

## Sorption of High Explosives to Water-Dispersible Clay: Influence of Organic Carbon, Aluminosilicate Clay, and Extractable Iron

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Explosives in soils can present environmental problems for military installations. Fine, mobile particles represent the most reactive fraction of the soil and, therefore, are expected to adsorb explosives and potentially facilitate their transport. The objective of this study was to determine the relative significance of phyllosilicate clay, organic matter, and two forms of extractable iron in adsorption of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by the colloidal water-dispersible clay (WDC) fraction of the soil. The WDC fraction of two mineral and one organic soil was separated and then treated to remove organic carbon (OC) and several forms of iron ( $Fe_o$ , oxalate extractable, and  $Fe_d$ , dithionite-citrate extractable). Adsorption coefficients were determined for whole soils, untreated, and treated WDC. For mineral soils, adsorption of TNT and RDX on the WDC was greater than on the whole soil. The presence of OC increased explosives sorption by WDC. When OC was removed, iron interfered with TNT sorption. In the presence of OC, removal of  $Fe_o$  decreased RDX adsorption and increased TNT adsorption indicating different adsorption mechanisms. Organic carbon was a more significant indicator of explosives adsorption by WDC than clays or iron oxides and hydroxides. Therefore, OC is the most likely medium for facilitated transport of TNT and RDX.

PREVIOUS research has demonstrated contamination of live-fire training ranges with residues of high explosives (HE) (Pennington et al., 2002). Anticipation of the extent to which migration of HE occurs is vital to assessments of contamination behavior/transport and appropriate range management. Specifically, 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are common HE that have been detected on live-fire ranges and due to their dissimilar chemical structure are expected to exhibit different behavior in the environment. Previous studies of adsorption by soils and transport of explosives in solution phase (review by Pennington and Brannon, 2002) indicated significant adsorption of TNT relative to much less adsorption of RDX. Therefore TNT tends to be a sediment contaminant, and RDX tends to be leached further down in the soil profile and is a common groundwater contaminant. The aspect of HE fate that was not studied previously is transport in association with mineral and organic colloidal material. However, significant contribution of colloids to transport of several other contaminants has been demonstrated (de Jonge et al., 2004). Strong adsorption of TNT to dissolved organic carbon (DOC) ( $K_{DOC} = 41-68 \text{ mL g C}^{-1}$ ) observed by Eriksson et al. (2004) suggests that colloid-facilitated transport may be contributing to TNT movement.

The clay-sized (colloidal) fraction of the soil consists of silica, iron, aluminum, manganese, titanium oxides and hydroxides, phyllosilicate minerals, and organic compounds. The portion of clay that can be mobilized by water is operationally defined as water-dispersible clay (WDC). According to Grolimund et al. (1998), soil colloidal particles mobilized in situ are highly poly-disperse and irregular in shape with an upper size limit of 1  $\mu\text{m}$ . Water-dispersible clay is also highly heterogeneous in mineral composition and enriched in OC and sesquioxides relative to whole soil (Kjaergaard et al., 2004).

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**Abbreviations:** AOE, acid oxalate extraction; CEC, cation exchange capacity; DCE, dithionite-citrate extraction; DOC, dissolved organic carbon;  $Fe_d$ , dithionite-citrate extractable iron;  $Fe_o$ , acid oxalate extractable iron; HE, high explosives; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; HPLC, high performance liquid chromatography;  $K_d$ , adsorption coefficient;  $K_{OC}$ , adsorption coefficient normalized to fraction of organic carbon; OC, organic carbon; POC, particulate organic carbon; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; TNT, 2,4,6-trinitrotoluene; SA, surface area; WDC, water-dispersible clay.

Soil adsorption coefficients ( $K_d$ s) for most common military explosives, including TNT and RDX, were reviewed by Branon and Pennington (2002) and Tucker et al. (2002). Significant linear regression between  $K_d$  values and soil OC content indicated that adsorption to organic matter is the main mechanism of RDX interaction with the soils (Tucker et al., 2002). Adsorption isotherms for RDX are generally linear and reversible (Tucker et al., 2002) confirming partitioning as the principal sorption mechanism. Haderlein et al. (1996) showed that RDX does not exhibit specific adsorption to clay surfaces as shown for nitroaromatic compounds; however, it can participate in hydrogen bonding with clays (Ainsworth et al., 1993). The presence of iron oxides that coat clay particles may also affect sorption. Ainsworth et al. (1993) used a combination of OC, CEC, clay content, pH, and  $Fe_d$  to predict RDX adsorption. However, Szecsody et al. (2004) observed no dependence of RDX adsorption on OC,  $Fe_d$ , or clay content in studied sediments.

TNT and its metabolites interact with soil organic compounds (Pennington et al., 1995; Li et al., 1997; Eriksson and Skyllberg, 2001; Eriksson et al., 2004). Li et al. (1997) suggested binding of TNT to non-polar groups and binding of amino-transformation products of TNT to polar groups in humic acids. Thorn and Kennedy (2002) defined the mechanism of this interaction by showing that amino-transformation products of TNT undergo nucleophilic addition reactions with quinone and other carbonyl groups in the soil humic acid to form both heterocyclic and nonheterocyclic condensation products. Eriksson and Skyllberg (2001) observed differences in binding of TNT (and its degradates) to DOC and particulate organic carbon (POC). They concluded that the association with DOC is mainly of ionic character involving specific DOC sites, while nonspecific hydrophobic partitioning happens in POC.

