Journal of Hazardous Materials 173 (2010) 343–348

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effect of soil organic matter chemistry on sorption of trinitrotoluene and 2,4-dinitrotoluene

Neera Singh[a,*], Anne E. Berns[b], Dieter Hennecke[c], Jennifer Hoerner[c], Werner Koerdel[c], Andreas Schaeffer[d]

[a] Division of Agricultural Chemicals, Indian Agricultural Research Institute, New Delhi-110012, India
[b] Forschungszentrum Juelich GmbH, Institute of Chemistry and Dynamics of the Geosphere, Institute 4: Agrosphere, 52425 Juelich, Germany
[c] Fraunhofer Institute of Molecular Biology and Applied Ecology, 27392 Schmallenberg, Germany
[d] RWTH University, Chair of Environmental Biology and Chemodynamics, Worringerweg 152074, Aachen, Germany

ARTICLE INFO

Article history:
Received 28 April 2009
Received in revised form 26 June 2009
Accepted 19 August 2009
Available online 25 August 2009

Keywords:
Trinitrotoluene
2,4-Dinitrotoluene
Sorption
NMR spectroscopy
Organic matter chemistry

ABSTRACT

The sorption of organic contaminants in soil is mainly attributed to the soil organic matter (SOM) content. However, recent studies have highlighted the fact that it is not the total carbon content of the organic matter, but its chemical structure which have a profound effect on the sorption of organic contaminants. In the present study sorption of two nitroaromatic contaminants viz. trinitrotoluene (TNT) and 2,4-dinitrotoluene (2,4-DNT) was studied in different SOM fractions viz. a commercial humic acid, commercial lignin and humic acid and humin extracted from a compost. ^{13}C-DP/MAS NMR studies indicated that the structural composition of the organic carbon in different SOM fractions was different. The order of sorption of the nitroaromatics in the different sorbents was: humic acid-commercial > humic acid-compost > humin ~ lignin. Among the aliphatic and aromatic carbon fractions (representing bulk of SOM matrix), adsorption parameter $K_f(1/n)$ for nitroaromatics sorption correlated well with the aliphatic carbon ($r = 0.791$ for TNT and 0.829 for 2,4-DNT) than the aromatic carbon ($r = 0.634$ for TNT and $r = 0.616$ for 2,4-DNT). However, among carbon containing functional groups, carbonyl carbon showed strong positive correlation with sorption of TNT ($r = 0.991$) and 2,4-DNT ($r = 0.967$) while O-alkyl carbon showed negative correlation ($r = 0.832$ for TNT and $r = 0.828$ for 2,4-DNT). The study indicates that aliphatic domains in the SOM significantly affect the non-specific sorption of both the nitroaromatic contaminants.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The contaminant's interactions with the soil organic matter (SOM) are central to understanding the fate and transport of chemicals in the soil environment. It has been well demonstrated by several researchers that the retention capacity of soil/sediment for an organic contaminant is dominantly controlled by its total organic matter content [1–3]. This association between the contaminant and the SOM limits its bioavailability to soil biota and causes the contaminant stability and prolonged persistence in the environment. Therefore, understanding the fundamental sorption mechanism of contaminant in SOM is of utmost importance for optimizing the efficiency of remediation techniques and improving the accuracy of risk assessment models. The comprehension of the sorption mechanism has progressed from setting the simple correlation of sorption with the SOM content to considerations taking into account the specific structural and chemical properties of SOM. Studies indicate that SOM characteristics like polarity, molecular weight, aromaticity and aliphaticity can be correlated to, and account for the difference in the sorption behaviour for a contaminant [4–7].

Recent reports have shown that the SOM is a heterogeneous substance consisting of two types of domains: expanded and condensed. Spectroscopic studies have shown that the expanded and condensed domains are mainly attributed to aliphatic and aromatic moieties [8,9]. Some reports suggest that aromatic components of SOM contribute to contaminant sorption [10–12]. Few other sorption studies are not in agreement with such a conclusion and suggested that aliphatic component of SOM contribute much to contaminant sorption [7,13–15]. However, Gunasekara and Xing [16] highlighted the importance of both aliphatic and aromatic moieties for contaminant's sorption in SOM. Thus, the capacity and affinity of SOM to retain organic contaminants significantly varies among samples of different origin. This may in be the reason why commercially available Aldrich humic acid is not preferred for studying the sorption of an organic contaminant as it will not give the realistic results [6].

