Influences on the sorption affinity of soil organic matter for non-ionic organic pollutants

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ABSTRACT

Sorption of non-ionic organic compounds to organic matter is usually characterized as a partitioning interaction, which is quantified by K_{oc}, the organic-C normalized partitioning coefficient. However K_{oc} for any single compound varies considerably between soils, often by a factor of 3-10. This study addresses some of the potential causes of this variability.

Forty-four soil cores were collected from a 2 ha paddock. Ten of these cores were selected for sorption measurements. The chemical composition of the soil organic matter (SOM) was determined using ^{13}C NMR analysis. It was found that K_{oc} for diuron was positively correlated with aryl C ($r^2 = 0.59$) and negatively correlated with O-alkyl C ($r^2 = 0.84$). There were no such correlations for phenanthrene K_{oc}.

A second set of experiments was carried out to investigate the effects of SOM–mineral interactions on the sorption properties of a selection of the soils. It was found that HF-treatment increased K_{oc} for both phenanthrene and diuron. The HF treatment removes mineral matter leaving the organic phase unaffected by the treatment. The increase in K_{oc} on HF-treatment soils provides strong evidence that interactions between organic matter and soil minerals block organic matter sorption sites. Furthermore, following HF-treatment, there was a positive correlation between K_{oc} for phenanthrene and aryl C and carbonyl C and a negative correlation with O-alkyl C. This suggests that the non-constancy of the relationship between organic matter chemistry and K_{oc}, for whole soils in the case of phenanthrene, may be a consequence of variability of the effect of organic matter-mineral interactions on K_{oc}.

The influence of lipids on the sorption of diuron and phenanthrene to soils was also investigated. Lipids are known to cover the surfaces of organic matter in soil. K_{oc} for diuron and phenanthrene were consistently higher for the lipid-extracted soils than for the whole soils (average of 31% for diuron and 29% for phenanthrene), indicating that lipids block sorption sites on the organic matter. Sorption experiments on one pair of HF-treated soils indicated that the blocking effects of minerals and lipids are independent, because lipid extraction and HF-treatment combined increased K_{oc} by more than either treatment alone.

In the last experiment, the effect of solvent conditioning on the sorption of diuron and phenanthrene was investigated. The K_{oc} values for compounds were consistently higher for solvent-treated whole soil and lipid-extracted soil than corresponding soils before solvent treatment. Solid-state ^{13}C NMR spectra of the solvent-treated soils indicated that there were no significant changes in the chemical structure of SOM caused by solvent treatment. Solvent treatment changes the physical conformation of the SOM, increasing its sorption affinity.

The key findings from the research are:
- Variations in sorption affinity for diuron are related to differences in the soil organic matter chemistry.
- SOM-mineral interactions can have a substantial influence on K_{oc} for non-ionic compounds.
- Lipids may block the active sorption sites on the SOM thereby diminishing sorption overall.

- Solvent conditioning can change the physical conformation of SOM and lead to enhancement sorption of diuron and phenanthrene.

DECLARATION

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1) Ahangar, A. G., R. J. Smernik, R. S. Kookana and D. J. Chittleborough. 2008. Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. Chemosphere 70: 1153-1160.

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5) Ahangar, A. G., R. J. Smernik and R. S. Kookana (2007). Can sorption properties be used to gauge the strength of organic matter-mineral interactions? 3rd International Conference on Mechanisms of Organic Matter Stabilisation and Destabilisation in Soils and Sediments, Adelaide, 23-26 September 2007.

6) Ahangar, A. G., R. J. Smernik and R. S. Kookana (2006). Changes in the sorption affinity of soil organic matter (Koc) with depth for two organic contaminants. Soil science solving problems: ASSSI-ASPAC-ACMS National Soils Conference, the University of Adelaide, 3-7 December 2006.

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10) Ahangar, A. G., R. J. Smernik and R. S. Kookana (2008). The effects of organic matter-mineral interactions and organic matter chemistry on the sorption of phenanthrene. The 12th international conference on integrated diffuse pollution management. Khon Kaen, Thailand 25-28 August 2008.