TNT can be sorbed to uncharged regions of phyllosilicate clays through electron donor-acceptor complexes between oxygen atoms of the siloxane surface and the six-carbon ring of TNT, called pi-bonding (Haderlein et al., 1996; Weissmahr et al., 1998; Weissmahr et al., 1999). The effect of this mechanism on overall TNT adsorption by natural low-OC sediments was demonstrated by Weissmahr et al. (1999).

A strong positive relationship between oxalate-extractable iron ( $Fe_o$ ) and  $K_d$ s for TNT indicated by Pennington and Patrick (1990) suggests participation of poorly crystalline iron oxides and hydroxides in adsorption of TNT. While Weissmahr et al. (1998) showed that several crystalline iron oxides (magnetite, hematite, lepidocrocite, and goethite) do not display significant sorption of TNT and other nitroaromatics, materials they tested had limited surface area (SA). Non-crystalline iron oxides possess much greater SA than their crystalline forms and may be responsible for sorption of TNT and possibly RDX. Poorly crystalline forms of iron are also more mobile (Jackson et al., 1986). Consequently, this amorphous iron can participate in facilitated transport of HE. On the other hand, Ainsworth et al. (1993) showed a negative relationship between dithionite-citrate extractable iron ( $Fe_d$ ) content and RDX and TNT adsorption, probably due to iron oxides interfering with sorption of explosives to OC and clays.

The objective of this study was to identify components con-

stituting WDC fraction(s) of soils (e.g., OC, iron oxides, phyllosilicate clays) that adsorb TNT and RDX and that are, therefore, potentially responsible for their facilitated transport in soils. This was achieved by defining and comparing partition coefficients for TNT and RDX adsorption by three different soils, WDC fraction of these soils, and WDC treated to remove OC,  $Fe_o$ , and  $Fe_d$ . The hypothesis was that TNT would interact strongly with OC and clay, while RDX would react primarily with OC.

## Materials and Methods

### Soils

Catlin silt loam (fine-silty, mixed, mesic, superactive Oxyaquic Argiudolls) collected in Champaign County, IL, Benndale fine sandy loam (coarse-loamy, siliceous, semiactive, thermic Typic Paleudults) collected in De Soto National Forest, Perry County, MS, and Kenner muck (euic, thermic, Fluvaquentic Medisaprists) collected in Bayou Segnette, Jefferson Parish, LA were used in this study. Soils represented a range of environments and climates: Catlin formed on a prairie, Benndale in a forest, and Kenner in a freshwater marsh.

Soil samples collected to a depth of 20 cm were air dried at room temperature, ground, and passed through a 2-mm sieve to obtain a uniform and representative sample. Soils were analyzed for cation exchange capacity (CEC) using the NaOAc method (USEPA, 1986), OC by combustion after acid pretreatment, and iron using acid ammonium oxalate (AOE) and dithionite-citrate extraction (DCE) (Soil Survey Staff, 1996). Particle size was determined by the hydrometer method (Gee and Or, 2002). Soil pH was measured in a 1:1 soil/water slurry using sympHony SB70P benchtop pH meter with glass combination pH electrode (VWR, West Chester, PA).

### Clay Removal and Treatment

Water-dispersible clay ( $\leq 2 \mu\text{m}$ ) was extracted from soils by repeated suspension in deionized water and sedimentation. Residues ( $>2 \mu\text{m}$ ) were oven dried and weighed to determine clay recovery by difference. Water-dispersible clay in decanted supernatant was flocculated using  $0.5 \text{ mol L}^{-1} \text{ CaCl}_2$  and concentrated by centrifugation. Samples were then treated to remove carbonates, OC, noncrystalline aluminosilicates and hydrous oxides, and free iron-aluminum oxides and hydroxides according to the following scheme (Fig. 1).

All samples were washed with  $1 \text{ mol L}^{-1} \text{ NaCl}$  solution and treated with  $1 \text{ mol L}^{-1}$  acetate buffer (pH 5) at  $70^\circ\text{C}$  to remove carbonates. Absence of  $\text{CO}_2$  bubbles indicated that soils did not contain carbonates. Organic carbon removal for treatments WDC-OC, WDC-OC- $Fe_o$ , and WDC-OC- $Fe_d$  was done by treatment with peroxide (30%  $\text{H}_2\text{O}_2$  on the  $70^\circ\text{C}$  water bath) (Kunze and Dixon, 1986). Noncrystalline aluminosilicates and hydrous oxides were removed using oxalate extraction at pH 3 in the dark as described in Jackson et al. (1986) (treatments designated WDC-OC- $Fe_o$  and WDC- $Fe_o$ ). Free iron-aluminum oxides and hydroxides (treatment WDC-OC- $Fe_d$ ) were removed using sodium citrate-dithionite extraction (Kunze and Dixon, 1986) to expose phyllosilicate clay surfaces. All samples were

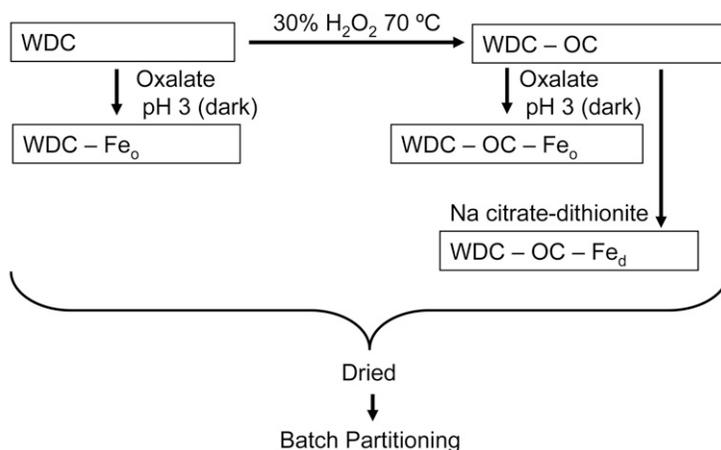


Fig. 1. Flow chart of water-dispersible clay (WDC) treatments. All WDC samples were treated with sodium acetate buffer to remove carbonates. OC = organic carbon,  $Fe_d$  = dithionite-citrate extractable iron,  $Fe_o$  = acid oxalate extractable iron.

washed three times with  $0.5 \text{ mol L}^{-1} \text{ CaCl}_2$  solution and then washed free of salts with deionized water until no  $\text{Cl}^-$  was detected by  $\text{AgNO}_3$  test and clays started to disperse. WDC was flash frozen in liquid nitrogen and lyophilically dried for storage.