The contamination of soil and groundwater by nitroaromatic munitions residues like 2,4,6-trinitrotoluene (TNT) and other

* Corresponding author. Tel.: +91 11 25841390; fax: +91 11 25846420.
E-mail address: drneerasingh@yahoo.com (N. Singh).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.08.090

aminonitrotoluenes have drawn public attention due to their toxic and mutagenic effects on organisms, including humans. Therefore, substantial efforts have been put into the remediation programmes of contaminated sites. Most of the TNT contaminated sites are bound to the areas used for incineration and dumping and those adjacent to the manufacturing units, where large volumes of processed water containing explosives are released. TNT has been reported in groundwater after leaching from disposal sites [17,18], thus, threatening drinking water resources.

Different types of binding mechanisms are responsible for the binding of TNT and its degradation products to SOM. Both physical partitioning and chemical/electrostatic interactions between contaminant and organic matter results in contaminant sorption. The hydrophobic partitioning reaction occurs mainly between non-polar organic contaminants and non-polar moieties of SOM and gives linear adsorption isotherms. Electrostatic interactions/covalent bond formation reactions occur between functional groups in the organic contaminant and SOM. These reactions are very specific unlike hydrophobic partitioning, which is non-specific in nature. Adsorption isotherms obtained due to specific interaction leads to non-linear isotherms. SOM has very complex structure and have both hydrophobic backbone having plenty of different types of reactive functional groups. Thus, both specific and non-specific adsorption mechanism are possible in TNT/metabolite and SOM. Achtnich et al. [19], Bruns-Nagel et al. [20] and Thorn et al. [21], studied binding of TNT in SOM using ^{15}N-labeled compound using nuclear magnetic resonance spectroscopy. Results suggested that reduced degradation products of TNT (diaminonitrotoluene and triaminotolunes) undergo 1,2-nucleophilic addition reactions with carbonyl groups or quinones, resulting in a covalent bonding to SOM [22].

The retention of TNT and its degradation products in soil is highly dependent on the SOM content of soil [23]. The sorption of nitroaromatics in soils is non-linear and concentration dependent, thus, a simple partition model does not adequately address their sorption mechanism [24,25]. However, little information is available on the role of SOM nature (aliphatic and aromatic domains) on the binding of nitroaromatic compounds. Therefore, in the present study we report the sorption of TNT and 2,4-DNT in four SOM fractions and the sorption is correlated to the structural composition of the organic carbon.

2. Materials and methods

2.1. Compounds

Analytical grade (97%) TNT was obtained from "Wehrwissenschaftliches Institut für Werk-, Explosiv- und Betriebsstoffe", Swisstal, Germany. 2,4-DNT was obtained from Sigma–Aldrich Seelze, Germany. Humic acid and lignin were purchased from Sigma–Aldrich. HPLC grade solvents used were locally purchased.

2.2. SOM fractions

Four sorbents were used in the present study. Commercially available humic acid and lignin (a main precursor of soil humic substances) were purchased from Sigma–Aldrich Chemicals and were used without any pre-treatment. Two other sorbents, humic acid and humin were extracted from commercially available compost. Briefly, 5 g of compost was extracted with 50 ml 0.1N NaOH under nitrogen for 24 h. After equilibration the tubes were centrifuged at 3000 rpm for 30 min and the supernatant was transferred into a separate bottle. Fresh sodium hydroxide solution was added and the procedure was repeated until the supernatant became clear in color. After ten alkali extractions the solid mass left behind was defined as humin. The humin fraction was de-ashed with a mixture of HF and HCl, washed using deionised water till free of halide ions and dried at 70°C.

To separate humic acid from fulvic acid, the supernatant was acidified to pH 2 using H_2SO_4 to precipitate humic acid. Humic acid was separated by centrifugation, de-ashed, washed with deionised water and freeze dried. The percent organic carbon content of HA-commercial, lignin, HA-compost and humin was 54.6, 64.9, 52.6, and 41.5% by weight, respectively.

2.3. DP/MAS ^{13}C NMR Experiments

A Varian INOVA^{TM} unity equipped with a 6 mm wide bore probe and operating at 75.475 MHz for ^{13}C was used to acquire the spectra. The samples were placed in zirconia rotors with boron nitride bottom and top spacers and Vespel® drive tips. The rotor spin rate was set at 7500 ± 1 Hz, so that spinning side bands occur at 100 ppm of the respective central band. The spectrum of the compost humic acid was recorded at a spin rate of 7000 Hz with spinning side bands at 93 ppm. Direct polarization (DP) spectra were acquired to allow for a quantitative evaluation of the spectra. The measurements were performed with a repetition time of 180 s, to allow for complete relaxation of the carbon nuclei, and a two-pulse phase modulation (TPPM) decoupling sequence which was optimized for the phase-shift angle (Φ) and pulse length (τ_W). During each experiment 1024 transients were acquired. The free induction decays (FID) were acquired with VNMRJ software (Version 1.1 RevisionD, Varian Inc., Palo Alto, CA, USA) and the spectra elaboration was done with Mestre-C software (Version 4.9.9.9; Mestrelab Research, Santiago de Compostela, Spain). All the FIDs were transformed by applying a 4k zero filling, an exponential filter function with a line broadening (LB) of 50 Hz and a second order polynomial with Bernstein algorithm for baseline correction [26]. The spectra were divided in five spectral regions [27]. Spinning side bands (SSB) were accounted for and the spectra were corrected (see Table A as electronic supporting material). This correction of the spectra has already been reported to be effective in improving the assessment of ^{13}C-CPMAS NMR spectra of humic substances [28], even though the SSB shapes may not be symmetrical in respect to the central band [29].

