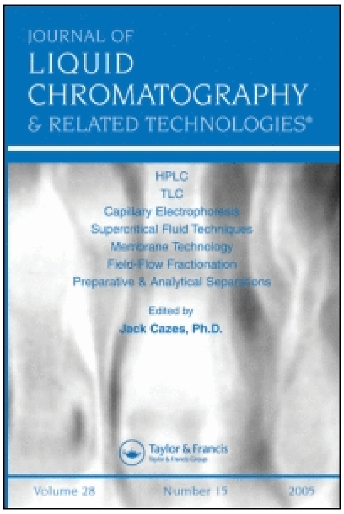

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Adsorption Study of RDX and TNT Explosives in Soils by HPLC

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To cite this Article Falone, Sandra Zago , Vieira, Eny Maria and Onuska, Francis I.(2006) 'Adsorption Study of RDX and TNT Explosives in Soils by HPLC', Journal of Liquid Chromatography & Related Technologies, 29: 11, 1645 — 1662
To link to this Article: DOI: 10.1080/10826070600678373
URL: http://dx.doi.org/10.1080/10826070600678373

Journal of Liquid Chromatography & Related Technologies®, 29: 1645–1662, 2006

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070600678373

Adsorption Study of RDX and TNT Explosives in Soils by HPLC

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Abstract: The environmental contamination by explosives has concerned the scientific community, due to their toxicity, mainly in those areas where the explosives are manufactured, stored, or still demilitarized. This paper describes the RDX and TNT interaction in different matrices. The Freundlich isotherms were used for the data mathematical treatment. The results indicated that the largest adsorption and the smallest desorption of the RDX and TNT explosives occurred in the peat in natura, with adsorption coefficient (Kd) of 24.88 and Freundlich dessorption value 37.56 of RDX explosive, and adsorption coefficient (Kd) 78.11 and Freundlich desorption value 110,31 of TNT explosive.

Keywords: Explosives, Adsorption, Desorption, Freundlich

INTRODUCTION

One of the most serious environmental problems facing the Army is the soil contamination by high explosives residues at sites where munitions has been formerly manufactured, stored, used, or demilitarized.[1]

Explosive compounds have been manufactured, stored, tested, and used at formerly used defense sites throughout the United States and military sites in

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Europe over the past century.[2] In Germany, there are a large number of sites where explosives and ammunition were produced before World War II.[3] In US, the Army alone has estimated that over 1.2 million tons of soil have been contaminated with explosives, and the impact of the explosives contamination in other countries has similar magnitude.[4]

The contamination of ground water and surface water by energetic materials at waste disposal sites, industrial production plants, firing ranges, and burning facilities represents a world wide environmental concern.[5] Modern explosives are nitrogen containing organic compounds with the potential to self-oxidate to small gaseous molecules (N_2, H_2O, and CO_2).[6] The munition products, cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and 2,4,6-trinitrotoluene (TNT)[7] are important explosives used by the US and European munitions industry.[8] These explosives are solid materials at room temperature, and sparingly soluble in the aqueous phase ($60\,\mathrm{mg \cdot L^{-1}}$ for RDX and $150\,\mathrm{mg \cdot L^{-1}}$ for TNT).[9–11] The probability of directly binding these contaminants either on the ground or near the surface, in soil or sediment samples is high since their solubility in water is high.[5]

RDX (T4, cyclonite, hexogen, trimethylen-trinitramin)[9] is a highly toxic material. It is a white, crystalline powder prepared by nitration of hexamethylene-tetramine (hexamine).[12] In human beings it affects primarily the central nervous system.[13] In acute toxicity studies in rats, the LD_{50} was found to be approximately $200\,\mathrm{mg \cdot kg^{-1}}$ in nonfasting rats, 50 to $100\,\mathrm{mg \cdot kg^{-1}}$ in fasting rats, and $600–100\,\mathrm{mg \cdot kg^{-1}}$ in mice.[10,12] The US EPA classifies RDX as a possible human carcinogenic compound,[8] but its toxicity is unknown.[14]

TNT (trinitrotoluol, trinitrotoluene, trotyl, tolite) is a pale yellow granulated crystal produced by the nitration of toluene with nitric and sulfuric acids mixed in several steps.[9] Wullbrand first synthesized it in 1865, and for many years it has been used as a major explosive in charges and bombs.[15] It is still widely used as an explosive and has been classified both as hazardous and a possible human carcinogenic (U.S. Environmental Protection Agency EPA) and mutagenic compound.[15,16] It can cause damage in the liver, and can give origin to anemia and pancytopenia, as a result of bone marrow failure.[6] Oral LD_{50} in rats are near $1.0\,\mathrm{g \cdot kg^{-1}}$and $0.6–1.0\,\mathrm{g \cdot kg^{-1}}$ in mice.[6,10]