Extracted and treated clays were analyzed for residual iron oxides (Soil Survey Staff, 1996), OC content (by combustion), and CEC (USEPA, 1986). External SA by nitrogen adsorption (Brunauer–Emmett–Teller [BET]) was determined using NOVA 3200e surface area analyzer (Quantachrome Instruments, Boynton Beach FL). In addition, WDC samples that had OC removed were examined using X-ray diffraction (XRD) to determine crystalline mineralogy of the clay fraction as described in Soil Survey Staff (1996).

### Batch Adsorption

Adsorption coefficients were determined by batch adsorption at five different concentrations using a mixture of unlabeled and radiolabeled RDX and TNT. Ring-labeled  $^{14}\text{C}$ -RDX with specific activity of  $19.82 \text{ mCi mmol}^{-1}$  was added at 0.2% of total solute, while  $^{14}\text{C}$ -TNT had specific activity of  $4.08 \text{ mCi mmol}^{-1}$  and amounted to 1% of total solute. Use of radioactive tracer allowed determining a sum of irreversible and reversible adsorption of RDX, TNT, and their transformation products. While for RDX it is expected that transformation and irreversible sorption were negligible, for TNT due to importance of transformation and irreversible adsorption an “apparent” adsorption coefficient was calculated for the sum of TNT and its products. No killing agents were added to the reactors potentially allowing both biotic and abiotic transformation of HE.

A series of preliminary experiments was conducted to select experimental conditions. Clay (or soil) to solution ratio was determined in preliminary studies to have about 10 to 30% of the solute adsorbed at the highest studied concentration (Roy et al., 1992). The ratios were 1:4 for Benndale soil TNT and RDX and Catlin RDX (4 g of soil in 16 mL of solution), 1:16 for Catlin TNT, 1:32 for Kenner RDX (0.5 g in 16 mL), and 1:160 for Kenner TNT (0.1 g in 16 mL). Clay/solution ratios were 1:20 for Benndale RDX and TNT and Catlin RDX, 1:40 for Catlin TNT, 1:160 for Kenner TNT, and 1:80 for Kenner

RDX. Within the soil or clay and solute combination the same ratio was used to ensure valid comparison of treatments.

Equilibration time was determined from kinetic adsorption curves established by shaking  $10 \text{ mg L}^{-1}$  radiolabeled RDX or TNT solutions with soils and clays for 0, 0.5, 1, 2, 6, 12, 24, 48, and 120 h on a reciprocating shaker at 180 excursions per minute. Equilibrium was considered established when the change in solution phase concentration over 24 h was less than 5% (Roy et al., 1992). This condition was satisfied at 24 h for most (76%) soils and clays, with several exceptions that are described below. Therefore, 24 h was used as equilibration time.

Batch adsorption was conducted in 25 mL glass centrifuge tubes. Soils and clays were ultrasonically dispersed in 8 mL of  $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$  solution, and then solutions of radiolabeled TNT and RDX were added. Resulting concentrations of TNT and RDX were 1, 2.5, 5, 7.5, and  $10 \text{ mg L}^{-1}$ . The samples were shaken for 24 h, centrifuged at 8288 relative centrifugal force for 60 min, and the aqueous phase removed and analyzed by liquid scintillation counting (Tri-Carb 2500TX Liquid Scintillation Analyzer, PerkinElmer Life and Analytical Sciences, Inc., Boston, MA). A sum of reversible and irreversible adsorption was determined from the decrease in solution phase radioactivity. All experiments were replicated at least twice, except for soil adsorption experiments which were replicated three times. For each set of experiments a blank with solution only was included to confirm the stability of test explosives and accuracy of solution additions. Measured blank TNT and RDX concentrations were not statistically different from calculated input concentrations.

Explosive concentrations in stock solutions were verified using high performance liquid chromatography (HPLC) (Waters HPLC, GenTech Scientific, Inc., Arcade, NY) and liquid scintillation. Standard USEPA Method 8330 (HPLC) (USEPA, 1994) was used with addition of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and the following degradation products: mono-, and diamino-nitrotoluenes, azoxy dimers of TNT, and mono-, di-, and tri-nitroso derivatives of RDX. The measured concentrations of TNT and RDX in stock solutions were within 1% of the target ( $30 \text{ mg L}^{-1}$ ), while HMX (an impurity in military-grade RDX) concentration was  $2.5 \text{ mg L}^{-1}$ .