2.4. Sorption–desorption studies

The sorption of TNT and 2,4-DNT in SOM fractions was studied using batch method. The SOM samples (10 mg for humic acids or lignin and 20 mg for humin so as to get sorption in the range of 30–75%) in 10 ml borosilicate stoppered glass tubes were supplemented with 5 ml of aqueous solution of TNT/2,4-DNT (solutions were fortified with 0.01 M $HgCl_2$ to prevent microbially mediated degradation of nitroaromatics). The sorption of TNT and 2,4-DNT was studied at six different concentrations ranging between 2.5 and 15 μg/ml and each concentration was replicated three times. Similarly maintained SOM samples, but without TNT or 2,4-DNT, served as controls. The samples were equilibrated at 20 ± 1 °C for 24 h, as preliminary studies indicated that equilibrium was attained after 24 h equilibration (results not given here). After equilibrium was attained, the samples were centrifuged at 6000 rpm for 30 min and the concentrations of TNT and 2,4-DNT in the supernatant were quantified using high performance liquid chromatography (HPLC). The amount of contaminant sorbed was calculated from the difference between the initial and the final solution concentrations. The mass balance calculations indicated that the TNT and 2,4-DNT were stable during the 24 h of equilibration period and there was no sorption of TNT or 2,4-DNT on the glass surface.

The desorption of TNT and 2,4-DNT was studied in the same samples as used for adsorption. After adsorption, the supernatant was decanted and was replaced with 5 ml of fresh distilled water

(fortified with 0.01 M $HgCl_2$). The suspension was again shaken on an end-over-end shaker for 24 h and then centrifuged. TNT and 2,4-DNT were analyzed in the supernatant by HPLC. Amounts of TNT or 2,4-DNT desorbed were calculated by subtracting the amount of TNT or 2,4-DNT in the entrapped solution after adsorption experiment from the solution concentration measured after the desorption experiment. Only one desorption was performed for each sample.

2.5. Analysis

TNT and 2,4-DNT in aqueous samples were quantified by HPLC (Dionex Summit HPLC analytical system) equipped with a Dionex UVD 340S UV-detector and a Raytest Ramona Star radio flow detector, connected in series. The column used was RP-18 Licrosphere 100 PR 18, 250 mm × 4 mm (MZ-Analysentechnik, Germany). The wavelength for UV detection was set to 230 nm. 20 μl samples were injected into the HPLC system equipped with an 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 to 10% B, 35–39 min 10% B to 80% B, 39–49 min 80% B.

3. Results and discussion

3.1. Carbon chemistry of SOM

Fig. 1 shows the DP/MAS ^{13}C NMR spectra of the SOM materials under analysis. The NMR spectra were divided by chemical shifts (ppm) into five regions: –(10) to 43 ppm = alkyl C (paraffinic); 43–90 ppm = O-alkyl, N-alkyl C; 90–108 = di-O-alkyl C; 108–160 = aryl and O-aryl C; 160–185 = carbonyl and amide C and were corrected for the spinning side bands (see Table A as electronic supporting material). The relative structural carbon percentage (RSCP) of the different SOM fractions is mentioned in Table 1. It was interesting to note that the humic acid isolated from compost was quite different from the commercially available humic acid. The commercial humic acid was rich in alkyl carbon content (37.1%) while the compost humic acid had low alkyl C content (15.2%). Chin and Weber [30] suggested that commercial and natural humic acids are quite different in their properties. Among all the SOM fractions, lignin had highest aryl carbon fraction (41.1%). Humin was the substrate with the highest proportion of O-alkyl carbon followed by the lignin (24%). Generally, carbonyl carbon contributed to the smallest proportion of the SOM carbon content.

