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CRREL

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September 1991

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U.S. Army Corps of Engineers
Cold Regions Research &
Engineering Laboratory

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Prepared for
OFFICE OF THE CHIEF OF ENGINEERS

PREFACE

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Role of Donor–Acceptor Interactions in the Sorption of TNT and Other Nitroaromatics from Solution

DANIEL C. LEGGETT

INTRODUCTION

Environmental contamination by TNT and other explosive-related compounds is an incipient problem in the U.S. and Europe (Periera et al. 1979, Spalding and Fulton 1988, Haas and Stork 1989, Jenkins et al. 1989, von Low et al. 1989). Consequently much attention is being given to water and soil analysis for those compounds, as well as to bio-uptake (Palazzo and Leggett 1986, Yinon and Hwang 1986), industrial hygiene (Hunt et al. 1980, Bishop et al. 1988) and forensic applications (Vouros et al. 1977, Krull et al. 1981, Voyksner and Yinon 1986). This means that a greater understanding of their environmental fate is needed, as well as reliable methods for their determination in a variety of matrices. Sorptive interactions play an important role in determining the environmental mobility of trace organics. I will examine here the nature of sorptive interactions involving TNT and similar compounds from dilute aqueous solution onto soils and model systems.

SORPTION ON SOILS

Several investigators have studied the sorption of TNT on soils and clay minerals (Sikka et al. 1980, Leggett 1985, Pennington and Patrick 1990). In all cases similar sorption isotherms were reported, some typical examples of which are shown in Figure 1. They are characterized by an initially steep rise followed by a region of nearly constant but positive slope. Thus, none of the most common isotherm models (linear, Freundlich and Langmuir) fit the data over the whole concentration range. One explanation for this type of isotherm is that two (or more) mechanisms operate simultaneously—one with lower capacity and higher energy, the other with higher capacity and lower energy (Leggett 1985)—corresponding to the participation of two (or more) types of site on the soil or clay.

Pennington and Patrick (1990) found that sorption coefficients K_S estimated from the linear model are strongly correlated with extractable iron and cation exchange capacity. This analysis could be criticized because the slopes are not constant; therefore, K_S cannot have one value over the entire range covered by the isotherms. Nevertheless, these single-valued sorption coefficients can be considered somewhat representative of trends in the data. The same investigators also found rather low correlation of K_S with soil organic carbon, which undoubtedly explains the failure of linear partitioning models to represent the sorption of TNT and the failure of octanol–water partition coefficients to provide reasonable estimates of K_S based on soil organic

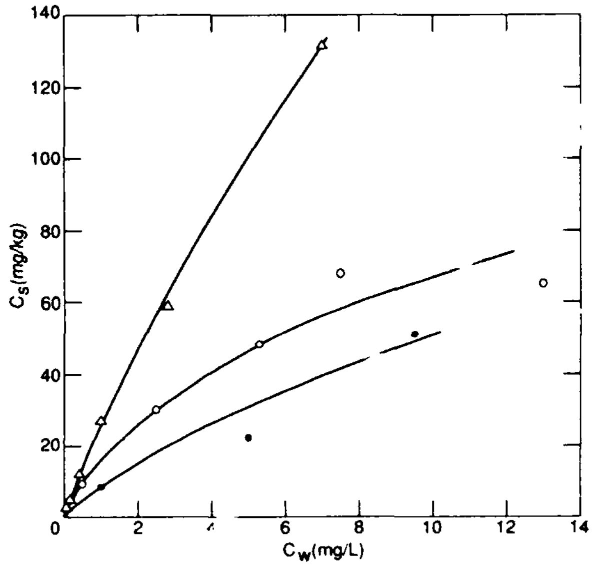

Figure 1. Some typical TNT sorption isotherms. (C_s and C_w are sorbed and solution concentrations, respectively.)

carbon. Experimental K_S values (Spanggord et al. 1985, Pennington and Patrick 1990) are greater than these estimates by as much as an order of magnitude. This means that although partitioning into soil organic matter may occur, it is not the dominant mechanism. Another mechanism that has been considered is hydrogen bonding to water coordinated by exchange cations (Leggett 1985). This mechanism is supported by spectroscopic evidence with similar compounds on clay minerals (Yariv et al. 1966, Fusi et al. 1982). The high-energy sites noted earlier were thought to be more likely due to strongly coordinating cations at edge sites such as aluminum and iron (Leggett 1985). Whether these compounds are coordinated through water or directly to cations apparently depends on the cation and the availability of water. Therefore, one must be cautious in comparing spectroscopic studies done at low moisture contents with adsorption studies done in aqueous suspensions. Hydrogen bonding can also occur through residual Si–OH groups on the mineral and free hydroxyl groups of the organic matter (Brodman et al. 1982, Winkler 1989). The main question in all surface H-bonding interactions with aromatic nitro groups is how strong they are in the presence of excess water. Apart from the strength of the interaction, binding should be stabilized by the hydrophobic effect.