Measured solution concentrations and calculated sediment concentrations were analyzed using linear, Freundlich, and Langmuir adsorption isotherms. The linear isotherm is described by the following equation:

$$S = K_d C,$$

where  $S$  is the concentration in sediment ( $\text{mg kg}^{-1}$ ),  $K_d$  is the adsorption coefficient ( $\text{mL g}^{-1}$ ), and  $C$  is the contaminant concentration in solution ( $\text{mg L}^{-1}$ ). The Freundlich isotherm is described by:

$$S = K_f C^n,$$

where  $K_f$  is the Freundlich adsorption coefficient and  $n$  is an empirical parameter that indicates the affinity of the compound for the adsorbent. Langmuir equation is:

$$S = Q b C / (1 + b C),$$

where  $b$  is the Langmuir constant for the adsorption reaction and  $Q$  is the monolayer sorption capacity ( $\text{mg L}^{-1}$ ). Parameters from the equation that described the data the best (largest  $R^2$ ) for majority of the treatments were compared between the treatments to elucidate the effect of treatments on adsorption. Statistical comparisons of adsorption isotherm slopes were performed using the method of difference between two independent regressions (Steel and Torrie, 1980). The  $\alpha = 0.05$  level of significance was used. Comparisons were done using SAS software (SAS Institute Inc., 2004).

## Results and Discussion

### Characterization of Water-Dispersible Clay

Catlin, Benndale, and Kenner soils had 18, 20, and 55% clay, pH of 7.5, 5.0, and 4.8, and WDC of 16, 8, and 7% of total soil, respectively. Water-dispersible clay fraction was enriched in OC and both forms of iron ( $\text{Fe}_o$  and  $\text{Fe}_d$ ) compared to whole soils (Table 1), in agreement with previous reports (Kjaergaard et al., 2004). The only exception was OC in Kenner muck, where OC was less than in whole soil because of the large amount of plant residues in the whole soils. Water-dispersible clay also had higher CEC than whole soils: 2.5 times higher for Catlin, 4.5 times for Benndale, and 1.3 times for Kenner muck. Benndale WDC was considerably enriched in iron (12 times for  $\text{Fe}_d$ ), while for other soils iron enrichment of WDC was not as pronounced.

None of the chemical treatments to WDC (peroxide, AOE, or DCE) completely removed iron or OC (Table 1). Peroxide treatments decreased OC concentrations three to five times compared to untreated WDC. Acid oxalate extraction of OC-containing WDC also removed an average of  $3.2 \text{ g kg}^{-1}$  OC, amounting to 5% of OC for Catlin WDC, 25% for Benndale WDC, and 1% for Kenner WDC. Dithionite-citrate extraction was more efficient than AOE in removal of iron and resulted in the lowest residual concentrations of both  $\text{Fe}_o$  and  $\text{Fe}_d$ . For mineral soils, removal of OC also decreased  $\text{Fe}_d$  by half indicating that OC protects iron oxides during DCE. This was not observed for  $\text{Fe}_o$ . In the Kenner WDC, removal of OC increased iron content as the total fraction of mineral components in WDC increased.

**Table 1. Properties of whole soils, untreated, and treated water-dispersible clay (WDC).**

	OC†	$\text{Fe}_d$	$\text{Fe}_o$	CEC	SA
	$\text{g kg}^{-1}$	$\text{mg g}^{-1}$	$\text{cmol}_c \text{ kg}^{-1}$	$\text{m}^2 \text{ g}^{-1}$	
Catlin silt loam	42.3	4.77	4.95	39	–
Kenner muck	353.5	1.73	1.82	122	–
Benndale fine sandy loam	8.9	0.88	0.76	11	–
Catlin WDC	51.5	20.24	9.24	95	18.1
Catlin WDC- OC	13.1	10.05	8.94	68	59.1
Catlin WDC- OC- $\text{Fe}_d$	9.2	0.92	1.48	64	50.3
Catlin WDC- OC- $\text{Fe}_o$	14.5	8.29	6.16	60	52.1
Catlin WDC- $\text{Fe}_o$	48.8	7.87	5.53	84	19.2
Kenner WDC	292.0	1.88	2.27	158	6.1
Kenner WDC- OC	49.5	3.55	5.49	55	14.0
Kenner WDC- OC- $\text{Fe}_d$	43.7	0.34	1.03	48	19.6
Kenner WDC- OC- $\text{Fe}_o$	51.4	2.07	2.36	49	21.5
Kenner WDC- $\text{Fe}_o$	289.0	0.63	0.93	144	4.0
Benndale WDC	15.7	10.44	4.52	47	55.0
Benndale WDC- OC	5.2	5.32	3.16	46	42.6
Benndale WDC- OC- $\text{Fe}_d$	4.3	1.28	1.09	36	67.0
Benndale WDC- OC- $\text{Fe}_o$	5.1	3.91	1.81	44	60.4
Benndale WDC- $\text{Fe}_o$	11.8	4.97	1.22	42	47.1

† OC = organic carbon by combustion after acid treatment;  $\text{Fe}_d$  = dithionite-citrate extractable iron,  $\text{Fe}_o$  = acid oxalate extractable iron; CEC = cation exchange capacity by sodium acetate method; SA = surface area by nitrogen adsorption.

Organic carbon removal decreased CEC in the Kenner (2.9 times) and Catlin (1.4 times) soils. Iron extraction did not have an appreciable effect on CEC indicating that both phyllosilicate clays and iron and aluminum oxyhydroxides serve as surfaces for cation exchange. However, as shown later, TNT is adsorbed differently by clays and oxyhydroxides.

The surface area of WDC was inversely related to OC content of the soils (Table 1). For Catlin and Kenner soils, removal of OC resulted in an increase in SA in agreement with Kjaergaard et al. (2004). Benndale soil, which had low OC content, did not exhibit this behavior. Increase in SA was attributed to increased access to clay surfaces, which were inaccessible when OC bound clay particles together.