Therefore, the US EPA has set a lifetime health advisory concentration in drinking water of $0.002\,\mathrm{mg \cdot L^{-1}}$ for RDX and $2\,\mathrm{ng \cdot mL^{-1}}$ for TNT.[17]

Soils contaminated by high explosives such as TNT and RDX represent a significant risk to human health. Incinerations are the most effective remediation method, but they are expensive, destroy soil fertility, and generate concern about air emissions. Bioremediation is often effective, but it cannot be applied to highly contaminated sites, requires long treatment times, and often produces toxic and/or mutagenic products.[18] Moreover, the interactions between these nitroaromatic compounds and complex soil matrix have not been extensively studied and very few references can be found.[19] However, there is some evidence that RDX and TNT can be strongly adsorbed by soil organic matrix, having a major influence on their availability, mobility, bioreactivity, and persistence.[20]

Soil organic matter is a mixture made by plant and animal residues at various stages of decomposition, substances microbiologically and chemically synthesized from the breakdown products, bodies of living and dead microorganisms, and small animals and their decomposing residues.[21] To simplify this very complex system, soil organic matter is usually subdivided into nonhumic and humic substances. Nonhumic substances include those with still recognizable chemical characteristics such as carbohydrates, proteins, peptides, amino acids, nucleic acids, purines, pyrimidines, fatty acids, waxes, resins, pigments, and other low molecular weight organic substances. In general, these compounds are relatively easily degraded in soils and have short life spans.[22]

Humic substances are classified into three fractions: humic acids (HA) soluble in alkaline solutions, fulvic acids (FA) soluble in alkaline, and acid solutions and humin, which is supposedly inert. The separation scheme currently accepted by most specialists in humic substances is the separation of the humic substances in three fractions: (I) humic acid (HA), which is soluble in dilute alkali but precipitates when the alkaline extract is acidified; (II) fulvic acid (FA), which is the humic fraction that remains in solution when the alkaline extract is acidified, soluble in both dilute alkali and dilute acid; and (III) humin, which is the humic fraction that cannot be extracted from soils by dilute base or acid.[23]

This paper describes the adsorption/desorption of RDX and TNT in soil matrices, with and without organic matter, and the possible development of inexpensive soil amendments that can be applied to enhance the adsorption of energetic compounds on military trining ranges, limiting the potential of these compounds to migrate to groundwater.[24,25]

Linear, Freundlich, and one and two site Langmuir equations are the most commonly used equations to describe sorption reactions at equilibrium.[26] The Freundlich isotherms were used in this study.[27] The Freundlich equation is $S = Kf \cdot C^b$, where C is the solute concentration in solution ($\mu g \cdot mL^{-1}$), S is the solute concentration associated with the solid phase of the soil (μg^{-1}), Kf is the Freundlich coefficient ($cm^3 \cdot g^{-1}$), and b is an empirical dimensionless parameter. For $b = 1$, the retention is linear, $S = Kd \cdot C$, where Kd is the distribution coefficient ($cm^3 \cdot g^{-1}$). For $b < 1$, the retention is type L, and for $b > 1$, the retention is type S. As Kd value increases, the capacity of adsorption of organic substances by soil also increases. Kd values between 0–24 represent short adsorption, between 25–49 middle adsorption, between 50–149 great adsorption, and 150 or more high adsorption.[28]

The compounds investigated are listed in Figure 1, namely, RDX (I) and TNT (II).

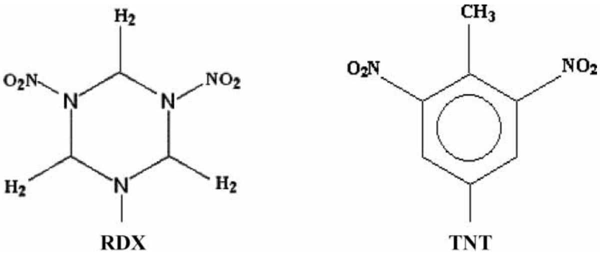

Figure 1. Structure of RDX and TNT.

EXPERIMENTAL

Chemicals

Methanol, acetonitrile, and calcium chloride were purchased from Aldrich Chemical Co (Milwaukee, Wis. USA). The water was purified using a Milli-Q-reagent grade water purification system (Millipore Corp., Bedford, Mass., USA).

The RDX and TNT standard working solutions were prepared by diluting the standard stock solutions containing these analytes at a concentration of 1,000 mg mL^{-1} each (Supelco, Bellefonte, Penn., USA). The solutions were stored at 4°C in the dark.

Calibration Curves and Limits of Detection and Quantification

The solutions used to obtain the calibration curves were prepared by dilution of the standards solutions, with concentrations ranging from 0.1 to 12 $mg \cdot L^{-1}$. The linearity of the RDX and TNT calibration curves are expressed by the following equations: for RDX, $y = 25.968\ X + 1.2494$, with $R^2 = 0.9979$, and for TNT, $y = 47.214\ X + 3.3423$, with $R^2 = 0.9985$.

