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Sorption–Desorption of Trinitrotoluene in Soils: Effect of Saturating Metal Cations

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Abstract Clay minerals in soils control the sorption and mobility of nitroaromatics in munitions contaminated soils. Therefore, effect of exchangeable cations (NH_4^+, K^+, Ca^{2+}, and Al^{3+}) on sorption–desorption of trinitrotoluene (TNT) was studied in two reference soils viz sandy loam and silty clay. Compared to control soils, K^+ ion saturation significantly increased TNT sorption in both the soils, while other cations decreased TNT sorption. Effect of K^+ saturation on sorption of TNT was more pronounced in organic matter poor sandy loam soil (seven times) then silty clay (two times). Desorption followed the reverse trend and greater amounts of sorbed TNT were retained in the K^+ saturated soils.

Keywords Trinitrotoluene · Exchangeable cations · Sorption · Desorption

Nitroaromatic munition residues like 2,4,6-trinitrotoluene (TNT) and other nitro- and aminonitrotoluenes have caused wide spread soil and ground water contamination at military installations and disposal sites in United States and Europe (Levsen et al. 1993). To assess and eventually to control the mobility and reactivity of such hazardous pollutants, the molecular interactions and environmental factors that determine the sorption behavior must be understood.

Considerable literature is available on sorption and transport of TNT and related nitroaromatics in natural and model soil systems. Like most of the organic pollutants partitioning of TNT into soil organic matter is the major sorption mechanism in soils having appreciable fraction of organic matter (Eriksson and Skyllberg 2001). However, in soils having low organic carbon content, other natural surfaces may also become important or may even dominate the overall sorption process. Among the natural surfaces these are the clays which play a significant role in binding nitroaromatics, and not the other natural minerals like aluminium and iron hydroxide and oxides, carbonate and quartz. Nitroaromatics bind to clay minerals by electron donor-acceptor (EDA) complex formation between siloxane oxygen of clay and nitroaromatics (Haderlein and Schwarzenbach 1993; Haderlein et al. 1996; Weissmahr et al. 1997; 1999). It has been observed that the type and nature of exchangeable metal cation present at clay surface significantly controls the EDA complex formation. High surface density of strongly hydrated cations (Na^+, Ca^{2+}, Al^{3+}) reduces the accessibility of siloxane sites for nitroaromatics, while small and weakly hydrated cations (K^+ and NH_4^+) allow better EDA complex formation. Formation of EDA complex depends on the nature of clay: highly negatively charged clays, like smectites, have the greatest capacity to bind nitroaromatics. However, these studies have been performed using purified clay systems and no information is available on the effects of these exchangeable metal cations on nitroaromatics sorption behavior in natural soil systems. Therefore, the present investigation reports the effect of exchangeable metal cations on TNT sorption in two natural soils from the German reference soil system.

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Materials and Methods

Two uncontaminated reference soils varying in their physicochemical properties were chosen from the set of soils provided by the German reference soil system (Bussian et al. 2004) and were named as sandy loam and silty clay. The physicochemical characteristics (Table 1) of the soils were determined using standard analytical procedures. The soil pH was measured at 1:2.5 soil:solution ratio (w/v) in 1 N KCl solution (Jackson 1967); organic carbon (OC) content by dry combustion method (Jackson 1967) and soil mechanical fractions employing the international pipette method (Black 1965).

Analytical grade (97%) TNT was obtained from Wehrwissenschaftliches Institut fur Werk-, Explosive- and Betriebsstoffe, Swisstal, Germany. HPLC grade solvents used were locally purchased.

To study the effect of saturating cations on sorption of TNT in both soils, batch sorption studies were performed. Soil samples (5 g) in 50 ml borosilicate stoppered glass tubes were supplemented with 25 ml of 0.1 M solution of saturating cations (NH_4^+, K^+, Ca^{2+}, and Al^{3+} as their chloride salts). Samples were fortified with TNT in 0.01 ml of methanol and four concentrations of TNT ranging between 2.5 and 10 μg/ml were taken. Each concentration was replicated three times. Similarly maintained soil samples, but not fortified with TNT, served as control. Samples were equilibrated at 20 ± 1°C for 24 h. After equilibrium was attained, soil samples were centrifuged at 3,000 rpm for 15 min and concentration of TNT in supernatant was quantified using high performance liquid chromatography (HPLC). The amount of TNT sorbed was calculated from the difference between the initial and final solution concentrations. The mass balance calculations indicated that TNT was stable during the 24 h of equilibration period and there was no sorption of TNT on the glass surface. The desorption of TNT was studied in the same soil as used for the adsorption. After adsorption, the supernatant was decanted and was replaced with 25 ml of fresh 0.1 M solution of respective saturating cation. Soil–water suspension was again shaken on an end over end shaker for 24 h and then centrifuged. TNT was analyzed in the supernatant by HPLC. The amount of TNT desorbed was calculated by subtracting the amount of TNT in the entrapped solution after adsorption experiment from the solution concentration measured after desorption experiment. Only one desorption was performed for each sample.