Mineralogical composition of all three soils was mixed. Benndale WDC contained vermiculite, kaolinite, and quartz, with traces of mica. Catlin WDC had smectite, vermiculite, illite, kaolinite, and quartz. The WDC fraction of Kenner muck soil contained smectite and quartz with traces of mica and kaolinite. Grolimund et al. (1998) showed that mineralogical composition of in situ mobilized soil colloidal particles was highly heterogeneous and similar to that of the total clay fraction.

### Batch Adsorption on Soils

Preliminary adsorption experiments showed that for two of the three soils RDX and TNT concentrations changed less than 5% between 24 and 48 h of equilibration. Therefore, 24-h equilibration was used in subsequent sorption studies.

The RDX sorption was best characterized using linear isotherms ( $R^2 \geq 0.99$ ) (Table 2) in agreement with published reports (Ainsworth et al., 1993; Xue et al., 1995; Singh et al., 1998; Tucker et al., 2002; Yamamoto et al., 2004). The  $K_d$  val-

**Table 2. Regression parameters for RDX adsorption data for whole soils, untreated, and treated water-dispersible clay (WDC). Best  $R^2$  for the treatment is shown in bold.**

Soil	Treatment	Linear		Freundlich			Langmuir		
		$K_d$	$R^2$	$K_f$	$n$	$R^2$	$Q$	$b$	$R^2$
Catlin		2.03	0.994 **	2.44	0.89	<b>0.995 **</b>	39.93	0.07	0.990 **
Kenner		36.19	<b>0.993 **</b>	43.14	0.84	0.978 **	230.08	0.25	0.973 **
Benndale		0.78	<b>0.992 **</b>	1.22	0.74	0.961 **	6.70	0.25	0.930 **
Catlin	WDC	4.01 a†	<b>0.999 **</b>	3.61	0.77	0.840 **	1.71	16.38	0.517 *
	WDC- OC	1.72 d	<b>0.985 **</b>	1.37	1.12	0.803 *	0.16	17.97	0.124 ns
	WDC- OC- Fe <sub>d</sub>	2.02 d	<b>0.996 **</b>	1.98	0.63	0.552 ns‡	0.32	-3.37	0.849 *
	WDC- OC- Fe <sub>o</sub>	2.54 c	<b>0.995 **</b>	3.49	0.60	0.843 *	-3.37	1.46	0.596 ns
	WDC- Fe <sub>o</sub>	3.46 b	<b>0.998 **</b>	3.64	0.81	0.906 *	1.71	9.31	0.712 ns
Kenner	WDC	21.95 a	<b>0.997 **</b>	26.80	0.89	0.995 **	560.32	0.05	0.995 **
	WDC- OC	3.07 b	<b>0.959 **</b>	2.44	1.13	0.812 **	0.95	-0.20	0.346 ns
	WDC- OC- Fe <sub>d</sub>	2.72 b	<b>0.920 **</b>	1.88	1.20	0.790 **	1.87	-0.25	0.284 ns
	WDC- OC- Fe <sub>o</sub>	2.99 b	<b>0.910 **</b>	1.36	1.36	0.860 **	12.78	-17.78	0.000 ns
	WDC- Fe <sub>o</sub>	19.02 a	<b>0.985 **</b>	22.81	0.91	0.973 **	1382.15	0.02	0.974 **
Benndale	WDC	1.28 abcd	<b>0.898 **</b>	1.99	0.56	0.621 **	11.25	-0.30	0.351 *
	WDC- OC	1.44 bc	<b>0.961 **</b>	2.53	0.57	0.702 **	-5.49	0.81	0.376 *
	WDC- OC- Fe <sub>d</sub>	0.85 d	0.892 **	0.68	1.04	0.775 **	-0.50	-0.53	<b>0.966 **</b>
	WDC- OC- Fe <sub>o</sub>	0.97 cd	0.768 **	1.09	0.80	0.846 **	4.91	0.63	<b>0.891 **</b>
	WDC- Fe <sub>o</sub>	1.78 ab	<b>0.959 **</b>	1.82	0.69	0.606 **	1.00	-3.39	0.557 **

\*- regression significant at 95%.

\*\* - regression significant at 99%.

† Numbers followed by the same letter within soil are not different at 95% level.

‡ ns - regression not significant at 95%.

ues varied with soil OC content: Kenner > Catlin > Benndale. When  $K_d$ s were normalized to OC,  $\log K_{OC}$  values (2.01 for Kenner, 1.69 for Catlin, and 1.94 for Benndale) fell within the range of previously reported values for soils and sediments ( $2.26 \pm 0.56$ ) (calculated from review by Brannon and Pennington, 2002).

TNT adsorption could be best described using Langmuir isotherms (Pennington and Patrick, 1990); however, all iso-

therms resulted in highly significant relationships (Table 3). Determined  $K_d$ s increased with OC increase similarly to RDX. When compared to the literature values for soils ( $\log K_{OC}$  of  $2.53 \pm 0.42$ ) (calculated from review by Brannon and Pennington, 2002), all three soils were within the reported range (Kenner: 2.91, Catlin: 2.63, Benndale: 2.30).