Instrumentation and Chromatographic Condition

Analysis was carried out through the high performance liquid chromatography method (Shimadzu LC-9) with an RP-18 ODS-Redxchrom column (150 mm × 4.6 mm × 5 mm) and UV-vis detector with wavelength set at 230 nm. The mobile phase methanol/water (60/40 v/v) and methanol/water (50/50 v/v) were used for RDX and TNT, respectively, operating in the isocratic mode at 22°C temperature with 1.5 mL min^{-1} flow and an injected volume of 20 μL. These conditions were selected after the experimental studies.

Sorption/Desorption Experiment

The adsorption isotherms were obtained by mixing either 1.0 g of soil in natura, roasted soil, peat in natura, or roasted peat, or 0.1 g of soil humic acid or peat humic acid with 10 mL of a 0.01 mol/L $CaCl_2$ solution in erlenmeyers of 150 mL. The mixtures were fortified with 1.0, 4.0, 7.0, and 10.0 $\mu g \cdot mL^{-1}$ explosives working solutions. The samples were shaken for 24 h at room temperature without modifying the soil and peat pH. After that the samples were centrifuged at 17.741 g during 20 min. The supernatant was collected and analysed by HPLC. The dessorption isoterms were obtained by adding 10.0 mL of 0.001 mol L^{-1} $CaCl_2$ solution to the erlenmeyers that were shaken for 24 h. Then the same procedure for the adsorption experiment was followed.[29]

The Kd values for RDX and TNT explosives were determinated within the quase-linear initial part of the adsorption isotherms by batch experiments in $CaCl_2$ solution. Concentrations of adsorbed explosives were calculated by the difference between adsorbed concentration and less desorbed concentration.

The aliquot of $CaCl_2$ solution was utilized to keep the ionic strength similar to the soil.

Soil and Peat

Soil samples were collected at Canchim farm, São Carlos, São Paulo, Brazil, and peat samples were collected at a peat-bog, on the border of Mogi-Guaçu River, Luiz Antonio, São Paulo, Brazil, from a depth of 15 cm. Afterwards, the samples were air-dried, homogenized, sieved in a 48–150 mesh and stored at 25°C until the analysis.

Extraction and Purification of the Humic Acid from Soil and Peat

The extraction and purification of the humic acid from peat and soil was done as the standard method described by Griffith et al. 1975.[30]

RESULTS AND DISCUSSION

Adsorption/Desorption of the RDX Explosive

Figure 2 shows the RDX adsorption and desorption isotherms in soil *in natura*. These isotherms showed an adsorption distribution coefficient value of 2.29, indicating a low adsorption, when compared to the values observed by

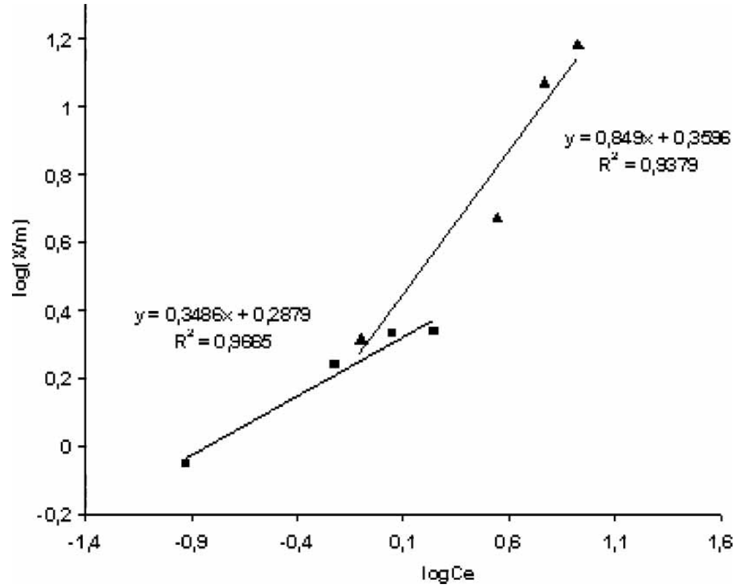

Figure 2. RDX adsorption (▲) and desorption (■) isotherms in soil *in natura*.

Lanças et al. (1994),[31] who studied the pesticides interaction with soil. However, a larger explosive concentration was observed in the soil than in the liquid phase. For desorption, the distribution coefficient value found was 1.94, suggesting that a small amount of the explosive was adsorbed.

Figure 3 shows the RDX adsorption and desorption isotherms in the roasted soil.

For RDX in the roasted soil, the Freundlich adsorption coefficient was 0.5, indicating that there was little interaction among the explosive and the possible inorganic constituents, as argilas, minerals, oxides and iron, and aluminum hydroxides, and also that this soil possesses a large quantity of those compounds, due to its rocky formation. In spite of the small adsorption value of 0.15, the desorption value was 2.97, suggesting that most of the explosive remained in the roasted soil. These results are in agreement with the results found in the literature.[26]

Figure 4 presents the RDX adsorption and desorption isotherms in the humic acid of the soil.