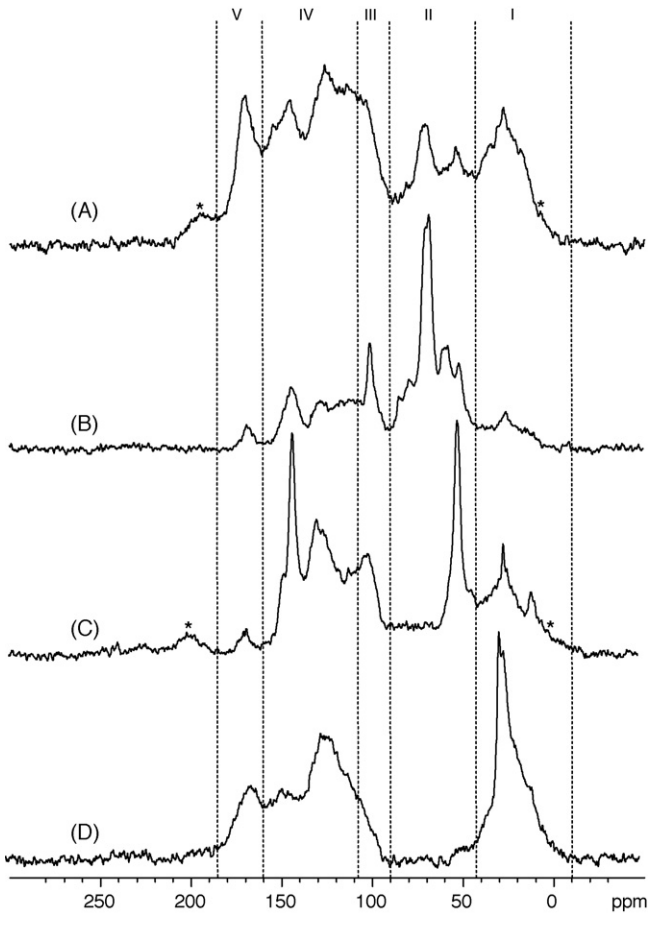

Fig. 1. ^{13}C-DP/MAS NMR spectra of the SOM fractions (A, humic acid-compost; B, humin; C, lignin; D, humic acid-commercial. Asterisk (*), spinning side band).

Table 1
Relative structural carbon percent (RSCP) of SOM fractions.

Substrate	Alkyl	O-Alkyl	Aryl	Carbonyl
Humic acid-commercial	37.1	0.4	43.9	13.1
Lignin	17.8	24.0	41.1	1.8
Humic acid-compost	15.2	18.8	38.9	11.1
Humin	9.4	52.1	26.1	2.2

3.2. Sorption experiment

The sorption data were fitted to the logarithmic form of the Freundlich equation:

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C$$

where, x is the amount of nitroaromatics sorbed (μg), m is the mass of the sorbent (g), C is the equilibrium concentration of the nitroaromatics (μg/ml) and K_f and $1/n$ are the Freundlich constants and are represented by the intercept and the slope of the isotherm, respectively. Freundlich adsorption isotherms and constants are presented in Fig. 2 and Table 2, respectively. K_f, which represents the amount of nitroaromatics adsorbed at an equilibrium concentration of 1 μg/ml, gives an estimate of the extent of adsorption at this concentration, while $1/n$ represents the variation in the adsorption with varying concentrations of nitroaromatics. All the sorbents exhibited non-linear isotherms for TNT and 2,4-DNT sorption with TNT isotherms showing more non-linearity as slope values for TNT were much lower than unity. The $1/n$ values for TNT and 2,4-DNT were less than one, indicating the L-type of adsorption isotherms [31]. The L-type adsorption isotherms are characterized by the strong interaction between the adsorbent and the adsorbate and adsorption decreases as the aqueous phase concentration of the nitroaromatics increases.

To ensure a meaningful comparison of K_f values of TNT and 2,4-DNT in different SOM samples, the $1/n$ (slope) values should be

Table 2
Parameters for TNT and 2,4-DNT adsorption in different SOM fractions.

Substrate	c [$\mu g^{(1-n)} g/ml^n$]	$1/n_{ads}$	r^2	K_d (μg/g)	K_{oc}
TNT					
HA-commercial	358.6	0.79	0.974	259.7	381.9
Lignin	195.5	0.69	0.979	121.7	121.4
HA-compost	282.5	0.83	0.995	217.0	306.6
Humin	159.8	0.85	0.985	131.5	266.2
2,4-DNT					
HA-commercial	476.1	0.93	0.997	465.1	749.7
Lignin	132.1	0.98	0.974	130.9	205.9
HA-compost	387.7	0.79	0.994	295.4	406.1
Humin	142.2	0.98	0.975	154.7	335.7

