

Introduction

Nitroaromatic compounds, such as 2,4,6-trinitrotoluene (TNT), are common munition-derived pollutants encountered at facilities used in the manufacturing, processing, and disposing of explosives. The environmental fate of TNT and other organic contaminants in soils is largely determined by its interaction with soil clay minerals and organic matter. Previous research has found that TNT is reversibly bound to soil and clay minerals under various conditions and environmental parameters. However, studies have reported desorption hysteresis in various soils. Currently, it is not well known how the interaction between clay minerals and organic matter could facilitate the sorption and/or desorption of TNT.

Objective

- Determine the effect humic substances have on the sorption/desorption of TNT on various homoionic smectitic clay minerals.

Materials and Methods

- Reference clays were purchased from the Source Clays Repository of the Clay Minerals Society (Columbia, MO). The reference clays used in this study were used as delivered and include a low charge smectite (SWy-2), a high charge smectite (SAZ-1) and hectorite (SHCa-1).
- Homoionic K⁺- and Ca²⁺-saturated clays were prepared by saturating the clays with 0.1 M KCl and CaCl₂ respectively. After saturation the clays were repeatedly washed with DI water until the ionic strength of the solution was below 0.01 M.
- Humic-clay complexes were prepared by dissolving humic acid in a minimal amount of 0.5 M NaOH and then brought to 1L volume in either 0.01 M KCl or 0.0033 M CaCl₂ (pH = 7.6-7.8) Each respective clay mineral was added to the solution at a ratio of 10:1 clay:humic acid (w:w). The clays were shaken with the humic acid solution for 3 days followed by multiple washings with 0.1 M KCl or CaCl₂ to remove excess humic acid and saturate the humic acid-clay complexes with K and Ca respectively.
- The clay and humic-clay complexes were frozen, freeze-dried, and stored in closed sample bags until use. The humic acid-clay complexes are referred to as K-HA-SWy, K-HA-SHec, K-HA-SAZ, Ca-HA-SWy, Ca-HA-SHec, and Ca-HA-SAZ (Table 1).
- Batch equilibrium experiments were performed in triplicate in polypropylene tubes with clay-solution ratios from 1:5 to 1:500 over a period of 24 hours. Desorption was performed by replacing the supernatant with an equal amount of 0.01 M KCl or 0.0033 M CaCl₂ solution and equilibrated for 24 hours.
- Analysis for TNT was performed on a ThermoFinnigan HPLC using a J'sphere ODS-H80, 5 μm, 150x4.6 mm C8 reverse phase column. Sample injection volumes were 10 μL with a mobile phase (82:18, v:v) of water:2-propanol and a flow rate of 1.5 mL min⁻¹.
- X-ray diffraction (XRD) measurements were performed using orientated clay slides prepared after desorption on a Phillips PW 1729 diffractometer using Cu Kα radiation.

Results

Table 1. Properties of reference smectite clays and humic-acid (HA)-clay complexes.

Clay	CEC [†] cmol(+) kg ⁻¹	External Surface Area* m ² g ⁻¹ (STDE)	Interlayer Charge*	Total Carbon %
SWy	76.4	31.85 (±0.22)	-0.55	--
K-HA-SWy				2.52
Ca-HA-SWy				2.18
SAZ	120	97.42 (±0.58)	-1.08	0.51
K-HA-SAZ				0.32
Ca-HA-SAZ				--
SHec	43.9	63.19 (±0.50)	-1.57	--
K-HA-SHec				8.38
Ca-HA-SHec				8.42

