om}/f_{min}) + (K_{whole} / K_{min} * f_{min}) \qquad [3]$$

Plotting f_a versus f_{om}/f_{min} for each soil should give an intercept of 1 when the SOM content is zero (i.e., 100% availability of sorptive surfaces). The sorption coefficients for sorption of a solute by SOM (i.e., K_{om}) and by the smectites in the OM-removed soil (i.e. K_{min}) would differ for different solutes. To determine the K_{min} (analogous to $K_{smectite}$) term in equation [3], the extent of sorption of each solute by peat soil and K^+-beidellite were described by fitting the data to the Freundlich equation as previously described. The n and K_f sorption parameters were used to determine the sorption per gram of sorbent (peat and K^+-beidellite) at an equilibrium concentration of 10 mg L^{-1}. Correlation coefficients describing the relationship between f_a values and the ratio of SOM to smectite content ($f_{om}/f_{smectite}$ or %OM/%smectite), to SOM content, to smectite content in unfractionated soils, to the sorption distribution coefficient (i.e., K_d) for solute sorption by K^+-beidellite, and to the ratio of sorption of solute by SOM and smectite at an equilibrium concentration of 10 mg L^{-1} ($K_{om}/K_{smectite}$) were obtained. If the calculated f_a values are reasonable, the intercept of a linear regression equation relating f_a with $f_{om}/f_{smectite}$ should tend to unity (i.e., no mineral blockage by SOM) when %OM tends to zero.

Statistical Analysis

The sorption coefficient (K_f) and the constant related to the sorption isotherm curvature (n) were estimated using the Freundlich equation, $Q=K_fC_e^n$. Comparisons of sorption isotherms were made by comparing the K_f and n values for each soil-solute system using nonlinear regression in SAS (SAS Institute, 1999). A significant difference between isotherms was assigned when there was a significant difference ($\alpha = 0.05$) between K_f and n or K_f values of compared isotherms (Laboski and Lamb, 2004).

RESULTS AND DISCUSSION

The Webster and Clarion soils contain significant amounts of smectite clays (13-24% smectite) (Table 4.1) and were therefore chosen as the study soils. The amount of free FeO_x associated with the Webster and Clarion soils is less than 1%. For p-NCB, 1,4-DNB, and 2,4-DNT sorption by FeO_x synthesized in the laboratory was negligible (data not reported). We therefore conclude that FeO_x did not contribute to sorption of p-nitrocyanobenzene (p-NCB), 1,4-dinitrobenzene (1,4-DNB), and 2,4-dinitrotoluene (2,4-DNT) in the soils studied. This is consistent with studies by Haderlein and Schwarzenbach (1993) who reported that NACs do not adsorb significantly to aluminum and iron (hydr)oxides, carbonates or quartz.

The sorption isotherms for p-NCB, 1,4-DNB, and 2,4-DNT sorption by each soil were L shaped (Figure 4.1–4.4). For the concentration range used for each solute, the amount sorbed did not plateau for any soil hence the suitability of the Freundlich equation to describe these isotherms (Table 4.2) (Chiou, 2002). Sorption of p-NCB, 1,4-DNB and 2,4-DNT by the Mg^{2+}-saturated soil was equal to or greater than that by the Mg^{2+}-saturated OM-removed soil (Figure 4.1-4.4). Removal of SOM may liberate clay surface sites, but the sorption by the liberated Mg^{2+}-exchanged clay sorption sites would be low due to the large hydrated radius of the Mg^{2+} cation. Cations with large hydrated radii obscure a greater portion of the clay interlayer sorption domain compared to cations with smaller hydrated radii resulting in lower NAC sorption by Mg^{2+}-saturated clays and soils compared to K^+-saturated clays and soils (Li et al., 2003; Sheng et al., 2002; Haderlein et al., 1996; Weissmahr et al., 1997, 1999; Johnston et al., 2002). In addition, sorption

Table 4.1. Physicochemical characteristics of Webster and Clarion soils (whole soil and soils from which SOM was removed).

WA, Webster A; WAO, Webster A OM-removed; WB, Webster B; WBO, Webster B OM-removed; CLA, Clarion A; CAO, Clarion A OM-removed; CLB, Clarion B; CBO, Clarion B OM-removed.

Soil	**Texture**	**pH**	**%OM**	**% clay-sized fraction**	**%smectite**	**Clay mineralogy**[†]	**% clay surface coverage**[‡]
WA	Clay loam	6.38	3.870	31	24	S,M/I,K,Q	38
WAO			0.225	-	-		2
WB	Clay loam	7.90	2.100	31	16	S,M/I,K,Q	31
WBO			1.210	-	-		17
CLA	Sandy clay loam	6.16	2.690	25	13	S,M/I,K,Q	49
CAO			0.380	-	-		7
CLB	Sandy clay loam	6.37	0.593	27	14	S,M/I,K,Q	10
CBO			0.075	-	-		1

[†] S, smectite; M/I, mica and/or illite; K, kaolinite; Q, quartz

[‡] Estimated basal smectite surfaces (see text)