**Table 3. Regression parameters for TNT adsorption data for whole soils, untreated, and treated water-dispersible clay (WDC). Best  $R^2$  for the treatment is shown in bold.**

Soil	Treatment	Linear		Freundlich			Langmuir		
		$K_d$	$R^2$	$K_f$	$n$	$R^2$	$Q$	$b$	$R^2$
Catlin		17.90	0.932 **	32.67	0.60	0.957 **	119.05	0.46	<b>0.982 **</b>
Kenner		285.23	0.831 **	499.01	0.63	0.894 **	1866.00	0.44	<b>0.972 **</b>
Benndale		1.77	<b>0.976 **</b>	2.78	0.73	0.975 **	13.71	0.29	0.946 **
Catlin	WDC	20.61 b†	0.939 **	48.48	0.48	<b>0.995 **</b>	114.29	1.01	0.973 **
	WDC- OC	8.90 d	0.941 **	21.17	0.53	0.955 **	69.89	0.48	<b>0.981 **</b>
	WDC- OC- Fe <sub>d</sub>	12.91 c	0.961 **	27.97	0.56	<b>0.991 **</b>	91.51	0.52	0.979 **
	WDC- OC- Fe <sub>o</sub>	13.20 c	0.964 **	28.35	0.56	<b>0.987 **</b>	92.64	0.52	0.984 **
	WDC- Fe <sub>o</sub>	26.40 a	0.863 **	71.64	0.40	0.931 **	140.45	1.66	<b>0.974 **</b>
Kenner	WDC	59.13 a	<b>0.979 **</b>	111.31	0.54	0.916 **	258.24	0.97	0.772 **
	WDC- OC	10.56 b	<b>0.952 **</b>	19.60	0.62	0.780 **	71.59	0.42	0.670 **
	WDC- OC- Fe <sub>d</sub>	12.80 b	<b>0.976 **</b>	21.44	0.70	0.877 **	102.63	0.29	0.720 **
	WDC- OC- Fe <sub>o</sub>	10.28 b	<b>0.978 **</b>	21.12	0.59	0.891 **	74.19	0.46	0.781 **
	WDC- Fe <sub>o</sub>	59.34 a	<b>0.972 **</b>	115.64	0.51	0.871 **	239.65	1.25	0.670 **
Benndale	WDC	4.69 bc	0.971 **	7.88	0.73	0.977 **	61.88	0.15	<b>0.983 **</b>
	WDC- OC	2.51 e	<b>0.964 **</b>	5.53	0.58	0.948 **	23.58	0.31	0.954 **
	WDC- OC- Fe <sub>d</sub>	3.86 cde	0.924 **	6.83	0.68	0.907 **	34.10	0.27	<b>0.927 **</b>
	WDC- OC- Fe <sub>o</sub>	3.74 d	<b>0.995 **</b>	5.19	0.81	0.983 **	45.54	0.14	0.961 **
	WDC- Fe <sub>o</sub>	6.43 a	<b>0.979 **</b>	12.42	0.61	0.928 **	41.03	0.51	0.727 **

\*\* - regression significant at 99%.

† Numbers followed by the same letter within the soil are not different at 95% level.

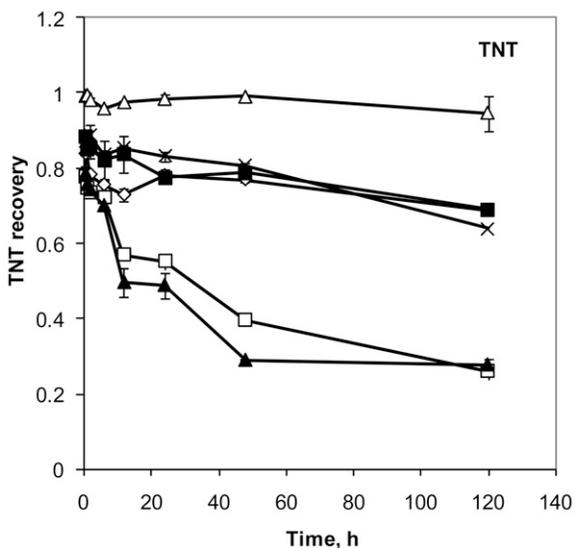
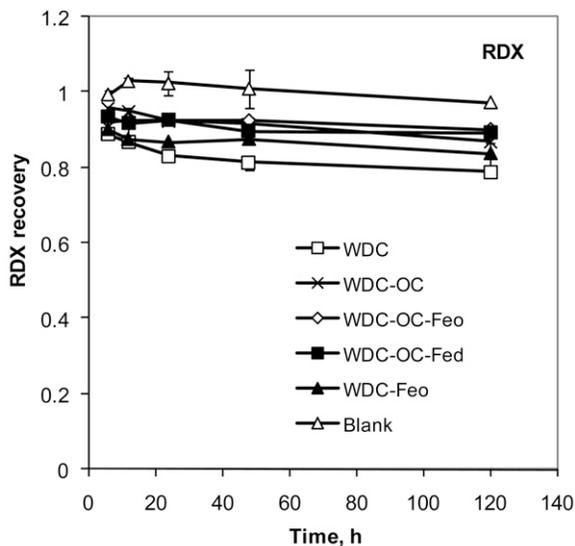


Fig. 2. TNT and RDX recovery in Catlin water-dispersible clay (WDC) over time. Each point is average of two replicates. Error bars equal one standard deviation

### Batch Adsorption on Water-Dispersible Clay

Kinetics of TNT and RDX sorption on Catlin WDC and whole soils were similar (Fig. 2). All WDC treatments reached equilibrium with RDX within 24 h. For TNT, WDC fractions that had OC removed reached equilibrium, but solution phase concentration of those with OC continued to decrease over time (Fig. 2). TNT has been demonstrated to transform to compounds that covalently bind to the soil OC (Thorn and Kennedy, 2002), which may explain continued removal of TNT from solution. Adsorption coefficients were determined at 24 h for comparisons with RDX  $K_d$  values.