Direct coordination of TNT by Fe^{+3} by charge transfer from nitro into iron d or sp^3d^2 hybrid orbitals (Harvey and Porter 1963) is a potentially important interaction but one for which we have no direct evidence. A theoretical molecular orbital analysis would be welcome. Sorption of TNT and other nitro compounds from the vapor phase onto stainless steel and several pure transition metals has been observed (Dravnieks 1966, Leggett 1977, Peebles et al. 1985).* It is also not clear how much influence water vapor has on this interaction. The potential sorption mechanisms identified thus far are consistent with the statistical correlation with extractable iron and exchange cations (Pennington and Patrick 1990) and with the experimentally observed sorption isotherms (Leggett 1985).

SORPTION AND PARTITIONING IN MODEL SYSTEMS

The previous section gave the evidence for association of TNT and other nitroaromatics with inorganic soil components. Weak statistical association of sorption with soil organic carbon also argues against the validity of the customary hydrophobic partition models (Chiou et al. 1979, Karickhoff et al. 1979, Briggs 1981) for TNT. The hydrophobic model essentially ignores any enthalpic interactions of compounds, or at least any differences among compounds, with the organic phase. However, it is becoming increasingly clear that the hydrophobic partition model is in need of refinement, both in terms of the differences in organic matter from soil to soil and the chemical behavior from compound to compound (Mingelgrin and Gerstl 1983, Gerstl and Mingelgrin 1984, Landrum et al. 1984, Garbarini and Lion 1986, Gauthier et al. 1987, Grathwohl 1990, Murphy et al. 1990). It is not hard to deduce why this is so. A general treatment of solubility and partitioning in solvent–water systems is known to require at least donor, acceptor and electrostatic terms besides a cavity term (Leo et al. 1971, Pierotti 1976, Snyder 1978, Watarai et al. 1982, Taft et al. 1985a,b, Kamlet et al. 1988, Cheong and Carr, 1989, Chin and Weber 1989, Buncel and Rajagopal 1990). Sorption in soil organic matter is a great deal more complex due to the multiplicity and self-interaction of functional groups that can be present, the spatial and temporal heterogeneity of soil organic matter, and steric affects not seen in solution. A complete description of sorptive behavior can certainly not now be, and probably never will be, realized. The best we can ever hope to achieve is to identify and measure those interactions that are most important. Some predictive capability will no doubt be possible but will never have the certainty of empirically determined sorption isotherms using a single compound and a single soil subsample. On the other hand, semi-quantitative generalizations often suffice for practical purposes, as evidenced by the success of the octanol–organic matter correlations (Chiou et al. 1979, Karickhoff et al. 1979, Briggs 1981). The important thing to realize is that these only work for compounds in which the cavity term is large enough to (statistically) obscure all other (enthalpic) contributions. For small polar or polarizable molecules such as nitrobenzenes and nitrotoluenes, I suggest that this condition is not satisfied.

Studies of solution complexing of nitroaromatics are numerous (Rao 1969), and trinitrobenzene is the quintessential electron-pair acceptor in studies involving charge transfer interactions. Some more recent investigations are described in Chudek et al. (1987), Rahda et al. (1987), Ayad et al. (1989) and Qureshi et al. (1989a,b, 1990). Thus, many substituted benzene compounds and even benzene itself can form π–π^*-type donor–acceptor complexes with nitroaromatics. Other indicators of donor–acceptor behavior in solution are solubilities in various solvents. For example, TNT is quite soluble in benzene and toluene but even more so in pyridine and acetone (Taylor and Rinkenbach 1923). A 20-fold enhancement of the solubilities of TNT, TNB and picric

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* Also, T.F. Jenkins, personal communication, 1973.

Table 1. Partition coefficients for some nitroaromatics in octanol–water and acetonitrile-saturated NaCl.