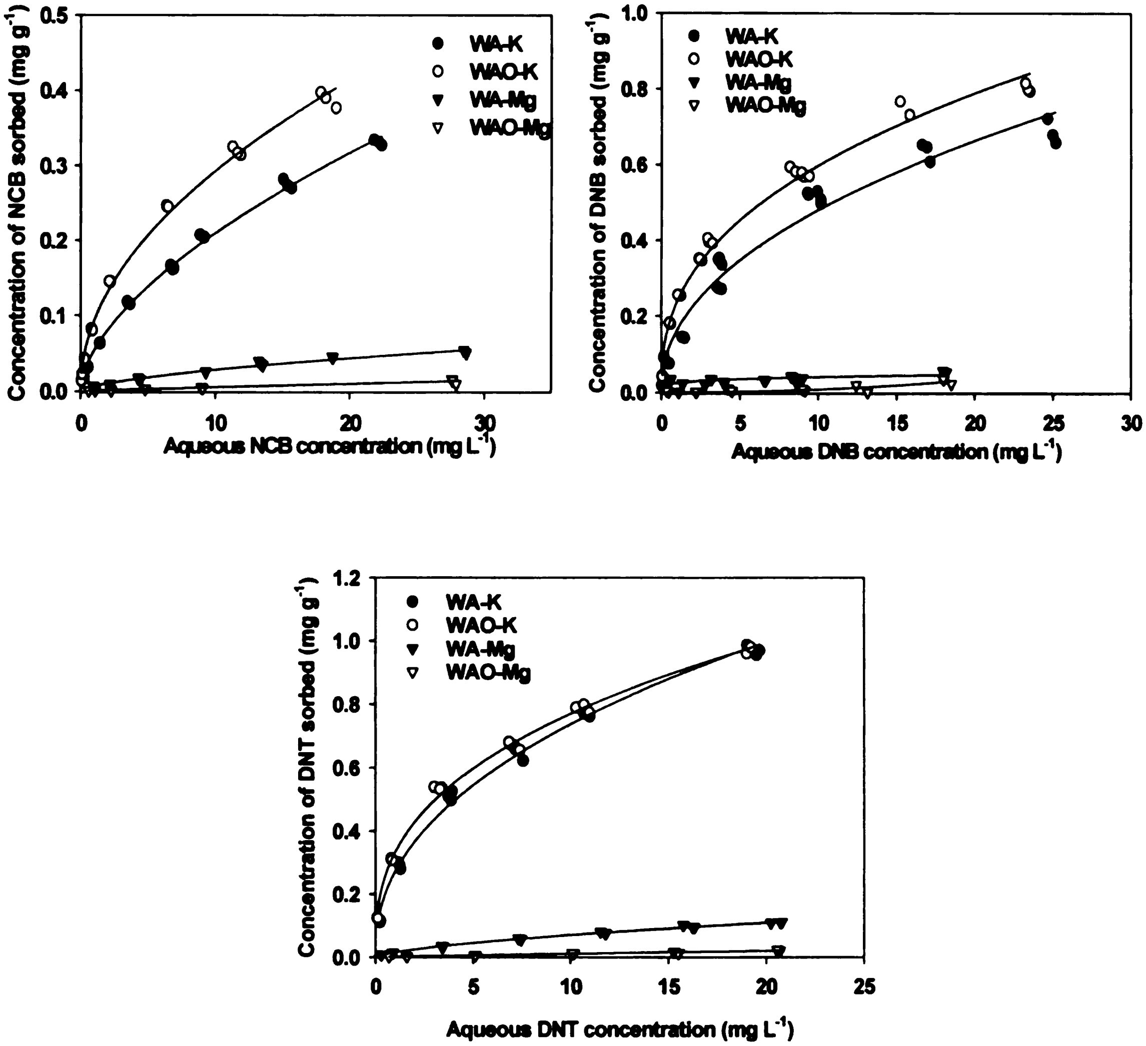

Figure 4.1. Isotherms for sorption of p-nitrocyanobenzene (p-NCB), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) by K^{+}- and Mg^{2+}-saturated Webster A (WA) and Webster A soil from which SOM was removed (WAO).