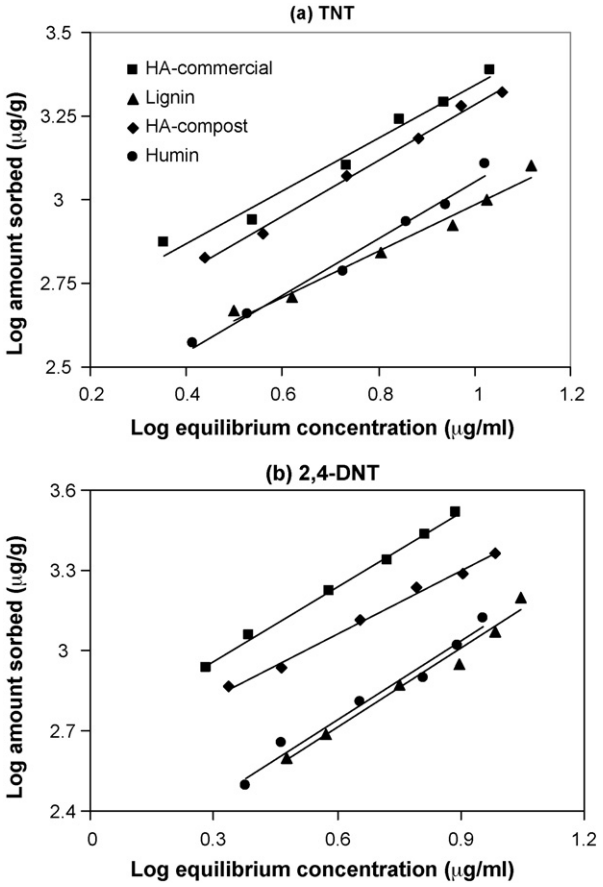

Fig. 2. Adsorption isotherms for TNT (a) and 2,4-DNT (b) in SOM fractions.

statistically equivalent. Thus, $K_f(1/n)$, i.e., the product of the Freundlich adsorption constant (K_f) and the isotherm slope ($1/n$), was chosen as the parameter for comparison [32]

The $K_f(1/n)$ values for TNT sorption in HA-commercial, lignin, HA-compost and humin were 283.3, 134.9, 234.5 and 135.8, respectively, suggesting that both humic acid samples have high affinity for TNT. Similarly, $K_f(1/n)$ values for 2,4-DNT sorption in different substrates were 442.8, 129.5, 306.3 and 139.4, respectively. Both humic acid samples exhibited higher sorption of 2,4-DNT than the TNT, while no difference in TNT/2,4-DNT sorption was observed in the lignin and humin samples. Generally, the sorption of organic compounds is correlated with their aqueous solubilities [30] and octanol–water partition (K_{ow}) coefficients [33]. Literature values for aqueous solubility of TNT and 2,4-DNT are 100–200 μg/ml and 270–273 μg/ml, respectively, while respective log K_{ow} values are 1.60 and 1.98. The aqueous solubility data do not explain the higher sorption of 2,4-DNT in humic acid samples as sorption is inversely related to the aqueous solubility. On the contrary, log K_{ow} values explained the higher sorption of 2,4-DNT in humic acid samples as higher the octanol–water partition coefficient higher will be the sorption.

The K_{oc} (normalizing the partition coefficient (K_d) to organic carbon of substrate; K_d values were calculated using single point adsorption value of 4 μg/ml) values showed same degree of variation as the Freundlich constant K_f or the partition coefficient K_d, suggesting that it not the total organic carbon content of the substrates that affects the sorption of both the nitroaromatic compounds in SOM fractions. Probably, the nature or chemistry of the organic carbon has some important role in determining the sorption of these nitroaromatics.

Table 3
Correlation coefficients (r) between the parameter $K_f(1/n)$ and the RSCP of sorbents for TNT and 2,4-DNT sorption.

Compound	Alkyl	O-Alkyl	Aryl	Carbonyl
TNT	0.791*	−0.832*	0.634	0.991**
2,4-DNT	0.829*	−0.828*	0.616	0.967**

* Significant at $p < 0.05$
** Significant at $p < 0.01$.