11) Smernik, R. J., A. G. Ahangar, R. S. Kookana and D. J. Chittleborough (2008). What can the sorption of organic molecules tell us about the nature of organic matter?

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12) Smernik, R. J., A. G. Ahangar, R. S. Kookana and D. J. Chittleborough (2008). Dual roles of organic matter chemistry and organic matter-mineral interactions in the sorption of organic pollutants. Palmerston North, New Zealand 1 - 5 December 2008.

CHAPTER 1

REVIEW OF LITERATURE

1. The importance of organic pollutants

Organic compounds constitute one of the most important classes of pollutants. Although the highest concentrations of organic pollutants are usually associated with human activity (e.g. in urban areas), they are also widely distributed, with some found in substantial concentrations on the most remote parts of the earth (Bargagli 2008). Organic pollutants are of concern due to their toxic effects on living organisms, human included. These toxic effects can be either acute or chronic and include disruption of the endocrine, reproductive and immune systems, neurobehavioral disorders and carcinogenicity. Organic pollutants can be introduced into the environment through natural processes (e.g. biomass burning), but most are introduced through human activity, either planned (e.g. the use of herbicides or pesticides) or as industrial waste and vehicle emissions.

The issue of organic pollutants first came to widespread public attention in 1962 with the publication of "Silent Spring" (Carson 1962), which recognised the impact of the synthetic pesticide DDT (dichloro-diphenyl-trichloroethane), used to control malaria-carrying mosquitoes, on the environment. In particular, DDT was found to bioaccumulate in birds and cause thinning of their eggshells and ultimately a lack of reproductive success. Since then, there has been an increased public awareness of the impacts of organic chemicals, an awareness that has peaked with several subsequent events including the human health effects from the widespread spraying of the defoliant "Agent Orange" (which contained highly toxic dioxins) during the Vietnam

War (Minh et al. 2008), and the huge oil spill from the tanker "Exxon Valdez", that contaminated a pristine Alaskan wilderness area (Boehm et al. 2007).

One of the challenges of dealing with organic pollutants is their great variety. The number of organic molecules generated by different industries increases every day. The sum of natural and man-made organic compounds in our environment is estimated at between 8 and 16 million, of which about 40000 are commonly encountered in daily life (Hou et al. 2003). Currently, more than 100,000 organic chemicals are available for purchase in Europe (European Commission 2006). It is clearly not possible to test the fate of each compound individually in every environment where it is likely to occur. Therefore extensive effort has been put into identifying, at a mechanistic level, the key features of both chemical and environment that control the environmental fate of organic pollutants.

2. The fate of organic pollutants in soils

Organic pollutants can undergo a number of processes in soils: they can be degraded biotically and abiotically, the low molecular weight organic pollutants have a tendency to volatilize, and they may also be lost by leaching (Semple et al. 2003). They can be bioaccumulated and adsorbed onto soil minerals and organic matter (Schwarzenbach et al. 1993). The fate of organic pollutants in a soil is affected by factors such as weather and climate, biological diversity and abundance, the amount and the nature of the soil minerals, and organic matter and pollutant properties such as solubility, polarity, hydrophobicity, and molecular structure (Reid et al. 2000; Semple et al. 2003; Doick et al. 2005).

2.1 Degradation

The ability of a soil to degrade organic pollutants depends on soil fertility and health, and most importantly the catabolic activity of the soil micro-organisms. A variety of eukaryotic and prokaryotic organisms are able to metabolize organic pollutants. There are two prerequisites that are needed for biodegradation: pollutants must be bioavailable and they must be biodegradable (Reid et al. 2000; Christopher et al. 2002). The rate of microbial decomposition is affected by several factors (Semple et al. 2003):

- the availability of pollutants to micro-organisms with the ability to degrade them;
- the population of the degrading micro-organisms;
- the activity of the degrading micro-organisms; and
- the nature and structure of the pollutants.

Catabolic activity can be enhanced in a number of ways, such as by adding specific enzymes, genetic modification of micro-organism, adding selected micro-organisms specific to the target pollutant and manipulating environmental conditions (e.g. denitrifying or aerobic conditions) (McNally et al. 1998; Semple et al. 2003).