TNT in aqueous samples was quantified by HPLC (Dionex Summit HPLC analytical system) equipped with Dionex UVD 340S UV-detector and Raytest Ramona Star radio flow detector, series connected. The column used was RP-18 Licrosphere 100 PR 18, 250 × 4 mm (MZ-Analysentechnik). Wave length for UV detection was 230 nm. Twenty microlitre samples were injected into HPLC system equipped with automatic injection system. The following HPLC conditions were used: temperature 40°C, flow 0.4 ml/min, solvent system methanol (A) and 0.02 TBA (tetrabutyl ammoniumbisulfate) (B); gradient: 0–35 min 80% B–10% B, 35–39 min 10% B–80% B, 39–49 min 80% B. The limit of detection for TNT was 0.1 μg and recovery of TNT from water samples at fortification levels of 0.1–5 μg/ml was more than 95%.

Table 1 Physicochemical properties of soils

Soil characteristics	Sandy loam	Silty clay
pH	5.52	6.62
Organic carbon (%)	0.97	2.49
Particle size analysis (%)		
Sand	71.0	12.8
Silt	23.8	52.7
Clay	5.2	34.5

Results and Discussion

Adsorption isotherms for TNT in both soils are shown in Fig. 1. The adsorption data was fitted to the Freundlich adsorption equation: $\log x/m = \log K_f + 1/n \log C$, where, x is the amount of TNT adsorbed (μg), m is the weight of the soil (g), C is the equilibrium concentration of TNT (μg/ml), and K_f and 1/n are the constants. The Freundlich constant K_f (intercept) represents the amount of contaminant adsorbed at an equilibrium concentration of 1 μg/ml. The constant 1/n (slope) is the measure of the intensity of sorption and reflects the degree to which sorption is a function of contaminant concentration. The values of correlation coefficients (Table 2) for all cases were very high ($R^2 > 0.982$), indicating that the Freundlich adsorption equation satisfactorily explained the results of TNT sorption in soils and the results were significant at 99% levels.

The slope (1/n) values for TNT adsorption isotherms in various treatments were <1 (except K^+ saturated sandy loam soil, where slope value was 1) suggesting nonlinear sorption isotherms for TNT in soils. Slope values of <1 indicate L-type adsorption isotherms, which are characterized by the decrease in the adsorption at higher aqueous concentration of the compound (Giles et al. 1960), thus sorption of TNT in these soils was concentration dependent. This type of adsorption isotherms are observed when the molecules are sorbed in a flat position, not suffering a strong competition from the water molecules, which explain the high affinity to sorbent for solute at low concentration. However, as the concentration increases sorption sites become limiting, therefore, sorption decreases.

Fig. 1 Adsorption isotherms for TNT in soils saturated with different metal cations