The adsorption distribution coefficient was 1.90, showing a low adsorption, and Freundlich desorption value was 1.13, demonstrating that there is more explosive retained in the acid originated from the humic acid of the soil than desorbed in the solution.

Figure 5 presents the RDX adsorption and desorption isotherms in the peat in natura.

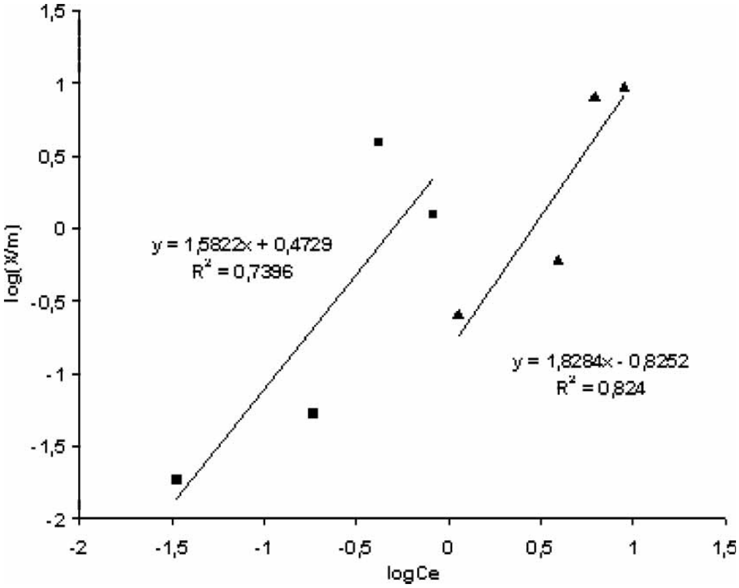

Figure 3. RDX adsorption (▲) and desorption (■) isotherms in the roasted soil.

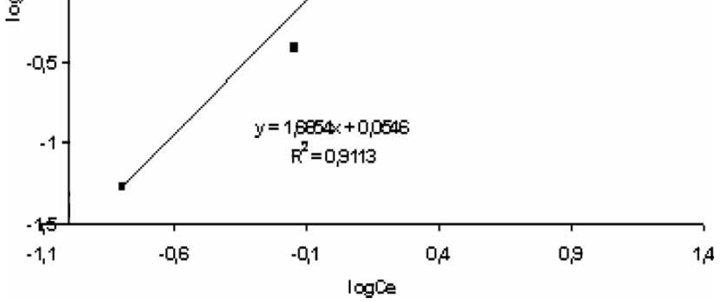

Figure 4. RDX adsorption (▲) and desorption (■) isotherms in the humic acid of the soil.

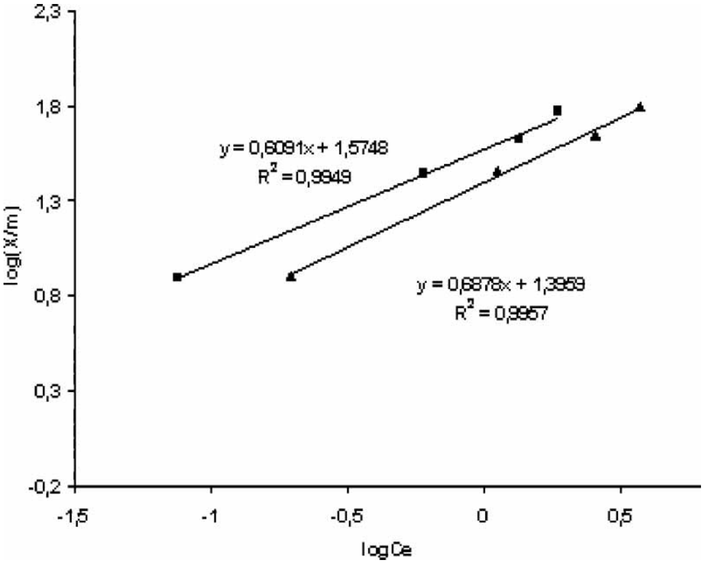

Figure 5. RDX adsorption (▲) and desorption (■) isotherms in the peat *in natura.*

The RDX explosive presented an adsorption value equal to 24.88 in the peat, probably due to its acidity, as it presents a great number of carboxilics and phenolics functional groups responsable mainly for the explosive interaction with the humic substances. It can be observed from the 37.56 value that the interaction of the explosive molecule is taking place in the interstice of the humic substances. As RDX is not well desorbed, there are few chances that the composition will be leached, translocated for the plants, or degraded, becoming non-toxicant molecules.

Figure 6 presents the RDX adsorption and desorption isotherms in the roasted peat.

Vieria et al. (1999)[32] observed that interactions can occur between the pesticides and explosives with the aluminum oxides and hydroxides, in agreement with the Freundlich constant values of 1.27 of 10.64 found for adsorption and desorption, respectively, presented in Figure 6.