*Data from Source Clays Repository †Cation exchange capacity

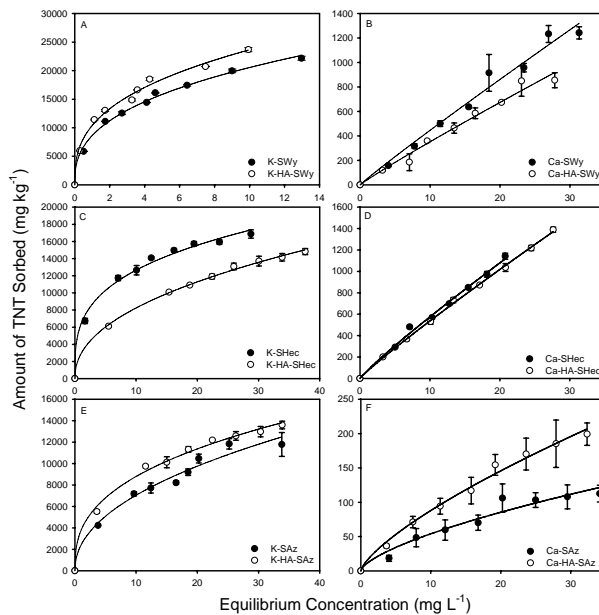


Figure 1. Sorption isotherms (Freundlich) representing 2,4,6-trinitrotoluene (TNT) sorption by reference smectite clays and the respective humic acid (HA)-clay complexes: (A) K-SWy/K-HA-SWy, (B) Ca-SWy/Ca-HA-SWy, (C) K-SHec/K-HA-SHec, (D) Ca-SHec/Ca-HA-SHec, (E) K-SAZ/K-HA-SAZ, and (F) Ca-SAZ/Ca-HA-SAZ.

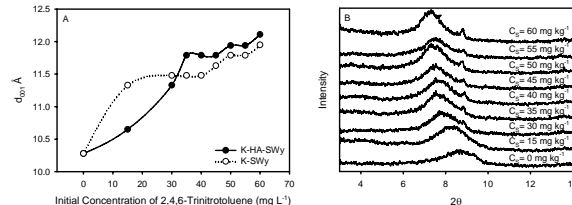


Figure 2. (A) The associated d-spacings for K-SWy and K-HA-SWy as a function of TNT in solution and x-ray diffraction patterns of oriented films of (B) K-HA-SWy.

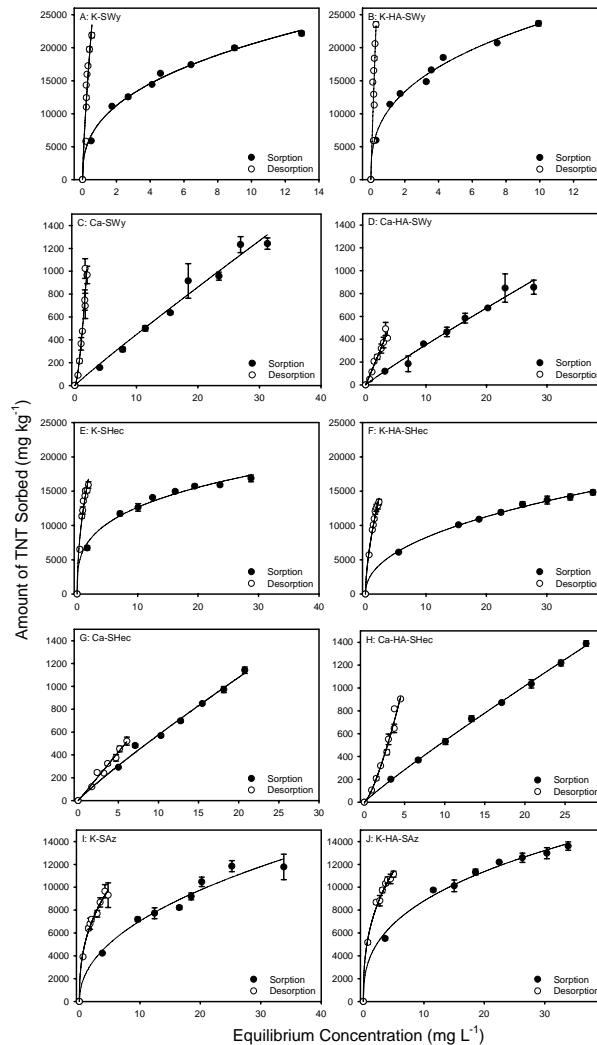


Figure 3. Sorption/desorption isotherms (Freundlich) representing TNT sorption by reference smectite clays and the respective humic acid (HA)-clay complexes. Sorption/desorption of TNT by (A) K-SWy, (B) K-HA-SWy, (C) Ca-SWy, (D) Ca-HA-SWy, (E) K-SHec, (F) K-HA-SHec, (G) Ca-SHec, (H) Ca-HA-SHec, (I) K-SAZ, (J) K-HA-SAZ.