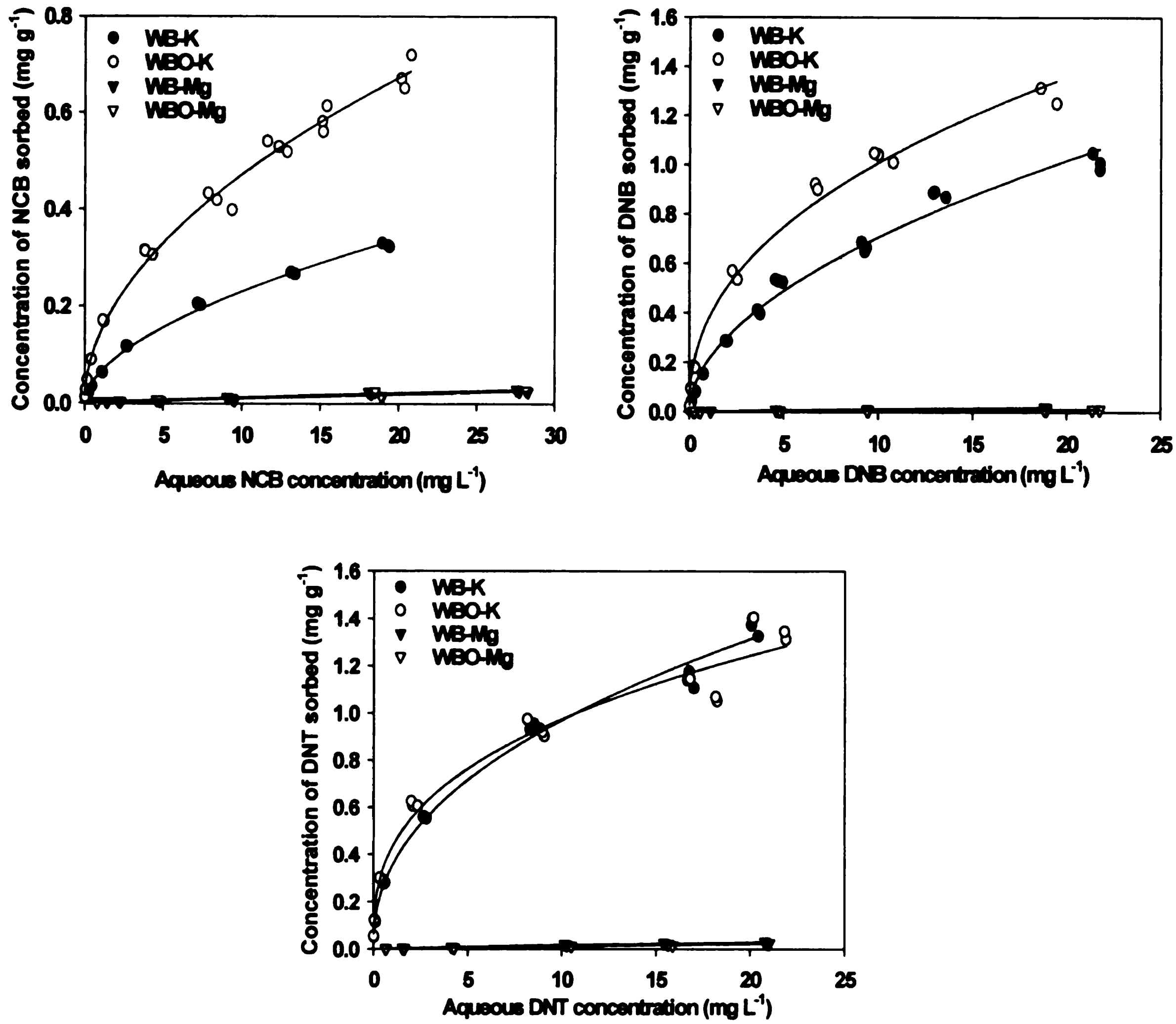

Figure 4.2. Isotherms for sorption of p-nitrocyanobenzene (NCB), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) by K^+- and Mg^{2+}-saturated Webster B (WB) and Webster B soil from which SOM was removed (WBO).

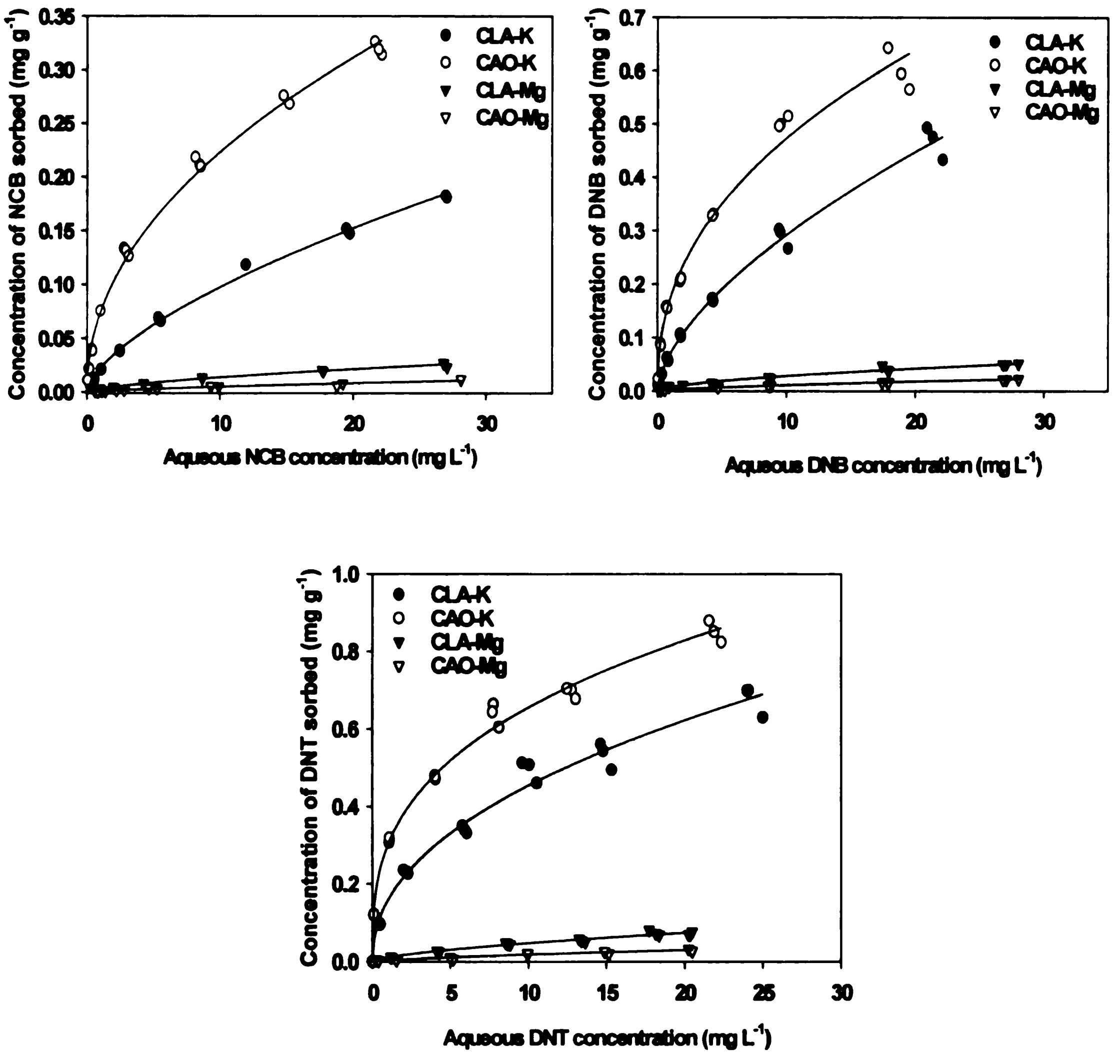

Figure 4.3. Isotherms for sorption of p-nitrocyanobenzene (NCB), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) by K^+- and Mg^{2+}-saturated Clarion A (CLA) and Clarion A soil from which SOM was removed (CAO).