2.2 Volatilization

The loss of organic pollutants from the surface of plants, soil and water in the vapour form is called volatilization. For most pesticides, volatilization is as important as degradation as a dissipation mechanism (Wolters et al. 2004). The physicochemical properties of the organic pollutant are key determinants of volatilization rates. In

particular, Henry's law constant (H) can be used to predict rates of volatilization from solution (Schwarzenbach et al. 1993);

$$H = (C_a / C_w) \, RT$$

where C_a is the concentration of the organic compound in air, C_w is the concentration of the organic compound in water, R is the universal gas constant (8.314 Pa / m^3.mol.K), and T is absolute temperature (K). Values of H>10 indicate very high air affinity and values of H<10^{-4}, very low air affinity.

Volatilization from the soil surface is a much more complex process, since molecules in soils are partitioned between three phases (solids, water-filled pores and gas-filled pores), which may not necessarily be in equilibrium due to slow rates of diffusion within, or transfer between the phases. Soil conditions, especially soil water content, and weather conditions (temperature, wind speed) can modify rates of volatilization by up to two orders of magnitude. More sophisticated models that take into account these factors have recently been developed (Wolters et al. 2004).

2.3 Leaching

Loss of chemicals through dissolution in a mobile water phase is called leaching. An understanding of an organic pollutant's mobility is important in evaluating its potential for ground water pollution. Pollutants most susceptible to leaching are those with low sorption and high water solubility (Regitano et al. 1997). Leaching of low solubility compounds is often mediated by association with other species. For example, Kim and Osako (2003) reported that the leachability of phenanthrene and

pyrene in sandy soils increased 10-fold when dissolved humic matter was present at a concentration of 126.2 mg/l. Other studies have also shown that the presence of dissolved humic material can increase the solubility of organic pollutants, which in turn enhances their leachability (Lassen et al. 1997).

2.4 Bioaccumulation

The tendency of chemicals to concentrate in biota generally is expressed as a bio-concentration factor (BCF), defined as the ratio of the chemical concentration in biota to that in its environment at steady state (Hamelink, 1977). The uptake of hydrophobic or lipophilic organic pollutants by organisms is a critical issue because they can accumulate in the food chain. BCF data for a given combination of chemical and organism are often not available and are time-consuming and expensive to determine. Therefore other parameters are used for BCF estimation such as octanol/ water partitioning coefficient (K_{ow}), water solubility of compounds and soil adsorption coefficient (K_{oc}) (Lu et al. 2000). Fish are typically used as targets for BCF assessment from aquatic environments because of their importance as a human food source and the availability of standardized testing protocols (Barron 1990). Plants are often used to measure BCF for soils. For example, Zhang et al (2004) suggested that vegetables, and in particular leaf vegetables, can act as an indicator of human exposure to PAHs. They reported that total PAH concentration in Chinese vegetables were between 8.6-111µg/g dry weight, corresponding to BCFs in the range 18 to 871 (Zhang et al. 2004).

2.5 Sorption

Sorption is a phase distribution process that includes adsorption or accumulation of sorbate at the interface of an aqueous phase and sorbent as well as absorption or partitioning from the aqueous phase into the sorbent matrix. In other words, sorption describes the transition of molecules from the solution phase to any phased fixed (perhaps temporarily) to any of the solid components of soil. Because the other processes that influence the fate of pollutants (degradation, volatilization, leaching and bioaccumulation) act entirely or primarily on the solution phase of the pollutant, sorption plays an over-arching role in the fate of organic pollutants in soils.

The term "sorption" has gained popularity as it does not imply a mechanism, whereas the terms "adsorption" and "absorption" do. Due to the complexity and heterogeneity of soils, both absorption and adsorption may occur at the same time, and it is often impossible to differentiate between the two. Adsorption specifically refers to sorption of molecules to the surface of solid components, whereas absorption refers to the movement of molecules, or partitioning, into a separate phase (Hassett and Banwart 2002).