Table 2. Summary of TNT sorption and desorption and XRD parameters for reference clays (SWy, SAZ, SHec) and humic acid (HA)-clay complexes.

Sorbert	Sorption			Desorption			Basal Spacing	
	K _f	N	r ²	K _d	N _d	r ²	C _s [†] = 0	C _s [†] = 40,60
K-SWy	8,640 a [‡]	0.38	0.999	36,541 a	0.74	0.977	10.28	11.95
K-HA-SWy	10,400 b	0.36	0.998	68,201 a	0.90	0.952	10.28	12.11
K-SHec	6,360 a	0.30	0.999	12,293 a	0.5	0.996	ND [§]	ND
K-HA-SHec	2,899 b	0.45	1.000	8,549 b	0.61	0.999	ND	ND
K-SAZ	2,387 a	0.47	0.996	5,260 a	0.39	0.998	12.11	12.28
K-HA-SAZ	3,748 b	0.37	0.999	6,172 b	0.38	0.999	10.78	11.33
Ca-SWy	50.02 a	0.95	0.994	354.01 a	1.56	0.979	14.98	14.98
Ca-HA-SWy	40.65 a	0.94	0.994	123.84 b	1.03	0.986	14.49	14.49
Ca-SHec	71.10 a	0.91	0.999	83.56 a	1.01	0.995	ND	ND
Ca-HA-SHec	64.19 a	0.92	1.000	121.18 b	1.35	0.993	ND	ND
Ca-SAZ	11.83 a	0.66	0.988	ND	ND	ND	14.98	14.98
Ca-HA-SAZ	16.43 a	0.73	0.998	ND	ND	ND	ND	ND

[†] Basal spacing at 0 and 40 (CaCl₂) or 60 (KCl) mg TNT kg⁻¹

[‡] different letters denote significant differences between clay and humic-acid clay complexes (p<0.01)

[§] Not determined

Summary

- Higher TNT sorption was observed for humic coated K-smectite (K-HA-SWy and K-HA-SAZ) compared to that without humic acid (K-SWy and K-SAZ). However, humic acid resulted in less TNT sorption to K-HA-SHec compared to K-SHec (Figure 1, Table 2)
- Humic acid had no effect on TNT sorption to Ca-saturated smectite (Figure 1, Table 2).
- TNT sorption was not readily reversible (hysteresis) after one desorption step in most of the humic acid-clay complexes and clay minerals. In K-saturated samples, humic acid either enhanced or inhibited desorption of TNT (Figure 3, Table 2)
- XRD analysis revealed that interlayer TNT sorption occurred in K-saturated clays with and without humic acid. Interlayer TNT sorption could have occurred in Ca-saturated clays, however, XRD analysis does not support or refute this possibility (Table 2, Figure 2).
- There was a slight increase in interlayer spacing in K-HA-SWy compared to K-SWy when the initial concentration was greater than 30 mg TNT kg⁻¹ soil (Figure 2a).
- XRD results infer that humic acid may have resulted in a greater amount of interlayer TNT sorption in K-saturated minerals, particularly K-SWy, however, the results of this study do not provide enough evidence to support this theory (Table 2).

Conclusions

- The K_f values determined from TNT sorption to homoionic clay minerals were similar to and support the findings of Haderlein et al., 1996.
- The TNT sorption parameters for humic acid-clay complexes and the desorption parameters for homoionic clay minerals differ from previous research. Contrary to our results, Li et al., 2004 observed no difference in sorption between K-saturated smectites and K-saturated humic acid-clay complexes for a structurally similar nitroaromatic compound, 4,6-dinitro-o-cresol. However, they did observe a similar degree of intercalation of 4,6-dinitro-o-cresol in the interlamellar region of the clay with an increase in pesticide sorption.
- Our results indicate that organic matter has potential to impact the sorption and desorption of TNT to clay minerals.

Acknowledgements

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