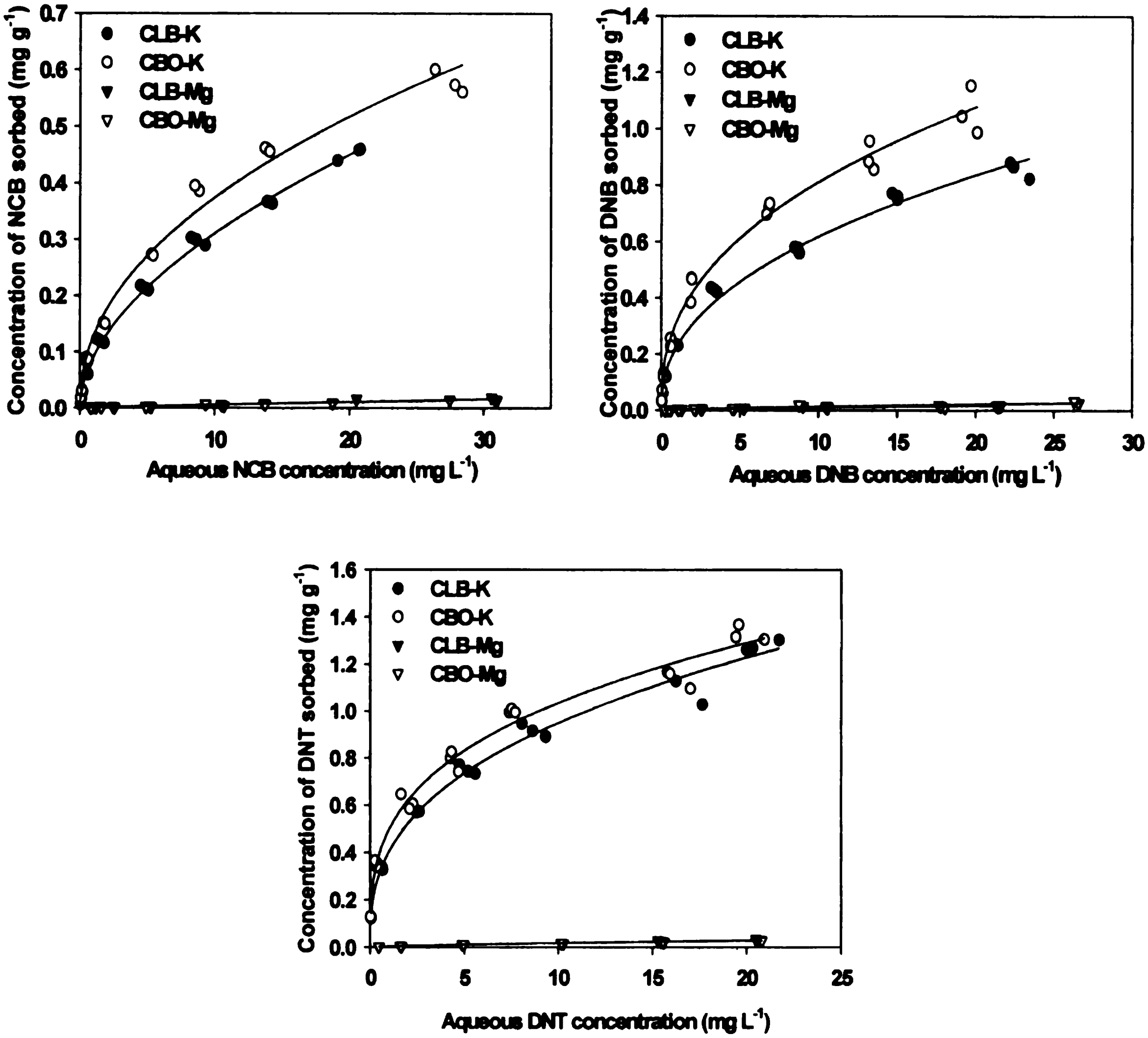

Figure 4.4. Isotherms for sorption of p-nitrocyanobenzene (p-NCB), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) by K$^+$- and Mg^{2+}-saturated Clarion B (CLB) and Clarion B soil from which SOM was removed (CBO).

Table 4.2. Freundlich equation K_f and n values for p-nitrocyanobenzene, 1,4-dinitrobenzene and 2,4-dinitrobenzene sorption by K^+- and Mg^{2+}-exchanged Webster and Clarion (A and B horizons) whole soils and soils from which SOM was removed.

Soils		**p-Nitrocyanobenzene**		**1,4-dinitrobenzene**		**2,4-dinitrotoluene**	
		K_f	**n**	**K_f**	**n**	**K_f**	**n**
Webster A	K^+-whole	0.0527	0.5989	0.1627	0.4690	0.2702	0.4358
	K^+-OM removed	0.0921	0.5022	0.2373	0.4004	0.3304	0.3687
	Mg^{2+}-whole	0.0067	0.6216	0.0205	0.2975	0.0152	0.6637
	Mg^{2+}-OM removed	0.0001	0.8939	0.0022	0.6476	0.0016	0.8480
Webster B	K^+-whole	0.0634	0.5589	0.2092	0.5283	0.3615	0.4183
	K^+-OM removed	0.1446	0.5129	0.3681	0.4420	0.4384	0.3294
	Mg^{2+}-whole	0.0017	0.8495	0.0019	0.7414	0.0030	0.7463
	Mg^{2+}-OM removed	0.0012	0.8824	0.0009	0.8481	0.0015	0.9068
Clarion A	K^+-whole	0.0220	0.6464	0.0703	0.6182	0.1586	0.4569
	K^+-OM removed	0.0734	0.4844	0.1689	0.4337	0.3013	0.3381
	Mg^{2+}-whole	0.0025	0.7402	0.0080	0.5596	0.0100	0.6861
	Mg^{2+}-OM removed	0.0010	0.7061	0.0023	0.7167	0.0035	0.7301
Clarion B	K^+-whole	0.0902	0.5386	0.2341	0.4338	0.4112	0.3556
	K^+-OM removed	0.1293	0.4643	0.3309	0.3821	0.5029	0.3066
	Mg^{2+}-whole	0.0007	0.9551	0.0026	0.6026	0.0038	0.6942
	Mg^{2+}-OM removed	0.0012	0.7166	0.0025	0.7327	0.0043	0.6377

of NACs through direct coordination of the NO_2 group with the interlayer cation is hindered by the waters of hydration for more highly hydrated cations (e.g., Mg^{2+}) resulting in lower energies of interaction between the NAC and the cation and hence lower NAC sorption compared to less strongly hydrated cation systems (e.g., K^+) (Li et al., 2004). Hence, the clays in the Mg^{2+}-saturated OM-removed soil are relatively inactive as sorbents for sorption of the NACs. The SOM in the Mg^{2+}- saturated whole soil is the principal sorbent phase hence with its removal p-NCB, 1,4-DNB and 2,4-DNT sorption decreases in the Mg^{2+}-saturated OM-removed soil (Figure 4.1-4.4).