This matrix is rich in metals, mainly aluminum, which can interfere in the explosive adsorption. Such interference can be verified by the low value found for the adsorption distribution constant, equal to 1.27, as there is no organic matter. It can also be verified that the explosive does not desorbe very well, allowing the detection of a large amount of residual, which can be attributed to the possible interactions of the RDX nitro groups, as they easily react with the inorganic compounds present in the soil.

Figure 7 presents the RDX adsorption and desorption isotherms in the humic acid part of the peat, with adsorption and desorption distribution coefficients of 2.05 and 1.96, respectively.

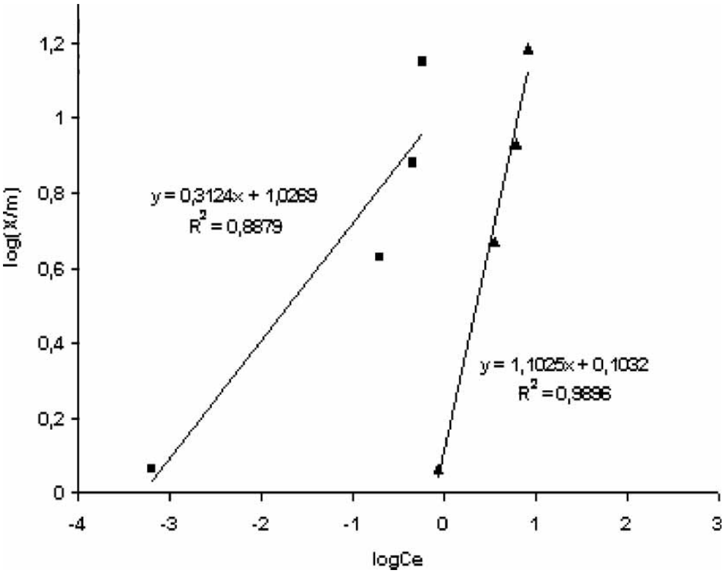

Figure 6. RDX adsorption (▲) and desorption (■) isotherms in the roasted peat.

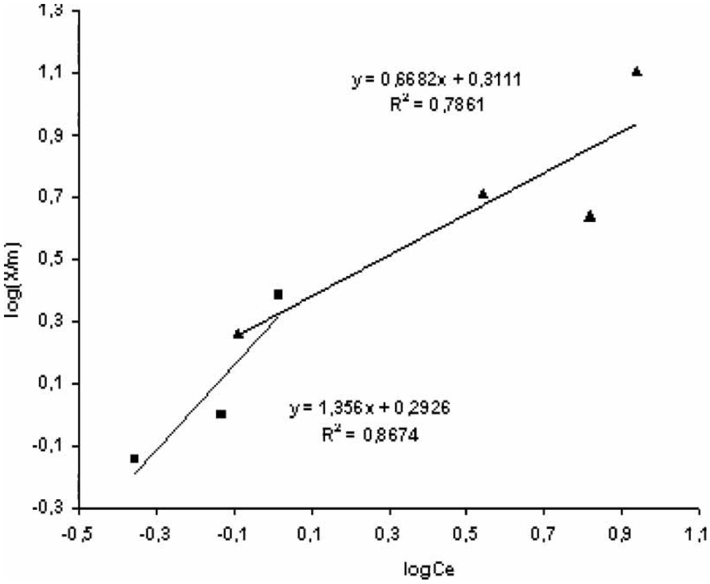

Figure 7. RDX adsorption (▲) and desorption (■) isotherms in the humic acid part of the peat.

The values found for the distribution coefficients suggest that there was a small interaction of the explosive with the matrix, probably due to the weak interactions between the humic acid and RDX, although it can be observed that there is a larger amount adsorbed in the matrix than liberated in the solution. This behavior can be explained by the functional groups present in the humic acid that are responsible for the interaction with organic molecules, as explosives.

The Freudlich constants values found for the different matrices shown from Figure 2 to Figure 7 are presented in Table 1.

The data in Table 1, show that the adsorption values found for RDX in the adsorption process in soil matrices, AH of the soil peat, and AH of the peat are lower than 1, presenting isotherms like type L. In this case, there is a decrease in the availability of the sites responsible for the adsorption as the concentration of RDX increases. The same occurs for the desorption, since soil, peat, and roasted peat matrices also present isotherms of this type. The other matrices present isotherms of type S. Such behavior is observed when the initial adsorption is low and it increases as the number of adsorbed molecules increases. Only in the adsorption process, the value for the peat is almost 1, presenting a C type isotherm. In this case, there is a partitioning constant between the solute and the solution, corresponding to the linear isotherm aspect. The value of Kd obtained for the peat in natura is probably due to the organic matter of the soil, as the peat possesses 60% of organic matter, corresponding to humic acid, fulvic acid, humin, and the non-humic substances. Analyzing the Kfa value of the peat in natura with the humic acid extracted from it, it can be observed that RDX interacted more with the other representatives, such as fulvic acid, humin, non-humic substances, and inorganic components than the humic acid, since it is possible to verify that the peat in natura presented a medium Kd adsorption of 24.88, and a low desorption value, as observed by the high value of Kd equal to 37.56.