Solute	*log* P_{aw}	*log* P_{ow}
Benzene	2.56	2.13*
Toluene	2.91	2.73*
Nitrobenzene	2.49	1.85*
2-Nitrotoluene	2.87	2.30*
3-Nitrotoluene	2.90	2.45*
4-Nitrotoluene	2.86	2.42*
1,3-Dinitrobenzene	2.61	1.49†
2,4-Dinitrotoluene	2.92	1.98†
2,6-Dinitrotoluene	3.03	2.02**
1,3,5-Trinitrobenzene	2.78	1.18**
2,4,6-Trinitrotoluene	3.30	1.86**

* Sangster (1989).
† Hansch and Leo (1979).
** Jenkins (1989).

acid in chloroform compared to carbon tetrachloride suggest that they can be electron donors as well as acceptors, presumably by forming H-bonds through the nitro groups (Marvel et al. 1940). Thus, it appears that several types of charge transfer are possible, depending on the nature of the donor or acceptor molecule, and two types may occur cooperatively within the same complex (Rahda et al. 1987, Qureshi et al. 1989b, Qureshi et al. 1990).

Liquid–liquid partitioning systems can also give information on donor–acceptor behavior in solution. For example, in the octanol–water system, nitro groups on aromatic rings lower the partition coefficient P_{ow} relative to the unsubstituted parent compound (Hansch and Leo 1979). Nitro groups must confer some degree of hydrophilicity to aromatic compounds by H-bonding with water molecules. On the other hand, we have studied partitioning of nitroaromatics in the acetonitrile–water system by salting out the organic phase with sodium chloride (Leggett et al. 1990, in press). When the data are expressed as partition coefficients and plotted vs P_{ow} (Table 1, Fig. 2), a relationship both to P_{ow} and the number of nitro groups n becomes apparent. In this case, however, the contribution of the nitro group to the partition coefficient is positive. Since acetonitrile is a weaker H-bond donor than water (Snyder 1978), H-bonding to the nitro groups doesn't explain the partitioning of aromatic nitro compounds between water and acetonitrile. Probably acetonitrile donates a pair of electrons to aromatic rings made deficient by the nitro group. The H-bond basicity of acetonitrile has been investigated using several reference acids (Gurka and Taft 1969, Gutmann 1978, Abraham et al. 1989, Catalan et al. 1990), but ours (Leggett et al., in press) appears to be the first report using an aromatic π-acceptor.

A fourth type of evidence of donor–acceptor interactions of nitroaromatics derives from their behavior on reversed-phase HPLC columns. In this case, capacity

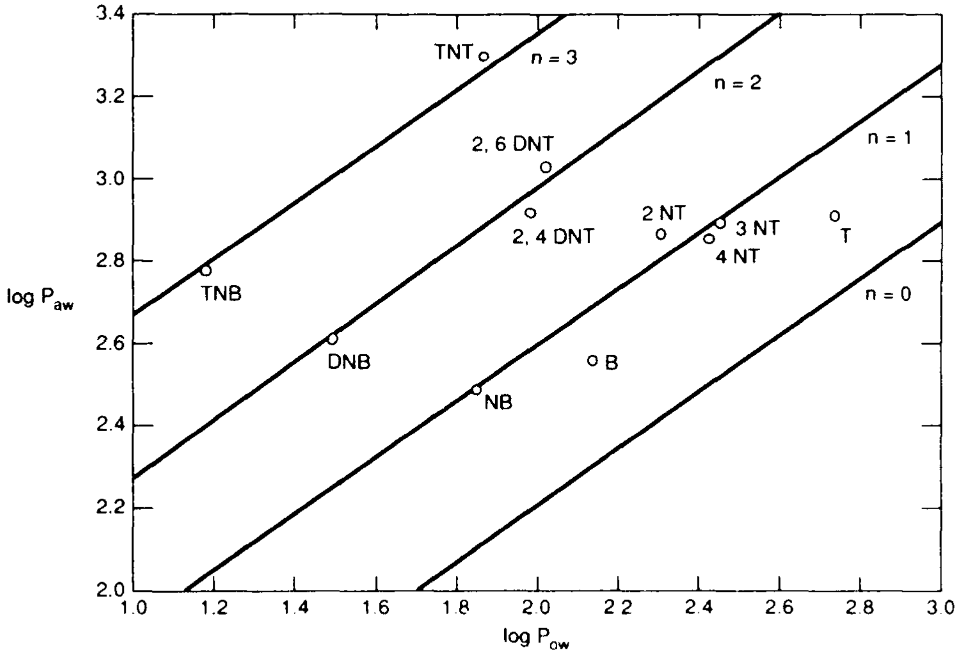

Figure 2. Plots of log P_{aw} *vs log* P_{ow} *for nitroaromatics. Solid lines are of log* $P_{aw} = 0.70 \log P_{ow} + 0.39n + 0.80$ *for different values of* n.