The K^+-saturated soils (unfractionated and OM-removed) sorbed p-NCB, 1,4-DNB and 2,4-DNT to a greater extent compared to Mg^{2+}-saturated soils (Figure 4.1-4.4). These results are consistent with several studies that report stronger sorption of NACs by smectite clays saturated with cations of relatively low hydration energies (e.g. K^+, Cs^+) compared to that by systems saturated with cations of relatively higher hydration energies (e.g. Ca^{2+}, Mg^{2+}) (Li et al., 2003; Boyd et al., 2001; Sheng et al., 2001, 2002; Haderlein et al., 1996; Weissmahr et al., 1997, 1999; Johnston et al., 2001, 2002) and with the fact that smectite is the most abundant clay mineral in the Webster and Clarion soils (Chapter 3). This result can be attributed, in part, to direct interaction between NO_2 groups of the NACs and K^+; complexation of this nature is inhibited by the stronger hydration of Mg^{2+} in the Mg^{2+}-saturated soils (Boyd et al., 2001; Johnston et al., 2001, 2002; Sheng et al., 2002; Li et al., 2003). Lower hydration of K^+ (versus Mg^{2+}) on the exchange sites also manifests larger adsorption domains between exchangeable cations for NOC sorption which facilitates interaction of the solute with the clay basal surface (Lee et al., 1990;

Jaynes and Boyd, 1991a, b; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Weissmahr et al., 1997, 1998). Also, lower hydration of K^+ (versus Mg^{2+}) gives rise to smaller interlayer distances of ~3 Å which are optimal for the solute to interact with opposing siloxane sheets and thereby minimize its contact with water. In Chapter 1 we reported similar trends for p-NCB sorption by surface soils.

The K^+-saturated OM-removed soils sorbed more p-NCB, 1,4-DNB and 2,4-DNT than the K^+-unfractionated soils (Figure 4.1-4.4). Removal of SOM, therefore, increased sorption of the NACs by each soil although SOM undoubtedly acts as an independent sorptive sink for these solutes (Sheng et al., 2001). This suggests that SOM obscures sorptive surfaces in soils. This effect is most likely related to obscuration of smectite surfaces since they are the clays having the greatest affinities for NACs. It is possible to observe the suppression of sorption in the presence of SOM because of the preferential sorption of p-NCB, 1,4-DNB and 2,4-DNT to smectite clays compared to SOM as well as the use of systems saturated with cations (e.g., K^+) that facilitate relatively significant sorption by smectites. Literature reports decreased sorption of organic solutes to smectite clays when associated with SOM (Liu et al., 2002; Celis et al., 1997; Pusino et al., 1992, 1994). Although these studies indicated that the presence of SOM associated with smectite clays results in decreased sorption of solutes by the clays, these studies utilized synthetic clay-SOM complexes. Our data indicates that in natural soils, removal of SOM from soil increases sorption of solutes indicating that in natural soils, as in synthetic systems, SOM obscures clay surfaces for sorption of NACs.

The f_a values (i.e. the fraction of mineral surfaces that are available in unfractionated soil for solute sorption) derived using the Karickhoff and alternative equations, are given in Tables 4.3, 4.4 and 4.5, respectively. The f_a values derived using Karickhoff's equation and K^+-saturated peat were similar to those derived using Mg^{2+}-saturated peat (Tables 4.3, 4.4). For each equation, the f_a values differed across soils for each NOC. For p-NCB, 1,4-DNB and 2,4-DNT, the f_a values calculated for each soil using the Karickhoff (1984) equation [1] (Tables 4.3, 4.4) were similar to those calculated using the equation [2] we proposed in Chapter 2 (Table 4.5). Considering the NACs (p-NCB, 1,4-DNB and 2,4-DNT) both equations yielded f_a values for Clarion B that were greater than for Clarion A; f_a values for Webster A and B were similar (Tables 4.3, 4.4, 4.5). If all carbon (C) in SOM were assumed to cover the basal surfaces of soil smectites, the estimated maximal percent of the smectite basal surface covered by SOM (calculated using the Lagaly (1981) alkylammonium method as outlined in Chapter 3) in whole soil was greater for Clarion A (49%) compared to Clarion B (10%) and similar for Webster A (38%) and Webster B (31%) which follows the trend for the complement of the f_a vales (i.e., 1- f_a) for each horizon. One conclusion from this analysis is that the basal surfaces of smectite clays are partially covered by SOM as suggested by Stevenson (1994). We know that NACs intercalate between clay layers when they sorb to smectites (Sheng et al., 2001, 2002; Li et al., 2003). Small organic molecules can also occupy clay interlayer sites (Jaynes and Boyd, 1991a, b; Lee et al., 1989, 1990). Another plausible mechanism is that SOM blocks access to the interlayer of swelling clays.

Table 4.3. The f_a values for p-nitrocyanobenzene (NCB), 1,4-dinitrobenzene (DNB), and 2,4-dinitrotoluene (DNT) sorption by Webster (A and B horizons) and Clarion (A and B horizons) estimated using Karickhoff's equation [1] (using solute sorption by K^+-saturated peat to determine the K_{om} term).