Table 1. Freundlich constants obtained from the RDX graphs for different matrices

	RDX			
	Adsorption		Desorption	
Samples	Kd	1/n	Kd	1/n
Soil	2.29	0.85	1.94	0.35
Roasted soil	0.15	1.83	2.97	1.58
Humic acid of the soil	1.90	0.78	1.13	1.67
Peat	24.88	0.69	37.56	0.61
Roasted peat	1.27	1.10	10.64	0.31
Humic acid of the peat	2.05	0.67	1.96	1.36

Adsorption and Desorption of the TNT Explosive

Figure 8 presents the TNT adsorption and desorption isotherms in the soil *in natura.*

Hundal et al. (1997)[20] studied the interaction of TNT with 14 different types of soil, finding a Kd of approximately 9.0. Considering this value, it can be said that the Kd equal to 20.03 found for the TNT-soil interaction, presented a relatively high value, with a small quantity of free explosive in the solution. Almost all the TNT adsorbed did not desorbe, as observed by the high value of the distribution coefficient Kd equal to 83.09.

Figure 9 presents the TNT adsorption and desorption isotherms in the roasted soil.

TNT had a low adsorption in the roasted soil (Kd = 3.16), due to either a low interaction of the explosive with the compounds presents in the soil after the calcination, or the competition of some metals for the interaction sites that would be occupied by the explosive. However, it presented a desorption distribution coefficient, Kd equal to 39.98, indicating that there was an interaction between TNT and the representatives of the soil; meaning that the explosive probably will not be leached, degraded, or translocated for the plants.

Figure 10 presents the TNT adsorption and desorption isotherms in the humic acid of the soil.

The values found for the adsorption distribution coefficient was 9.09 and Freundlich desorption was 7.74, were lower when compared to the values determinated by IBAMA, 1990.[28] This fact suggets that a great amount of

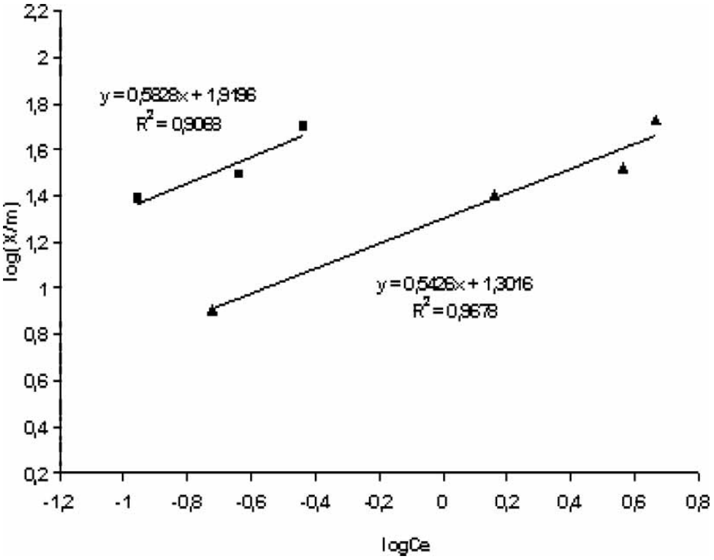

Figure 8. TNT adsorption (▲) and desorption (■) isotherms in the soil *in natura*.

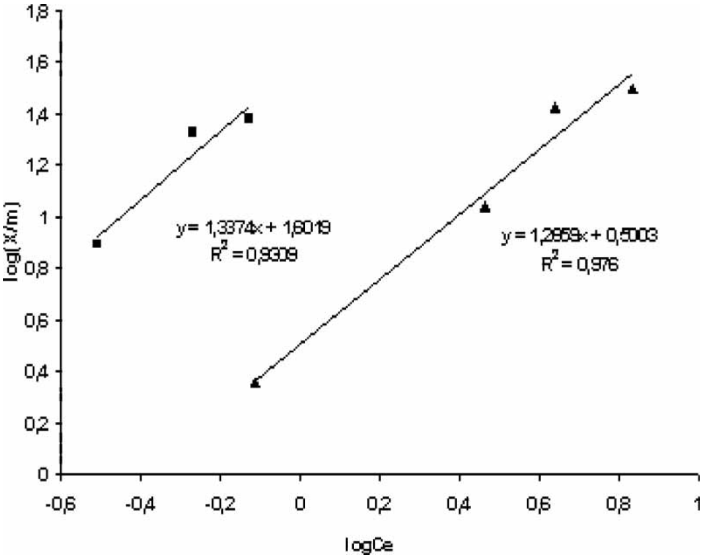

Figure 9. TNT adsorption (▲) and desorption (■) isotherms in the roasted soil.