Sorption is a key process in aquatic environments that controls the transformation, transport and distribution of organic pollutants between water, sediment and biota (Oliver and Charlton 1984). Sorbed organic molecules are generally less reactive, with lower chemical and biological activity. Therefore they are less toxic to the ecosystem and human health. Sorption can affect the biodegradation of organic pollutants in the environment and make them less available to the degrading organisms. In other words, the bioavailability and bioactivity of organic pollutants can

be directly influenced by the sorption phenomenon (Bailey and White 1964). The effectiveness and efficiency of many remediation technologies such as bioremediation are also dependent on sorption and more specifically the rate of desorption of organic pollutants. Sorption of organic pollutants by the natural environment and the impact of natural environmental heterogeneity on sorption phenomena are key factors controlling the fate of contaminants, evaluating the environmental risk presented by contaminants, and selecting and assessing the success of contaminated site remediation strategies.

3. Factors affecting sorption

Several factors have an effect on organic pollutant sorption to soils. They can be divided in three categories: the properties of the sorbate (pollutant), the properties of the sorbent and the properties of the aqueous phase.

3.1 Pollutant properties

3.1.1 Solubility. Water solubility of the organic pollutant is the most important determinant of the strength of sorption, solutes that have lower water solubilities having higher equilibrium sorption coefficients (Chiou et al. 1982, 1983). The solubility of an organic pollutant, in turn, depends on its molecular structure, as discussed below.

3.1.2 Ionization. A permanent electric charge on a compound increases its water solubility and hence decreases its tendency to sorb. Some neutral organic compounds,

i.e. those with either a basic or an acidic functional group, can be ionized in soil, depending on the pH, as they gain or lose H^+. The ionization of acidic or basic compounds strongly affects their sorption properties (Kah and Brown 2006).

3.1.3 Molecular size. The size of organic molecules can affect the sorption process through the molecular surface area and molecular volume of a compound (Calvet 1989). It has been shown that a basic determinant of the London-van der Waals force is the surface area of the molecule involved in the sorption process (Sabljic 1984). The molecular volume is related to water solubility which in turn can affect the sorption process of the organic molecules (Lambert 1967). Generally, the larger a molecule or the higher its molecular weight, the less soluble the compound tends to be.

3.2 Sorbent properties

3.2.1 Organic matter content. Numerous studies have found that soil organic matter is the most important soil component for sorption of non-ionic pollutants (Chiou, 1989; Wauchope et al. 2002). This is consistent with organic matter being most non-polar solid phase in soil. Most soil minerals are either charged (usually negatively) or have polar surface groups. The strong dipole interaction of such surfaces with water (which is strongly polar) results in water "out-competing" non-polar species for mineral surfaces. As a consequence, soil sorption affinities are often normalized to the organic carbon content of the soil, to decrease the variance in solute affinities between soils (Hamaker and Thompson 1972).

3.2.2 Surface area. Where sorption is dominated by adsorption (surface sorption) rather than absorption (partitioning), one would expect sorption to increase as surface

area increases (Chiou 2002). This is indeed the case for sorption of organic pollutants by clay minerals. It has been shown that affinity for organic compounds such as benzene, toluene and xylenes are lower for kaolinite, which has a lower specific surface area, than for montmorillonite and illite, which have higher specific surface areas (Li and Gupta 1994). It has also been demonstrated that the sorption affinity for DDT is four times higher for montmorillonite compared with kaolinite (Pierce et al. 1974). On the other hand, soil surface area is generally a poor predictor of the sorption affinity of organic compounds by soil for a number of reasons. First, much of the surface area of a soil is due to minerals that have low affinities relative to that of organic matter. Second, sorption to organic matter is likely to be at least in part an absorption rather than an adsorption process, and hence not dependent on surface area. An exception is sorption to charcoal, which does appear to scale with surface area (Bornemann et al. 2007).

3.2.3 Mineral surface properties. Two types of charge can be identified in soil minerals, permanent or constant charge and variable or pH dependent charge. Constant charge is a result of isomorphous substitution and is not influenced by pH, but variable charge results from protonation and deprotonation of the SiOH groups on clay surfaces, and thus it varies with pH. Therefore, the surface charge is variable on soil minerals such as kaolinite, metal oxides, oxyhydroxides, and hydroxides, and layer silicates coated with metal oxides. Some minerals (especially metal oxides) have a point of zero charge (PZC) at environmentally relevant pH. Such uncharged surfaces would be expected to have a higher affinity for non-polar organic molecules than permanently or variably charged mineral surfaces.