NAC used	Concentration (mg L^{-1})	Iowa Webster A	Iowa Webster B	Clarion A	Clarion B
Nitrocyanobenzene	5	0.55 (0.02)	0.44 (0.02)	0.27 (0.01)	0.78 (0.04)
	10	0.60 (0.02)	0.46 (0.02)	0.32 (0.01)	0.82 (0.02)
	15	0.63 (0.03)	0.47 (0.02)	0.35 (0.01)	0.84 (0.02)
	20	0.65 (0.03)	0.47 (0.02)	0.37 (0.01)	0.86 (0.03)
Dinitrobenzene	5	0.70 (0.03)	0.64 (0.02)	0.49 (0.04)	0.76 (0.01)
	10	0.74 (0.03)	0.68 (0.02)	0.57 (0.06)	0.79 (0.03)
	15	0.76 (0.03)	0.71 (0.03)	0.62 (0.08)	0.81 (0.04)
	20	0.78 (0.04)	0.73 (0.04)	0.66 (0.09)	0.82 (0.05)
Dinitrotoluene	5	0.86 (0.02)	0.94 (0.04)	0.59 (0.01)	0.89 (0.04)
	10	0.89 (0.02)	1.00 (0.06)	0.63 (0.01)	0.92 (0.06)
	15	0.90 (0.02)	1.04 (0.07)	0.65 (0.02)	0.93 (0.07)
	20	0.91 (0.02)	1.06 (0.08)	0.67 (0.03)	0.94 (0.08)

For NCB and DNB, across each concentrations, f_a values for Clarion A < Webster B < Webster A < Clarion B ($p < 0.05$). For DNT, across each concentrations, f_a values for Clarion A < Webster A = Clarion B < Webster B ($p < 0.05$). For Clarion A, Webster A and Webster B, at each concentration, the f_a values for NCB < DNB < DNT. For Clarion B, at each concentration, the f_a values for NCB < DNB = DNT. Standard deviations in parentheses.

Table 4.4. The f_a values for p-nitrocyanobenzene (NCB), 1,4-dinitrobenzene (DNB), and 2,4-dinitrotoluene (DNT) sorption by Webster (A and B horizons) and Clarion (A and B horizons) estimated using Karickhoff's equation [1] (using solute sorption by Mg^{2+}-saturated peat to determine the K_{om} term).

NAC used	**Concentration ($mg\ L^{-1}$)**	**Iowa Webster A**	**Iowa Webster B**	**Clarion A**	**Clarion B**
Nitrocyanobenzene	5	0.61 (0.02)	0.46 (0.02)	0.35 (0.01)	0.79 (0.05)
	10	0.65 (0.02)	0.48 (0.02)	0.39 (0.01)	0.83 (0.02)
	15	0.68 (0.03)	0.48 (0.02)	0.42 (0.01)	0.85 (0.02)
	20	0.70 (0.03)	0.49 (0.02)	0.44 (0.01)	0.87 (0.03)
Dinitrobenzene	5	0.74 (0.02)	0.65 (0.02)	0.53 (0.04)	0.77 (0.01)
	10	0.77 (0.03)	0.69 (0.02)	0.60 (0.06)	0.79 (0.03)
	15	0.79 (0.03)	0.71 (0.03)	0.65 (0.08)	0.81 (0.04)
	20	0.80 (0.04)	0.73 (0.04)	0.68 (0.09)	0.82 (0.05)
Dinitrotoluene	5	0.90 (0.05)	0.95 (0.05)	0.62 (0.04)	0.90 (0.04)
	10	0.93 (0.06)	1.01 (0.06)	0.66 (0.05)	0.93 (0.06)
	15	0.95 (0.07)	1.05 (0.07)	0.69 (0.05)	0.94 (0.07)
	20	0.96 (0.07)	1.07 (0.08)	0.71 (0.06)	0.95 (0.08)

For NCB and DNB, across each concentrations, f_a values for Clarion A < Webster B < Webster A < Clarion B ($p < 0.05$). For DNT, across each concentrations, f_a values for Clarion A < Webster A = Clarion B < Webster B ($p < 0.05$). For Clarion A, Webster A and Webster B, at each concentration, the f_a values for NCB < DNB < DNT. For Clarion B, at each concentration, the f_a values for NCB < DNB = DNT. Standard deviations in parentheses.

Table 4.5. The f_a values for p-nitrocyanobenzene (NCB), 1,4-dinitrobenzene (DNB), and 2,4-dinitrotoluene (DNT) sorption by Webster (A and B horizons) and Clarion (A and B horizons) estimated using our alternative equation [2].

NOC used	Concentration (mg L^{-1})	Iowa Webster A	Iowa Webster B	Clarion A	Clarion B
Nitrocyanobenzene	5	0.61 (0.02)	0.46 (0.02)	0.35 (0.01)	0.79 (0.05)
	10	0.65 (0.02)	0.48 (0.02)	0.39 (0.01)	0.83 (0.02)
	15	0.68 (0.03)	0.48 (0.02)	0.42 (0.01)	0.85 (0.02)
	20	0.70 (0.03)	0.49 (0.03)	0.44 (0.01)	0.87 (0.03)
Dinitrobenzene	5	0.73 (0.03)	0.65 (0.02)	0.53 (0.05)	0.77 (0.01)
	10	0.78 (0.03)	0.69 (0.02)	0.60 (0.07)	0.80 (0.03)
	15	0.81 (0.03)	0.72 (0.03)	0.65 (0.08)	0.82 (0.04)
	20	0.83 (0.04)	0.74 (0.04)	0.69 (0.09)	0.83 (0.05)
Dinitrotoluene	5	0.88 (0.03)	0.95 (0.04)	0.61 (0.01)	0.91 (0.05)
	10	0.91 (0.02)	1.02 (0.06)	0.65 (0.01)	0.93 (0.06)
	15	0.93 (0.02)	1.05 (0.06)	0.68 (0.02)	0.95 (0.07)
	20	0.94 (0.03)	1.08 (0.08)	0.70 (0.03)	0.96 (0.08)

For NCB and DNB, across each concentrations, f_a values for Clarion A < Webster B < Webster A < Clarion B ($p < 0.05$). For DNT, across each concentrations, f_a values for Clarion A < Webster A = Clarion B < Webster B ($p < 0.05$). For Clarion A, Webster A and Webster B, at each concentration, the f_a values for NCB < DNB < DNT. For Clarion B, at each concentration, the f_a values for NCB = DNB < DNT. Standard deviations in parentheses.