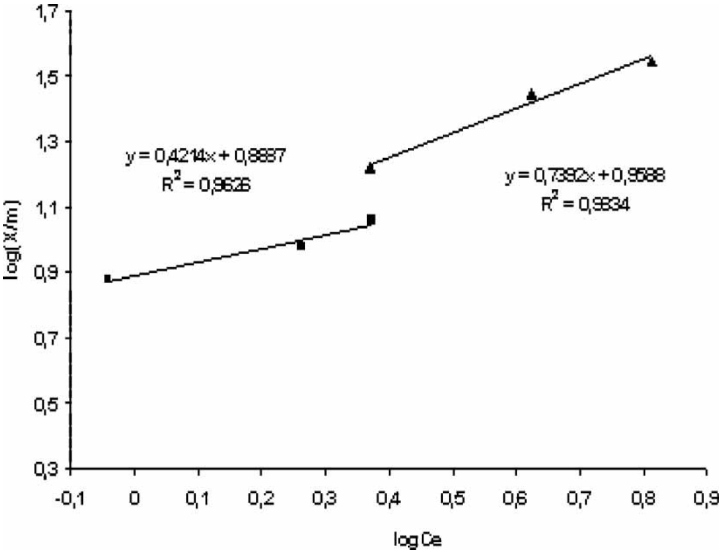

Figure 10. TNT adsorption (▲) and desorption (■) isotherms in the humic acid of the soil.

the compound that was adsorbed has been desorbed. However, the value of the adsorption constant of TNT is higher than the desorption, indicating that this compound can also be leached.

Figure 11 presents the TNT adsorption and desorption isotherms in the peat in natura.

According to Hundal et al.[20] the sorption of TNT depends on both the characteristics of the soil and its time of contact with the TNT. These isotherms do not present hysteresis, where an irreversible reaction occurs between the molecule of the explosive and the representatives of the soil.

In this system, a high adsorption distribution coefficient value can be observed (Kd = 78.10), indicating that there is a large interaction between the molecule of the explosive and the representatives of the peat. Considering the amount of adsorbed explosive, probably it has not been desorbed, which can be observed by the high value of the distribution coefficient for desorption (Kd = 110.31). The remaining amount observed is high if compared with other matrices, probably due to the representatives that might have had stronger affinity for the molecule of the explosive.

Figure 12 presents the TNT adsorption and desorption isotherms in the roasted peat.

These isotherms presented a distribution coefficient equal to 3.36 for adsorption, and a Kd equal to 6.66 for desorption. Analyzing these values, it can be verified that the small amount adsorbed has not been desorbed.

Figure 13 presents the TNT adsorption and desorption isotherms in the humic acid of the peat.

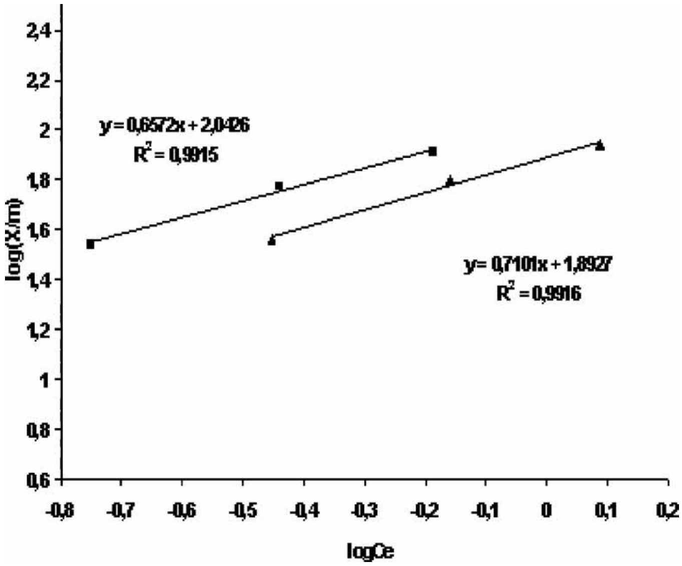

Figure 11. TNT adsorption (▲) and desorption (■) isotherms in the peat *in natura.*

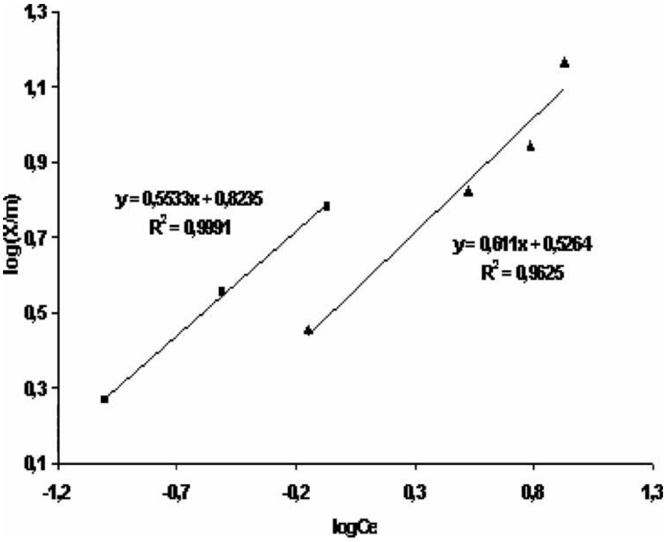

Figure 12. TNT adsorption (▲) and desorption (■) isotherms in the roasted peat.