Table 2. Capacity factors on LC-CN and octanol–water partition coefficients for some nitroaromatics.

Solute	*log* k'*	*log* P_{ow}†
Benzene	–0.328	2.13
Toluene	–0.180	2.73
Nitrobenzene	–0.215	1.85
2-Nitrotoluene	–0.076	2.30
3-Nitrotoluene	–0.056	2.45
4-Nitrotoluene	–0.066	2.42
1,3-Dinitrobenzene	–0.119	1.49**
2,4-Dinitrotoluene	0.021	1.98**
2,6-Dinitrotoluene	–0.022	2.02*
1,3,5-Trinitrobenzene	–0.149	1.18*
2,4,6-Trinitrotoluene	0.045	1.86*

* Jenkins (1989).
† *Sangster (1989).*
** Hansch and Leo (1979).

factors k' on a cyanopropyl stationary phase (Jenkins et al. 1989) are plotted vs P_{ow} (Table 2, Fig. 3). The capacity factor k' is linearly related to a partition coefficient, so the plot is analogous to that shown in Figure 2 and with almost identical results; both the capacity factor on cyanopropyl and the partition coefficient in acetonitrile are functions of the number of nitro groups on an aromatic nucleus as well as P_{ow}. In the case of acetonitrile–water partitioning, the nitro group contribution appears to be nearly constant, and except for benzene and toluene, an extended Hansch-type LFER would accommodate the polar interaction:

$$\log K_{aw} = a \log K_{ow} + bn + c \qquad (1)$$

where n is the number of nitro groups and a, b and c are constants. Retention on the cyanopropyl stationary phase appears to be a more complex function of n, possibly n^x where $0 < x < 1$. Partition coefficients of compounds with multiple chlorine substitution were also better fit with a power function (Kaiser 1983). Enhanced retention of aromatics due to nitro substitution has also been recorded on a number of other donor stationary phases, including aryl ether (Mourey and Siggia 1979), pyrene (Lochmuller et al. 1983), anthracene (Verzele and Van de Velde 1985) and propylaniline (Murphy et al. 1986), as well as on bentonite (Leggett 1985).

ORGANIC CHARGE TRANSFER IN SOIL

Since nitroaromatics readily participate in donor–acceptor interactions and can both donate and accept electrons depending on the environment, sorption will only occur if donors or acceptors or both are present in the soil. We have already discussed the likelihood of coordination by iron and exchangeable cations, which are types of charge transfer. The occurrence of donor–acceptor interactions between xenobiotics and soil organic matter has been discussed (Ziechmann 1972, Lindqvist 1982), and spectroscopic evidence has been