To get more insight on the role of chemistry of organic carbon of various SOM fractions on the sorption of TNT and 2,4-DNT the RSCP data of the substrates (Table 1) was correlated with the $K_f(1/n)$ parameter of TNT and 2,4-DNT sorption. Due to the problem of overlap between aromatic and anomeric resonances in region III (108–90 ppm) [34,35], this region was not considered in the correlation with the sorption data. The results (Table 3) suggested that the sorption of TNT and 2,4-DNT in different substrates was positively correlated with the paraffinic C, aryl C and carbonyl C fractions of SOM while negatively correlated with the O/N-alkyl C content. Among alkyl and aryl C (representing bulk of SOM matrix), it was the alkyl C which better contributed for the non-specific sorption of nitroaromatics with correlation coefficient (r) values of 0.791 and 0.828 for TNT and 2,4-DNT, respectively. This indicates that 61% of variability in the sorption of TNT in SOM fractions can be attributed to the paraffinic carbon. Similarly, for 2,4-DNT sorption 69% variability in the sorption was accounted for by the paraffinic carbon. On the contrary, aryl C contributed nearly 40% of variability in the sorption of both the nitroaromatics. Carbonyl carbon content of SOM showed very high positive correlation with TNT ($r = 0.991$) and /DNT ($r = 0.967$) sorption. The carbonyl C content of SOM was responsible for 98% variation in TNT sorption while corresponding figure for DNT was 93%. A probable explanation for very high correlation in carbonyl carbon content and nitroaromatics sorption could be that carbonyl carbon which has positive charge, is electrostatically associated with the negatively charged nitro groups of TNT/DNT. The study suggests that aliphatic component of SOM has an edge as far as affinity for nitrotoluenes is concerned, but we cannot rule out the contribution of aromatic carbon in their binding. Earlier reports [13,14] have highlighted the importance of the aliphatic components of SOM in the sorption of phenanthrene.

3.3. Desorption experiment

The desorption parameters and isotherms for TNT and 2,4-DNT are shown in Table 4 and Fig. 3, respectively. The results indicate that 48–67% of sorbed TNT was released from various SOM fractions during desorption. The corresponding figures for the 2,4-DNT desorption varied between 37 and 56%, suggesting that 2,4-DNT was more retained by the SOM fractions. It was interesting to note that the lignin desorbed least amounts of TNT and 2,4-DNT. This result is opposite of the TNT and 2,4-DNT sorption behaviour in lignin

Table 4
Parameters for TNT and 2,4-DNT desorption in different SOM fractions.

Substrate	% Desorption	K_f	$1/n_{des}$	r^2	$(1/n_{des})/(1/n_{ads})$
TNT					
HA-commercial	67.1	274.7	0.86	0.989	1.09
Lignin	47.9	473.7	0.96	0.974	1.39
HA-compost	62.1	283.6	1.00	0.994	1.20
Humin	57.7	157.5	1.12	0.979	1.32
2,4-DNT					
HA-commercial	39.3	730.0	1.01	0.984	1.09
Lignin	37.3	765.9	1.14	0.976	1.16
HA-compost	56.3	418.7	0.74	0.995	0.94
Humin	55.1	188.9	0.95	0.931	0.97

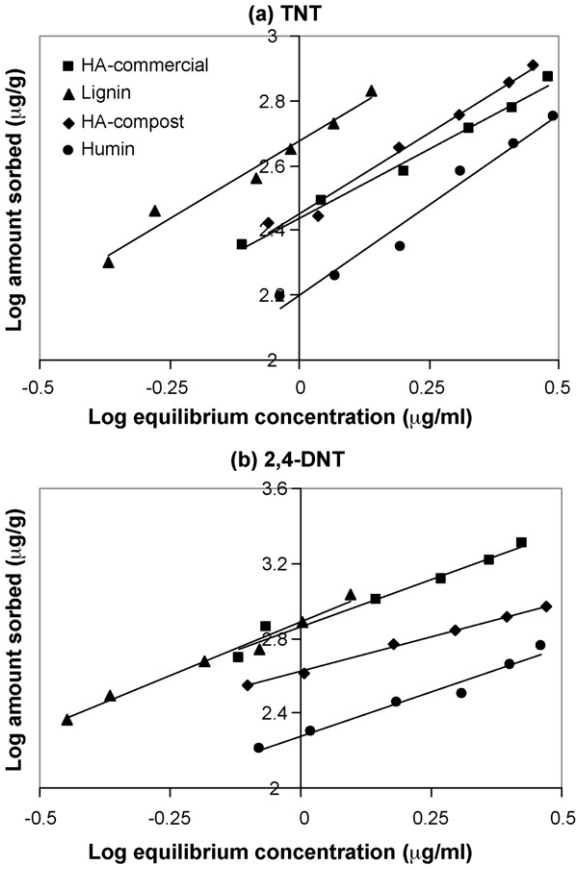

Fig. 3. Desorption isotherms for TNT (a) and 2,4-DNT (b) in SOM fractions.

where compared to other sorbents lignin adsorbed least amounts of these two nitroaromatics.