These isotherms presented a low value for the adsorption distribution coefficient Kd equal to 6.57, meaning that there is more explosive adsorbed in the soil than liberated in the solution. The Kd value equal to 4.24 suggests that a relatively small amount is found in the matrix.

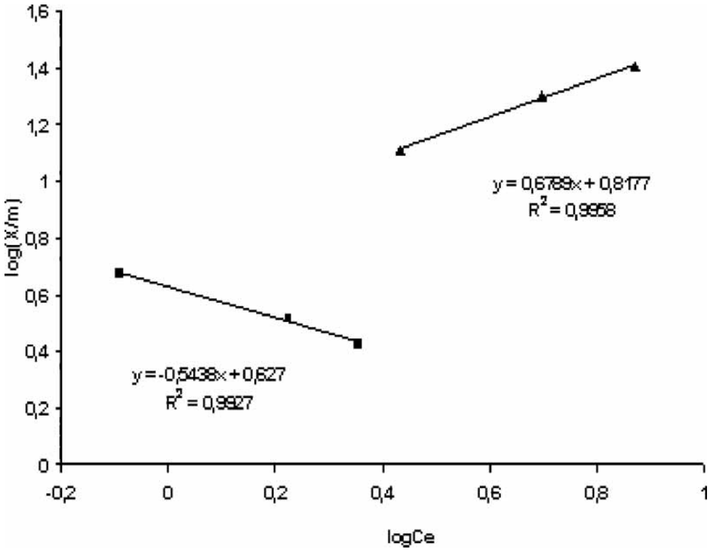

Figure 13. TNT adsorption (▲) and desorption (■) isotherms in the humic acid of the peat.

Table 2. Freundlich constants obtained from the TNT graphs for different matrices

TNT				
	Adsorption		Desorption	
Samples	Kd	1/n	Kd	1/n
Soil	20.03	0.54	83.09	0.58
Roasted soil	3.16	1.27	39.98	1.34
Humic acid of the soil	9.09	0.74	7.74	0.42
Peat	78.11	0.71	110.31	0.66
Roasted peat	3.36	0.61	6.66	0.55
Humic acid of the peat	6.57	0.68	4.24	0.54

According to Araújo et al. (2002),[33] the complexing capacity of the humic substances to modify the availability and the toxicological effects of metals may have occurred in this system, where probably there was a com petition of the metallic ions for the active sites of humic acid, with a small adsorption of TNT.

The Freundlich constants values found for the different matrices shown from Figure 8 to Figure 12 are presented in Table 2.

The study of TNT adsorption/desorption is an important process, as this explosive is easily degraded and possible transformations include the reduction of 1, 2, or 3 nitro groups to amine, and the joining of those groups can form dimers. The transformation products are typically observed in soils and water, and the transformation of those amino groups are softened by the mechanisms of the soils, through reactions with their components. Those mechanisms include linkage between reactive sites from explosive and the organic matter of the soil, through reactions with mineral surfaces and reversible adsorption.[34]

The TNT explosive presented type S isotherm for the roasted soil matrix, for the other matrices it presented type L isotherms. In the peat TNT system case, Kd value equal to 110.31 is high, as the explosive is totally adsorbed by the molecules of humic substances, without being desorbed. TNT may have a strong affinity for the representatives of the peat, as a high adsorption is observed in the peat as well as in the soil, still presenting low desorption if compared with the humic acids of the matrices.

CONCLUSIONS

For soil and peat in natura, the isotherms distinct non-linearity, and the Freundlich model provided the best description of the retention data. As indicated by the Kd values, RDX exhibited stronger affinity to the soil and peat than TNT, indicating that these compounds will not be lixiviated to the ground water, contaminating them.

The study of the RDX and TNT adsorption/desorption process in soil and peat values confirm the RDX and TNT adsorption.

However, the explosives showed a higher adsorption by the other peat and soil constituents as non-humic substances and inorganic compounds than the humic acid, as can be observed by the low values of Kd.

High performance liquid chromatography demonstrated to be suitable for the RDX and TNT analysis, showing short time analysis and good resolution.

ACKNOWLEDGMENTS

The authors would like to thank CAPES and FAPESP, Brazil, for the financial suport of the research.

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Received December 20, 2005
Accepted January 11, 2006
Manuscript 6801