3.2.4 SOM heterogeneity. SOM is not a single and homogeneous material but a mixture of materials including polysaccharides, lipids, lignin, protein, humic substances, kerogen and black carbon from combustion (Stevenson 1994), each of which is likely to have differing sorption properties for organic compounds. Different soils will contain different proportions of these components, and this has been identified as a likely cause of variability in K_{oc} between soils (Wauchope et al 2002).

Grathwohl (1990) carried out the first comprehensive study of the influence of organic matter chemistry on the sorption of non-ionic compounds, although some previous studies had already identified that K_{oc} varied for different organic matter sources (Garbarini and Lion 1986; Gauthier et al. 1987). Grathwohl (1990) showed that K_{oc} for organic matter in unweathered high-grade coals and shales was more than an order of magnitude higher than for soils or low-grade coals. He also found that weathering of geological organic matter (coal and kerogen) decreased its sorptivity. Both effects resulted in a positive correlation between K_{oc} and the atomic H/O ratio of organic carbon.

Many studies have tried to find a correlation between SOM structural properties and the sorption of soil organic matter. Gauthier et al (1987) examined the structure and composition of four humic substances using ^{13}C CPMAS NMR, and found the degree of aromacity played a key role in the sorption affinity of humic and fulvic acids. A number of other studies have also found strong correlations between aromacity and binding coefficients for a variety of sorbents and sorbates (Abelmann et al. 2005; Chin et al. 1997; Perminova et al. 1999). Probably the clearest example of this relationship for soils is the study of Ahmad et al (2001), in which the structure of soil

organic matter for twenty-seven soils from different ecological zones was investigated by ^{13}C NMR. It was shown that there was a positive and strong correlation between aromacity of organic matter and K_{oc} values of carbaryl and phosalone. They concluded that the aromatic content of soil organic carbon is a suitable predictor of the capacity of soil to absorb nonionic pesticides (Ahmad et al. 2001). A study of the composition and structure of sedimentary organic matter showed that aromatic carbon content of sediment and the amount of desorption-resistant phenanthrene were related to each other, but that not all the aromatic domains had the same affinity for phenanthrene (Golding et al. 2005).

On the other hand, several studies have found a relationship between aliphatic domains of organic matter and sorption affinity (Chefetz et al. 2000; Salloum et al. 2002; Mao et al. 2002). With the use ^{13}C NMR spectra, strong positive relationships have been reported between K_{oc} for pyrene and aliphatic C (Chefetz et al. 2000). In contrast, the relationship between aromacity and the sorption process for pyrene was very poor. It was suggested that the importance of aliphatic C is at least similar to the importance of aromatic groups with regard to adsorption of pyrene.

Salloum et al. (2002) suggested that organic matter rich in aliphatic carbon exhibited a higher sorption affinity for phenanthrene than highly aromatic materials such as humic acid. Moreover they tried to find a connection between SOM chemistry and the physical properties of SOM domains. They suggested that the aliphatic domains resemble rubbery-type carbon based on the different shape of sorption isotherms in aliphatic and aromatic domains. Mao et al. (2002) reported a positive and significant correlation between the amount of a specific type of aliphatic carbon – amorphous

nonpolar aliphatic poly methylene domains – and phenanthrene sorption capacity. Several recent studies also tried to classify two different types of organic matter domains according to their physical properties: a soft, rubbery, or amorphous domain and a hard, glassy or condensed domain (Huang et al. 2003; Xiao et al. 2004).

A number of studies have also reported that K_{oc} values increased with decreasing proportions of polar groups (Rutherford et al. 1992; Xing et al. 1994; Huang and Weber 1997; Kleineidam et al. 1999). For instance, a negative correlation was observed between sorption capacity of benzene and carbon tetrachloride and the organic matter polarity index of three high organic content soils (Rutherford et al. 1992). However, other researchers have not found such a relationship between polarity index and sorption capacity for nonionic organic compounds (Mao et al. 2002).