The slope of the Freundlich desorption isotherm ($1/n_{des}$) takes into account the non-linearity in the desorption isotherm and is the index of the intensity of desorption. The $1/n_{des}$ values indicate that the desorption isotherms were nearly linear (except for the 2,4-DNT desorption isotherm in HA-compost, which appears to be non-linear (L-type)). In general, the $1/n_{des}$ values were higher than the $1/n_{ads}$ values and desorption of nitroaromatics showed hysteresis. The hysteresis (H) was quantified using the $(1/n_{des})/(1/n_{ads})$ ratio. The hysteresis is negative when the $(1/n_{des})/(1/n_{ads})$ ratio is greater than one, while, it is positive when the $(1/n_{des})/(1/n_{ads})$ ratio is less than one. Generally, the desorption for TNT and 2,4-DNT showed a negative hysteresis except for 2,4-DNT in HA-compost and humin. The K_f values for TNT and 2,4-DNT desorption were higher than the corresponding sorption values in all the SOM fractions. This further indicates that the sorption of both the nitroaromatic is irreversible and a considerable amount of sorbed nitroaromatic was retained in the matrix.

The study indicates that different SOM fractions have different structural composition for carbon and these SOM fractions with varying RSCP of organic carbon have varying affinity for nitroaromatic contaminants. Therefore, the structural chemistry of SOM plays an important role in the sorption of nitroaromatic compounds. The non-specific sorption of both TNT and 2,4-DNT in SOM fractions was mainly controlled by the aliphatic (mainly alkyl) fraction of SOM constituting.

Acknowledgement

Neera Singh was supported by a research fellowship from the Alexander von Humboldt Foundation, Bonn, Germany.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.08.090.

References

[1] C.T. Chiou, Theoretical considerations of the particle uptake of nonionic compounds by soil organic matter, in: B.L. Sawhney, K. Brown (Eds.), Reaction and Movement of Organic Chemicals in Soils, Soil Sci Soc Am, Madison, WI, 1989, pp. 1–29.
[2] B. Xing, J.J. Pignatello, B. Gigliotti, Competitive sorption between atrazine and other organic compounds in soils and model sorbents, Environ. Sci. Technol. 30 (1996) 2432–2440.
[3] P.B. Hatzinger, M.E. Fuller, D.S. Rungmacol, L. Rachel, J. Robert, Enhancing the attenuation of explosives in surface soils at military facility: sorption–desorption isotherms, Environ. Toxicol. Chem. 23 (2004) 306–312.
[4] P. Grathwohl, Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations, Environ. Sci. Technol. 24 (1990) 1687–1693.
[5] B. Xing, W.B. McGill, M.J. Dudas, Sorption of alpha naphthol onto organic sorbents varying in polarity and aromaticity, Chemosphere 28 (1994) 145–153.
[6] Y.P. Chin, G.R. Aiken, K.M. Danielsen, Binding of pyrene to aquatic and commercial humic substances: The role of molecular weight and aromaticity, Environ. Sci. Technol. 31 (1997) 1630–1635.
[7] B. Chefetz, A.P. Deshmukh, P.G. Hatcher, E.A. Guthire, Pyrene sorption by natural organic matter, Environ. Sci. Technol. 34 (2000) 2925–2930.
[8] B. Xing, Sorption of naphthalene and phenanthrene by soil humic acids, Environ. Pollut. 111 (2001) 303–309.
[9] B. Xing, Z. Chen, Spectroscopic evidences for condensed domain in soil organic matter, Soil Sci. 164 (1999) 40–47.
[10] M.D. Johnson, W. Huang, W.J. Weber jr, A distributed reactivity model for sorption of soils and sediments. 13. Simulated diagenesis of natural sediment organic matter and its impact on sorption/desorption equilibria, Environ. Sci. Technol. 35 (2001) 1680–1687.
[11] X. Wang, B. Xing, Sorption of organic contaminants by biopolymer derived chars, Environ. Sci. Technol. 41 (2007) 8342–8348.
[12] A.G. Ahangar, R.J. Smernik, R.S. Kookana, D.J. Chittleborough, Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron, Chemosphere 70 (2008) 1153–1160.
[13] J.D. Mao, S. Hundal, M.L. Thompson, K. Schmidt-Rohr, Correlation of poly(methylene)-rich amorphous aliphatic domain in humic substances with sorption of a nonpolar organic contaminant, phenanthrene, Environ. Sci. Technol. 36 (2002) 929–936.
[14] M.J. Salloum, B. Chefetz, P.G. Hatcher, Phenanthrene sorption by aliphatic-rich natural organic matter, Environ. Sci. Technol. 36 (2002) 1953–1958.
[15] M.J. Simpson, P.C.E. Johnson, Identification of mobile aliphatic domains in soil humin by solid state ^{13}C-nuclear magnetic resonance, Environ. Toxicol. Chem. 15 (2006) 52–57.
[16] A.S. Gunasekara, B. Xing, Sorption and desorption of naphthalene by soil organic matter: Importance of aromatic and aliphatic components, J. Environ. Qual. 32 (2003) 240–246.
[17] V.H. Lenke, G. Daun, D. Bryniok, H.-J. Knackmuss, Biologiche sanierung vonrüstungsaltlasten, Spektrum der Wissenschaft Okt (1993) 106–108.
[18] M. Hildenbrand, V. Neumann, REV-reactor and soil column studies of sorption and migration of explosives in Elsnig sandy aquifers, Acta Universitatis Carolinae Geologica 39 (1995) 131–135.
[19] C. Achtnich, E. Fernands, J.M. Bollag, H.J. Knackmuss, H. Lenke, Covalent bonding of reduced metabolites of ^{15}N-TNT to soil organic matter during a bioremediation process analyzed by ^{15}N-NMR spectroscopy, Environ. Sci. Technol. 33 (1997) 4448–4456.
[20] D. Bruns-Nagel, H.D. Knicker, O. Drzyzga, U. Butehorn, K. Steinbach, D. Gemsa, E. von Loew, Characterization of ^{15}N-TNT residues after an anaerobic-aerobic treatment of soil/molasses mixtures by solid state ^{15}N-NMR spectroscopy. 2. Systematic investigation of whole soil and different humin fractions, Environ. Sci. Technol. 34 (2000) 1549–1556.
[21] K.A. Thorn, J.C. Pennington, C.A. Hayes, ^{15}N NMR Investigation of the reduction and binding of TNT in an aerobic bench scale reactor simulating windrow composting, Environ. Sci. Technol. 36 (2002) 3797–3805.
[22] K.A. Thorn, K.R. Kennedy, ^{15}N NMR Investigation of the covalent binding of reduced TNT amines to soil humic acid, model compounds, and lignocellulose, Environ. Sci. Technol. 36 (2002) 3787–3796.
[23] N. Singh, D. Hennecke, J. Hoerner, W. Koerdel, A. Schaeffer, Mobility and degradation of trinitrotoluene/metabolites in soil columns: effect of soil organic carbon content, J. Environ. Sci. Health 43A (2008) 682–693.
[24] L.S. Hundal, P.J. Shea, S.D. Comfort, W.L. Powers, J. Singh, Long-term TNT sorption and bound residue formation in soil, J. Environ. Qual. 26 (1997) 896–904.
[25] J. Eriksson, U. Skyllberg, Binding of 2,4,6-trinitrotoluene and its degradation products in a soil organic matter two-phase system, J. Environ. Qual. 30 (2001) 2053–2061.
[26] D.E. Brown, Fully automated base-line correction of 1D and 2D NMR spectra using Bernstein polynomials, J. Magnetic Res. Ser. A 114 (1995) 268–270.