The f_a values for p-NCB, 1,4-DNB, and 2,4-DNT were strongly negatively correlated (61-88%) with the ratio of SOM to smectite contents (%OM/%smectite) in soils; the percent correlation being in the order p-NCB > 1,4-DNB > 2,4-DNT (Table 4.6). This is reasonable since smectites have the highest affinity for NACs among soil clays (Chapter 1). The f_a values for p-NCB, 2,4-DNT and 1,4-DNB were moderately negatively correlated with the %OM contents of the soil horizons with 45-51%, 24-27% and 21-33% of the difference in f_a values between soil horizons attributed to differences in SOM contents, respectively (Table 4.6). The f_a values for p-NCB, 2,4-DNT and 1,4-DNB were weakly correlated with the %smectite contents of the soil horizons with 17-21%, 31-33% and 33-43% of the difference in f_a values between soil horizons attributed to differences in smectite contents, respectively (Table 4.6). Linear regression analysis of the f_a values and the ratios of SOM to smectite contents of the soil horizons indicates that the f_a values calculated are reasonable since, for each regression, the intercepts are approximately equal and all approach unity at 0% SOM (Table 4.6). The f_a values for the NACs, for each soil horizon, decreased in the order 2,4-DNT > 1,4-DNB > p-NCB, suggesting that the mechanism driving sorption site availability is influenced, in part, by the nature of the solute.

Data analysis revealed that the f_a values for the Webster A, Webster B and Clarion A soils across solutes were strongly negatively correlated with $K_{om}/K_{smectite}$ with 68-89% of the differences in f_a values between solutes attributed to differences in the relative affinities of the solute for SOM and smectite in these soils (Table 4.7). For each of these soils, the f_a values and $Q_{beidellite}$ (i.e., sorption distribution coefficient for sorption of each

Table 4.6. Correlations between f_a values for sorption of p-nitrocyanobenzene (NCB), 1,4-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT) estimated using Karickhoff equation [1] (using solute sorption by K^+-saturated peat to determine the K_{om} term) and our alternative equation [2] and percent organic matter (%OM), percent smectite (%smectite) and ratio of organic matter to smectite (%OM/%smectite).

Correlations were performed across the Webster and Clarion (A and B horizons) soils ($\alpha = 0.5$).

Equation used	**NOC used**	**%OM**	**%smectite**	**%OM/%smectite**	**Intercept**
Karickhoff	DNT	-0.27	0.31	-0.64	1.07 (0.08)
	DNB	-0.33	0.33	-0.75	0.92 (0.06)
	NCB	-0.51	0.17	-0.88	0.85 (0.04)
Alternative	DNT	-0.24	0.33	-0.61	1.08 (0.08)
	DNB	-0.21	0.43	-0.66	0.91 (0.06)
	NCB	-0.45	0.21	-0.83	0.85 (0.04)

Standard deviations in parentheses

Table 4.7. Amount of solute sorbed to K^+-beidellite ($Q_{beidellite}$) and peat (Q_{peat}) soil at an equilibrium concentration of 10 mg L^{-1} and the ratio of extents of p-nitrocyanobenzene (NCB), 1,4-dinitrobenzene (DNB), and 2,4-dinitrotoluene (DNT) sorption by SOM and K^+-beidellite. Regression correlations between f_a values estimated using Karickhoff equation [1] (using solute sorption by K^+-saturated peat to determine the K_{om} term) and our alternative equation [2] and $Q_{bedellite}$ and the ratio of extents of solute sorption by SOM and K^+-beidellite ($K_{om}/K_{smectite}$).

Equation used	NOC used	$Q_{beidellite}$ (mg g^{-1})	Q_{peat} (mg g^{-1})	$Q_{peat}/Q_{beideillite}$ = $K_{om}/K_{smectite}$	Correlations							
					$Q_{beidellite}$ (mg g^{-1})				$K_{om}/K_{smectite}$			
					WA	WB	CLA	CLB	WA	WB	CLA	CLB
Karickhoff	DNT	3.8261	1.5427	0.4032	0.93	0.92	0.94	0.49	-0.72	-0.68	-0.89	-0.11
	DNB	3.2088	1.0550	0.3288								
	NCB	1.4520	1.0119	0.6969								
Alternative	DNT	3.8261	1.5427	0.4032	0.92	0.92	0.92	0.47	-0.71	-0.67	-0.88	-0.09
	DNB	3.2088	1.0550	0.3288								
	NCB	1.4520	1.0119	0.6969								

NAC to K^+-beidellite clay at an equilibrium concentration of 10 mg L^{-1}) were strongly correlated with >90% of the difference in f_a values for each soil across NACs attributed to the difference in affinity of each NAC for smectite clay (Figure 4.5, Table 4.6). These results suggest that the greater the extent of sorption of the NAC to swelling clays, the less impact SOM may have on availability of sorptive surfaces in soils. For Clarion B, f_a values were negatively correlated with $K_{om}/K_{smectite}$ with 9-11% of difference in f_a values for this soil across solutes attributed to differences in the relative affinities of the solute for SOM and smectite clay in this soil. The f_a values for Clarion B, across solutes, were correlated to $Q_{beidellite}$ with 47-49% of the difference attributed to difference in affinity of each NAC for smectite clay. This may be due to the small initial amounts of SOM in this soil which we propose covers only 10% of the clay surface in whole soil (Chapter 3). Thus we suggest the efficacy of SOM to obscure sorptive clay surfaces in this case is probably minimal.

Our data suggest that f_a values for NACs approach 1 in cases where the NAC is strongly sorbed (presumably by smectite) and the OM/smectite ratio low. For example, f_a values for 2,4-DNT sorbed by the Webster B soil approach 1 (Table 4.3, 4.4). Since in theory f_a can not be larger than 1, it was of interest to test our method for evaluating f_a using a compound that sorbs more strongly to smectite clays than DNT, viz., 1,3,5-trinitrobenzene (1,3,5-TNB) (Haderlein et al., 1996). We measured sorption of 1,3,5-TNB to K^+- and Mg^{2+}-exchanged Webster B whole and OM-removed soils using a batch equilibrium technique (Figure 4.6), and calculated f_a values for the selected concentrations 5, 10, 15, and 20 mg L^{-1}, as previously described. The determined f_a

values were close to unity ranging from 1.05 ± 0.04 to 1.09 ± 0.09 and 1.06 ± 0.04 to 1.10 ± 0.09 using equation [1] and [2], respectively, for data analysis. This observation helps validate our approach for the experimental evaluation of clay mineral surface availability. These results suggest that the relative SOM and smectite contents of the soil horizons as well as the nature of the solute, primarily its adsorption capacity to swelling clays, influence the efficacy of SOM to obscure sorptive surfaces of soil clays and therefore influence the availability of these sites in whole soil for the sorption of NACs.