The influence of organic matter chemistry on K_{oc} is discussed in greater detail in chapter 2.

3.2.5 SOM-mineral interactions. A number of studies have reported that soil minerals have an indirect effect on the sorption affinity of SOM. Njoroge et al (1998) found that K_d for 1, 2, 4-trichorobenze and tetrachloroethene decreased by about 100-fold down a soil profile. This decrease was much greater than could be explained on the basis of SOM content of the lower horizons. They attributed the decrease in K_{oc} with soil depth to the association of the SOM with the clay mineral of the soils and the possible effect of this intimate association on SOM accessibility, sorptivity or both.

Salloum et al. (2001) found that K_{oc} values for isolated humic acid and humin from soils are in most instances higher than those for the source soil samples, and suggested SOM-mineral interactions may decrease the sorption affinity of whole soils for 1-naphthol. Bonin and Simpson (2007) reported that de-ashing a soil humin fraction increased its K_{oc}, indicating that soil clay minerals can influence the availability of sorption domains on SOM. The influence of organic matter-mineral interactions on K_{oc} is discussed in greater detail in chapter 3.

3.2.6 The effect of soil lipids. Lipids can decrease the sorption capacity of natural SOM by reducing the accessibility of sorption sites via competition, steric effects or sorption site deformation (Tremblay et al. 2005b). It has been reported that lipid removal can increase the sorption affinity of soils for organic compounds by as much as one order of magnitude and at the same time decrease sorption linearity (Kohl and Rice 1999; Tremblay et al. 2005b; Chilom et al. 2005; Drori et al. 2006). Wang and Xing (2007) also reported that K_{oc} for phenanthrene and 1-naphthol increased after lipid extraction for a peat soil and its humic and humin fractions. The influence of soil lipids on K_{oc} is discussed in greater detail in chapter 4.

3.2.7 SOM physical conformation. Some studies have shown that conditioning with solvent can change the sorption properties of soil, possibly by altering the physical conformation of SOM (Xia and Pignatello 2001; Lu and Pignatello 2002; Wang and Xing 2007). For example, Xia and Pignatello (2001) suggested that a "conditioning effect" led to enhanced sorption of $CHCl_3$ in a peat soil in which a high loading of sorbate caused molecules to penetrate the organic polymer matrix and swell its structure. Wang and Xing (2007) found that sorption affinity of humic acids as well as

humin for phenanthrene increased when they were conditioned with acetone for three days. The influence of the physical structure of organic matter on K_{oc} is discussed in greater detail in chapter 5.

3.3 Aqueous phase properties

3.3.1 pH. As discussed above, some organic pollutants have pH-dependent charge, and the charge of both organic matter and mineral sorbent phases vary with pH. Because the charge of both sorbent and sorbate affect sorption affinity, the pH of the solution phase (which is in equilibrium with the pH of the solid phase) is an important factor controlling sorption. When the pH of the solution is higher than the pK_a of an organic compound, the conjugate base (which has a negative charge) is the dominant species. As a consequence, sorption affinity for such molecules rapidly decreases with pH above the pK_a value. In contrast, for basic compounds, an increase in pH decreases the proportion of charged molecules, therefore increasing sorption affinity.

Since most organic pollutants are neither acidic nor basic, the main effect of solution pH on sorption affinity is through effects on the surface charge and conformation of the sorbent phases. Sorption of low polarity organic compounds, including those used in this study, depends very little on the soil pH (Karickhoff 1984; Delle Site 2001).

3.3.2 Salinity. The water solubility of hydrophobic compounds decreases with increasing ionic strength. This effect is called ''salting-out'' (Tremblay et al. 2005a). As a result, sorption affinity increases with increasing salinity (Karickhoff et al. 1979). For example, an increase in salinity from 0 to 0.34 M sodium chloride causes a 15% increase in pyrene sorption (Karickhoff et al. 1979). Sorption experiments on

four chlorinated benzenes and two chlorinated phenols at different ionic strengths (0.01, 0.05, and 0.5 M) have shown that the sorption capacity increased with increasing ionic strength of the background solution (Bakul and Asolekar 2001).