All RDX isotherms were linear ( $P > F < 0.01$ , Table 2, Fig. 3). For TNT, all isotherm models were highly significant (Table 3), but the linear isotherms resulted in the smallest error and largest  $R^2$  for 8 of the 15 treatments, including all Kenner WDC treatments. The rest of the TNT treatments were best

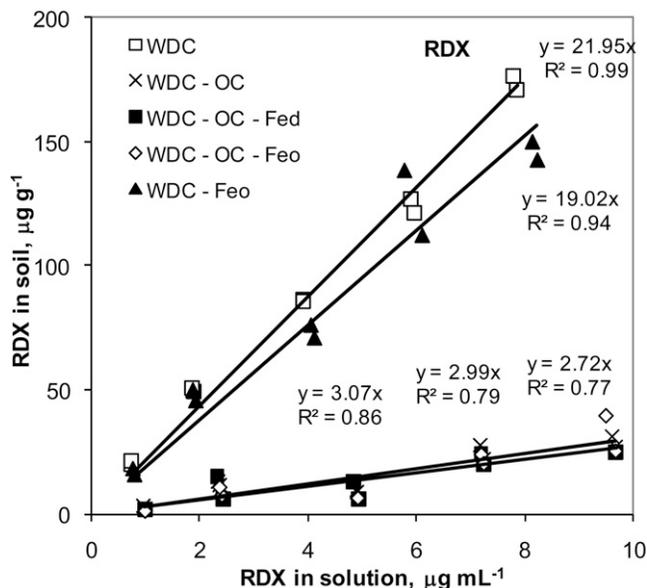


Fig. 3. Adsorption isotherms for RDX in Kenner water-dispersible clay (WDC). Data points for both replicates are shown.

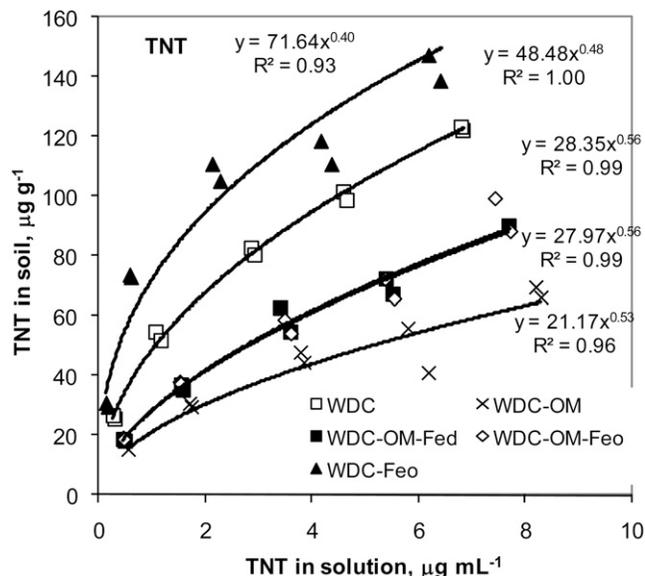


Fig. 4. Adsorption isotherms for TNT in Catlin water-dispersible clay (WDC). Data points for both replicates are shown.

described by Langmuir (four treatments) and Freundlich (three treatments) models. Since Freundlich and Langmuir isotherms describe conditions where sorption is limited by adsorbent capacity, the linear relationship observed for TNT in Kenner WDC may have been due to failure to reach adsorption capacity. The linear isotherm was used to compare the treatments.

For the mineral soils, both TNT and RDX sorption was greater for untreated WDC than for whole soils. This would be expected for fine material that is enriched in OC and phyllosilicate clays. For the organic soil, Kenner muck, this was not observed probably because OC content of Kenner WDC was smaller than in whole soil.

Removal of OC decreased TNT sorption for all three soils (Fig. 4, Table 3) supporting multiple studies that show TNT adsorption

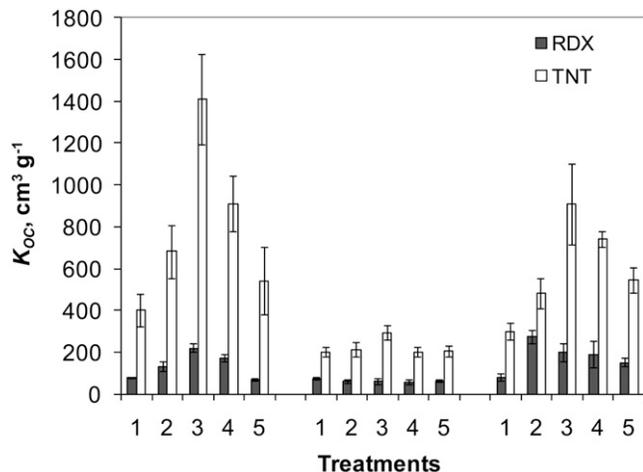


Fig. 5. Linear adsorption coefficients normalized to fraction of OC ( $K_{OC}$ ) for TNT and RDX adsorption by untreated and treated water-dispersible clay (WDC). Treatments indicated by numbers are: 1 = WDC, 2 = WDC-OC, 3 = WDC-OC-Fe<sub>o</sub>, 4 = WDC-OC-Fe<sub>d</sub>, 5 = WDC-Fe<sub>o</sub>. Error bars are 95% confidence intervals around the mean.

Average adsorption coefficients (mL g<sup>-1</sup>) for TNT and RDX in water-dispersible clay (WDC) before ( $\log K_d$ ) and after normalization for organic carbon ( $\log K_{OC}$ ), acid oxalate extractable iron ( $\log K_{Feo}$ ), and dithionite-citrate extractable iron ( $\log K_{Fed}$ ).