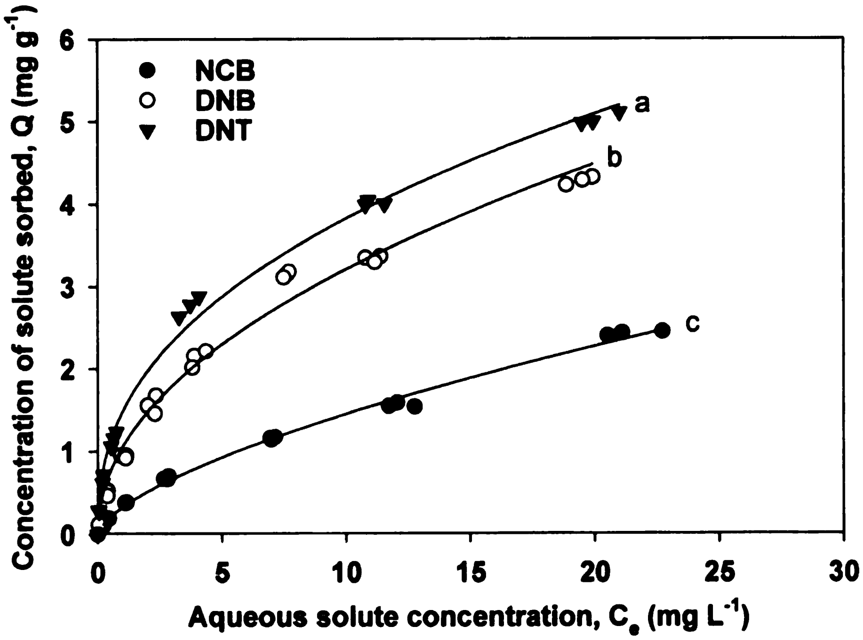

Figure 4.5. Isotherms for sorption of p-nitrocyanobenzene (NCB), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) by K$^+$-beidellite.

(isotherms with different letters are statistically different, $\alpha = 0.05$)

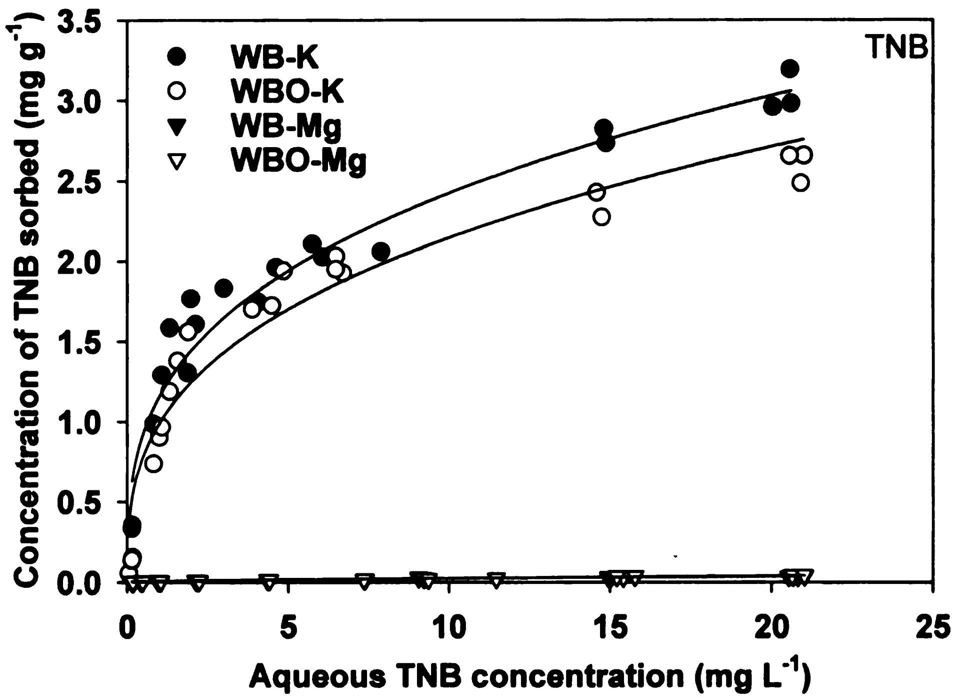

Figure 4.6. Isotherms for sorption of 1,3,5-trinitrobenzene by K^{+}- and Mg^{2+}-saturated Webster B (WB) and Webster B from which SOM was removed (WBO).

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CONCLUSION

The molecular and environmental factors that control the sorption of nitroaromatics (NACs) in the environment must be more accurately understood for the purposes of controlling their mobility and reactivity in the environment. Soil clays and soil organic matter (SOM) undoubtedly function in concert than as separate entities due to their intimate association in surface soils. Our studies indicate that adsorption of NACs by surface soils is strongly influenced by the nature of the dominant exchangeable cation. In addition, the association of SOM with clay reduces the availability of sorptive surfaces in soils, with availability being dependent on the relative contents of SOM and sorptive clays (and the nature of the clays) in the soil as well as the nature of the solute in the whole soil. We determined that the equation proposed by Karickhoff is best suited to compounds that sorb significantly to clays such as NACs such that the sorption to the clay fraction is large enough to facilitate accurate calculation of f_a. This issue was encountered when using diuron as the solute. Fate and transport models that utilize sorption parameters based on the additive effect of reference clay and humic material sorption may deviate from reality and may overestimate the amount of NAC sorbed.

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