[27] M.A. Wilson, NMR Techniques and Applications in Geochemistry and Soil Chemistry, Pergamon Press, London, UK, 1987.
[28] P. Conte, A. Piccola, B. van Lagen, P. Buurman, P.A. Jager, Quantitative aspects of solid state ^{13}C-NMR spectra of humic substances from soils of volcanic systems, Geoderma 80 (1997) 327–338.
[29] M.J. Duer, Solid State NMR Spectroscopy: Principles and Applications, Blackwell Science Ltd., Oxford, UK, 2002.
[30] Y.P. Chin, W. Weber, Estimating the effects of dispersed organic polymers on the sorption of contaminants by natural solids. I. A predictive thermodynamic humic substance organic solute interaction mode, Environ. Sci. Technol. 23 (1989) 978–984.
[31] C.H. Giles, T.H. McEvans, S.N. Nakhwa, D. Smith, Studies in adsorption. Part XI. A system of classification of adsorption isotherms and its use in diagnosis of desorption mechanism and measurement of specific surface areas of solids, J. Chem. Soc. 3 (1960) 3973–3993.
[32] Q. Wang, W. Yang, W. Liu, Adsorption of acetanilide herbicides on soils and its correlation with soil properties, Pestic. Sci. 55 (1999) 1103–1108.
[33] G.G. Briggs, Theoretical and experimental relationship between soil adsorption, octanol-water partition coefficient, water solubilities and bioconcentration factors and the parachor, J. Agric. Food Chem. 29 (1981) 1050–1059.
[34] J.D. Mao, K. Schmidt-Rohr, Accurate quantification of aromaticity and nonprotonated aromatic carbon fraction in natural organic matter by C-^{13}solid-state nuclear magnetic resonance, Environ. Sci. Technol. 38 (2004) 2680–2684.
[35] J.D. Mao, K. Schmidt-Rohr, Separation of aromatic-carbon C-^{13} NMR signals from di-oxygenated alkyl bands by a chemical-shift-anisotropy filter, Solid State Nucl. Mag. 26 (2004) 36–45.