	TNT			RDX		
	Avg.	Standard deviation	% Standard deviation	Avg.	Standard deviation	% Standard deviation
$\log K_d$	1.04	0.41	39	0.44	0.41	93
$\log K_{OC}$	2.65	0.28	11	2.04	0.24	12
$\log K_{Feo}$	0.41	0.65	159	0.12	0.66	537
$\log K_{Fed}$	0.34	0.82	242	0.05	0.86	1746

to natural organic compounds (Pennington et al., 1995; Li et al., 1997; Eriksson and Skyllberg, 2001; Thorn and Kennedy, 2002; Eriksson et al., 2004) but contrary to results of Charles et al. (2006) for related nitroaromatic compounds in soils. Strong influence of OC on TNT adsorption is also in disagreement with Pennington and Patrick (1990) who found that OC exerts less of an effect on adsorption of TNT than the mineral components of studied soils.

Removal of Fe<sub>o</sub> and Fe<sub>d</sub> from WDC-OC increased TNT sorption for Catlin, indicating that iron oxyhydroxides may be interfering with TNT sorption by phyllosilicate clays which were previously shown to serve as a substantial sink for TNT (Haderlein et al., 1996). This explanation is supported by a positive correlation between TNT adsorption and clay content and a negative correlation between TNT adsorption and Fe<sub>d</sub> observed by Ainsworth et al. (1993). A similar trend was observed in another mineral soil, Benndale, but differences were significant for WDC-OC-Fe<sub>o</sub> only. In organic Kenner WDC, removal of iron did not produce significant changes in  $K_d$  values, probably due to a much larger residual quantity of OC than in other soils (about 4.8%) (Table 1).

For RDX, peroxide treatment decreased sorption for Kenner soil 7 times and for Catlin soil 1.8 times (Fig. 3, Table 2) indicating partitioning of RDX to OC. Treatment of WDC-OC with oxalate or dithionite did not affect sorption suggesting that neither

iron and aluminum oxides, nor phyllosilicate clays adsorb RDX. Large variability in the RDX data for Benndale WDC precluded observation of consistent trends; few differences were significant.

When OC was present, removal of Fe<sub>o</sub> increased adsorption of TNT (differences were significant for Catlin and Benndale, non-significant for Kenner WDC) and decreased adsorption of RDX (significant for Catlin and nonsignificant for Kenner WDC). Decreased RDX adsorption could not be explained by loss of OC after AOE. While AOE decreased the amount of OC somewhat in WDC (Table 1), the difference was small compared to the observed decrease in RDX sorption (Table 2). As amorphous forms of Fe and Al associate with OC in the soils (Jackson et al., 1986) bonding to polar regions of organic matter (carboxylic-like and phenolic-like sites) (Weber et al., 2006), removal of iron and aluminum oxides is likely to increase polarity of the OC and, therefore, decrease non-polar interactions between RDX and OC.

A decrease in adsorption when OC was removed for both TNT and RDX supports OC as the principal medium for adsorption and facilitated transport of explosives in soils. The effects of Fe<sub>o</sub> removal on TNT and RDX sorption when OC was present indicates that different mechanisms are involved in sorption of these two compounds.

It may be suggested that oxalate-extractable oxyhydroxides suppress TNT sorption and promote RDX sorption by "neutralizing" -COOH and -OH groups in OC. RDX is adsorbed through non-polar interactions, and removal of Fe<sub>o</sub> causes release of some polar groups and results in a decrease in adsorption. TNT adsorption through covalent bonding of its transformation products to polar functional groups benefits from Fe<sub>o</sub> removal. Li et al. (1997), Ainsworth et al. (1993), and Eriksson and Skyllberg (2001) showed that TNT sorption to humic acids and soils increased with an increase in pH and, therefore, with dissociation of hydroxylic and carboxylic groups, confirming the importance of negatively charged functional groups in TNT adsorption.

After normalization for OC (dividing adsorption coefficients by measured OC concentrations), no difference in RDX sorption was observed between WDC treatments in Kenner muck (Fig. 5), indicating that OC was the dominant sorption phase. For the other two soils, RDX  $K_{OC}$  values were greater, more variable, and did not exhibit a consistent trend.  $K_{OC}$  values averaged more than four times larger for TNT than for RDX. The largest TNT  $K_{OC}$  values were observed for treatments where phyllosilicate clay surfaces were exposed (WDC-OC-Fe<sub>d</sub>), and smallest for untreated WDC, where other potentially reactive surfaces were covered with OC. While no single  $K_{OC}$  value was evident for these compounds (Fig. 5), the range of  $\log K_{OC}$  values was smaller, with smaller relative error than observed for  $\log K_d$  values (Table 4). Observed  $\log K_{OC}$  values were within the range reported in the literature,  $2.26 \pm 0.56$  for RDX and  $2.53 \pm 0.42$  for TNT (calculated from review by Brannon and Pennington, 2002). Normalization to Fe<sub>o</sub> and Fe<sub>d</sub> resulted in a much larger relative error compared to non-normalized data and data normalized to OC (Table 4). This indicates that iron oxyhydroxides are not an important phase for explosives sorption in WDC and supports previous conclusions by Ainsworth et al. (1993) and Weissmahr et al. (1998). All soils had mixed

mineralogy; therefore, no relationships between clay minerals and explosives sorption could be observed.

## Conclusions

For mineral soils, WDC adsorbed both TNT and RDX in excess of whole soil supporting potential movement of these explosives with mobile colloidal particles in soils. Treating WDC to remove OC and several forms of iron showed that phyllosilicate clays played a role in TNT adsorption. Iron oxides and hydroxides did not contribute to sorption directly, but decreased sorption by WDC and influenced sorption by OC. However, the strongest indicator of TNT and RDX adsorption by WDC was OC. This suggested that in high-OC soils mobile colloids could enhance movement of these explosives.

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