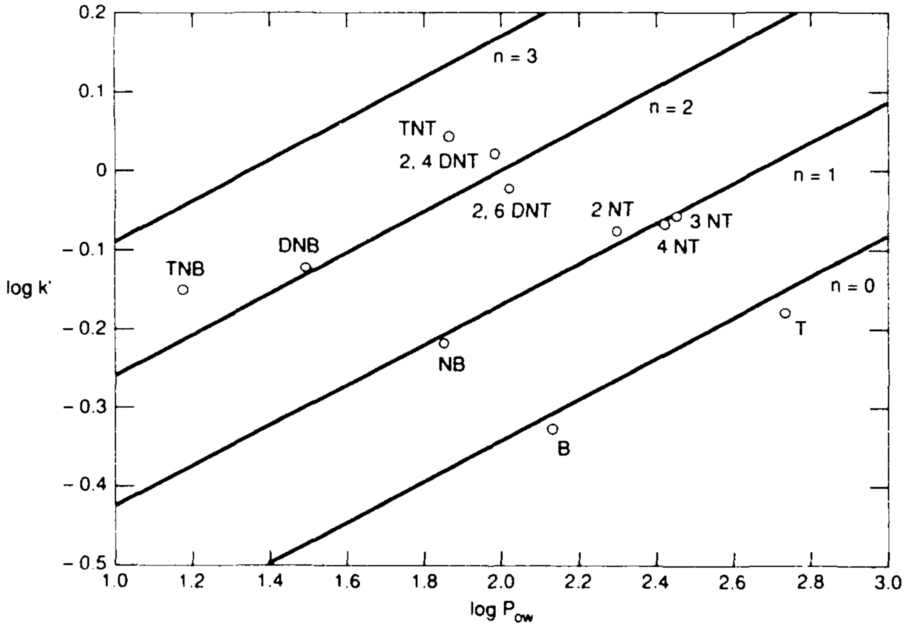

Figure 3. Plots of log k' *on LC–CN vs log*P_{ow} *for nitroaromatics. Solid lines are of log*k' *=* $0.26 \log P_{ow} + 0.17n - 0.86$ *for different values of* n.

presented for a number of compounds, including triazine herbicides (Senesi and Testini 1982), hydroquinones (Lindqvist 1982), tetrachlorobenzoquinone (Chloranil) (Melcer et al. 1987) and soil phosphatase enzyme (Gosewinkel and Broadbent 1986). Chloranil is a strong π acceptor (Ziechmann 1972) similar to TNT and other polynitroaromatics. Soil organic matter is known to contain many functional groups (Choudhry 1984) capable of acting as donors or acceptors or both (Abraham et al. 1989), including (but not limited to) carboxyl, carbonyl, aryl and alkyl hydroxyl, aryl ether and quinone. Hydroquinone–quinone structures are likely candidates (Wilson and Weber 1977, Choudhry 1984) for the role of humus in mediating many of the oxidation–reduction reactions in natural waters (Zimmerman 1981, Thurman 1986), including nitro reduction (Schwarzenbach et al. 1990). Reduction of TNT is known to be a principal mechanism affecting its fate in soil–water systems (Osmon and Andrews 1978, Periera et al. 1979, Pennington and Patrick 1990).* Ultimately, reduced TNT may bond covalently with humus (Hsu and Bartha 1974, Parris 1980). Photolysis of nitroaromatics in natural water is also known to be facilitated (sensitized) by humus (Mabey et al. 1983, Simmons and Zepp 1986), which may involve charge transfer with the sensitizing agent (Occhiucci and Patacchiola 1982). Interestingly, quinone oximes were isolated photoproducts of TNT many years ago (Schultz and Ganguly 1925). Reduction and photolysis of nitroaromatics could be considered examples of complete charge transfer, in which new compounds are formed irreversibly. Irreversible processes are important in the overall disposition of nitroaromatics and are ultimately responsible for their environmental fate.

Although organic donor–acceptor interactions of nitroaromatics are presumed to occur in soils, their relative importance is problematical. The statistical evidence noted earlier suggests that inorganic components (iron and cations) are more important than organic matter. However, if the number of organic donor–acceptor sites is not closely related to total organic carbon, the poor correlation with organic matter fraction could be misleading.

SUMMARY

Evidence was presented for the interaction of nitroaromatics in soil solution with specific donor–acceptor sites in soil, including nonlinear adsorption isotherms, the lack of correlation with soil organic carbon, the correlation with extractable iron, exchange cations and the number of nitro groups per aromatic ring. Possible mechanisms include H-bonding to coordinated water through the nitro groups and direct coordination to transition metals, the most abundant being iron. Association of nitroaromatics with organic matter is also strongly inferred from evidence of complexation in various model systems, including solvent–water partitioning and reversed-phase liquid chromatography, and the presence in soil organic matter of known donor–acceptor groups, including ketone, ether, hydroxyl and hydroquinone. Known electron carriers such as hydroquinones may be responsible for their reduction and irreversible coupling with soil organic matter. The statistical analysis of adsorption data on different soils suggests that sorption of TNT is predominantly to inorganic components. This simple interpretation could be in error, however, as the number of donor–acceptor groups on soil organic matter isn't necessarily related to the organic mass fraction in the soil.

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The evidence related to sorptive interactions of nitroaromatics is reviewed. Although evidence from a variety of organic model systems suggests that sorptive interaction of nitroaromatics with organic components will occur, the statistical evidence attributes greater importance of inorganic components over organic matter in soil sorption of TNT. It was concluded that donor–acceptor interactions are more important than purely hydrophobic effects in the sorption of nitroaromatics from solution onto soils and model sorbents. Furthermore, TNT in soil–water systems may become an ultimate recipient of charge, causing its reductive transformation and subsequent covalent bonding to soil organic matter components.

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