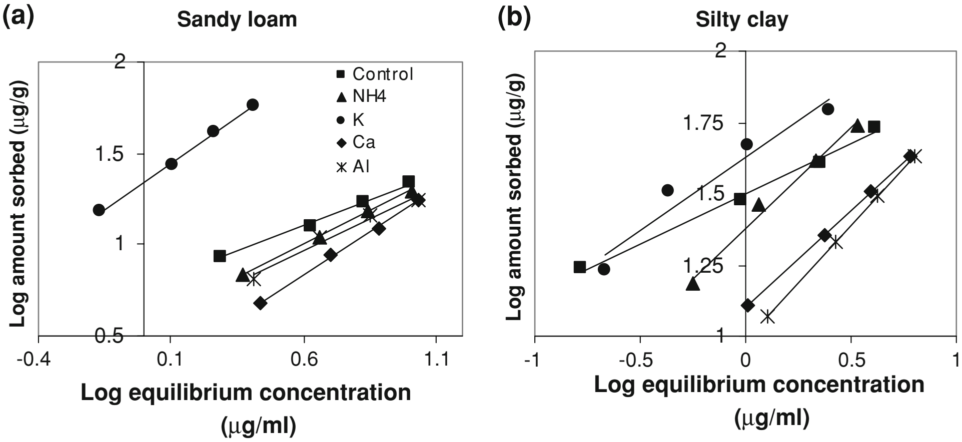

Table 2 Freundlich adsorption parameters of TNT in reference soils

Treatment	Sandy loam			Silty clay		
	K_f	1/n	r^2	K_f	1/n	r^2
Control	5.82	0.56	0.995	31.44	0.35	0.996
NH_4^+	3.64	0.79	0.999	23.97	0.71	0.991
K^+	22.10	1.01	0.999	42.69	0.52	0.940
Ca^{2+}	3.58	0.69	0.982	12.70	0.67	1.000
Al^{3+}	1.86	0.94	0.998	9.67	0.81	1.000

As both, K_f and 1/n, are the important coefficient for description of adsorption isotherms, especially in case of non-linear isotherms, therefore, as suggested by earlier workers, the product K_f * (1/n) was selected as the parameter of adsorption (Wang et al. 1999). K_f * (1/n) values for TNT sorption in the sandy loam soil saturated with NH_4^+, K^+, Ca^{2+}, and Al^{3+} ions were 2.88, 22.32, 2.47, and 1.75, respectively while value in control soil was 3.26. This suggests that except soil saturated with K^+, all other metal cations decreased TNT sorption in sandy loam soil. K^+ was very effective in increasing TNT sorption and compared to control TNT sorption in K^+ saturated soil increased by seven times. The K_f * (1/n) values for TNT sorption in silty clay soil after NH_4^+, K^+, Ca^{2+}, and Al^{3+} ions saturation were 17.02, 22.2, 8.51, and 7.83, respectively while value in control soil was 11.00. Thus, in silty clay soil monovalent cations saturation increased TNT sorption while, di- and trivalent cations decreased the sorption. Further, effect of K^+ saturation on increased TNT sorption was clearly visible in low organic carbon sandy loam soil. Earlier reports have shown that participation of clay in contaminant sorption is clearly visible only if soil OC content is less then 2%. At higher OC content, clay surfaces are masked by the organic matter and they do not contribute much towards contaminant sorption (Theng 1974). The results of the present study are in line with this fact. Higher adsorption of TNT in silty clay soil may be due to higher soil OC and clay content. Earlier studies on the effect of exchangeable cations on nitroaromatics sorption in pure clay system have shown that the presence of less bulky and weakly hydrated cation (K^+ and NH_4^+) at clay surfaces enhanced nitroaromatics sorption, while bulky and highly hydrated cations (H^+, Na^+, Ca^{2+}, Mg^{2+}, and Al^{3+}) prevented interaction of nitroaromatics with clay surfaces (Haderlein et al. 1996; Weissmahr et al. 1999).

Desorption of TNT was studied in the same soils after sorption. Desorption of TNT in soils was opposite of sorption and the greater amounts of sorbed TNT were retained in those soils which showed higher TNT sorption (Table 3). Thus, compared to control, except K^+ ion, all other metal cations resulted in greater desorption of sorbed TNT from both the soils. Like sorption, desorption too was concentration dependent and higher amount of sorbed TNT was desorbed from systems where TNT sorption was carried out at higher concentration. Thus, sorption was more irreversible at lower concentration. Further, sorption of TNT was more irreversible in silty clay soil than sandy loam soil suggesting stronger binding of TNT in silty clay

Table 3 Desorption parameters of TNT in reference soils

Cation	Soil	% Desorption at concentrations (µg/ml)			
		2.5	5.0	7.5	10.0
Control	Sandy loam	18.56	23.32	27.50	30.56
	Silty clay	0.35	0.82	2.57	5.89
NH_4^+	Sandy loam	42.88	45.33	46.77	46.88
	Silty clay	2.13	3.44	4.95	7.35
K^+	Sandy loam	20.36	19.96	19.91	19.95
	Silty clay	0.75	1.13	1.91	4.05
Ca^{2+}	Sandy loam	54.65	48.83	48.41	49.94
	Silty clay	9.82	13.62	16.17	19.76
Al^{3+}	Sandy loam	47.59	47.22	49.18	52.82
	Silty clay	21.15	23.58	24.46	26.09

soil. This study suggests that TNT desorption in the soils depends not only on the nature of saturating metal cation, but also to some extent on the sorbed phase concentration of TNT.

The results of the present investigation suggest that saturation of soils with metal cations can be exploited to control phase distribution and thus, transport of TNT in the soil profile. However, effect of saturating cations on TNT retention in the soils is site specific, therefore, detailed studies under actual field situations are recommended.

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