3.3.3 Co-solvents. Co-solvents, such as methanol and acetone, can decrease the sorption of organic pollutants by virtue of increasing their solution solubility. For hydrophobic organic chemicals, solubility has a log-linear dependence on the volume fraction of organic co-solvent (Rao et al. 1985; Lee and Rao 1996);

$$\log K_m = \log K_w - \alpha \sigma f_c$$

where K_m is the linear sorption coefficient in mixed solvents, K_w is the linear sorption coefficient in water, α is an empirical constant that reflects solvent–sorbent interactions, σ is the cosolvency power and f_c is the co-solvent volume fraction.

3.3.4 Solid-solution ratio. Although sorption of non-ionic compounds on soil is generally considered as partitioning between two phases and independent of sorbent concentration, in several instances an inverse relationship between sorbent concentration and partitioning coefficient has been reported (Grover and Hance 1970; O'Connor and Connolly 1980; O'Connor 1982). It has been demonstrated that sorption can be affected by the soil to water ratio. For example, a five-fold increase in the sorption of linuron was found on decreasing the soil to water ratio from 4:1 to 1:10 (Grover and Hance 1970).

3.3.5 Temperature. Where sorption is an exothermic process, the equilibrium constant should decrease with increasing temperature (Schwarzenbach et al. 1993). However, some studies have demonstrated sorption increased with increasing temperature, while others have observed no effect of temperature (Hance 1980; Hulscher and Cornelissen 1996). Sorption of organic pollutants occurs when the free energy of the sorption exchange (ΔG) is negative (Hulscher and Cornelissen 1996; Delle Site 2001);

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the change in Gibbs free energy (kJ mol^{-1}), ΔH is the change in enthalpy (kJ mol^{-1}), T is the absolute temperature (K) and ΔS is the change in entropy (kJ mol^{-1} K^{-1}).

The free energy of sorption can be negative because of the entropy or enthalpy terms or both of them. The enthalpy term describes the affinity of a chemical for the absorbing surface relative to its affinity for the solvent. The entropy term is related to the change in randomness or disorder of the system upon sorption (Hassett and Banwart 1989; Hulscher and Cornelissen 1996).

3.3.6 Solute concentration. One of the most important and widely-studied aspects of sorption of organic pollutants to soil is the effect of solute concentration on sorption affinity, given that, in theory, this should convey important information about sorption mechanisms. This aspect is discussed in detail in the following section.

4 Equilibrium Sorption Models

Sorption isotherm models attempt to describe how the concentration of a molecule in the sorbed phase varies as a function of its solution concentration at constant temperature. Sorption isotherm models can provide important information about the physicochemical processes of sorption. Several different equations have been developed to describe sorption isotherms. Some are derived from consideration of the sorption processes involved, whilst others are empirical. There are several considerations when choosing which equation to use when fitting a sorption isotherm. Clearly it should provide a good fit of the data, but one should also consider the number of fitted parameters and their physical meaning.

4.1 The Linear Partitioning Model

In the simplest model of the sorption process, sorption affinity is independent of solution concentration. A number of early studies (Chiou et al. 1979, 1983; Karickhoff et al. 1979; Means et al. 1980, 1982) showed no indication of curvature in sorption isotherms. This behaviour is described by the linear partitioning model, which can be expressed mathematically as;

$$K_d = (x/m)/C_e$$

where K_d is called the distribution coefficient, x/m is the concentration in the sorbed phase at equilibrium [µg/g] and C_e is concentration in solution at equilibrium [µg/ml].

As discussed above, for non-polar organic compounds, many studies have found a highly significant relationship between K_d of the compounds and the organic carbon content of the soil (Chiou 1979; 1983). Therefore, Hamaker and Thompson (1972) suggested that to decrease the variance in sorption coefficients, K_d should be divided by the organic carbon concentration (f_{oc}) of the soil to give the organic C normalized soil sorption coefficient (K_{oc});

$$K_{oc} = K_d / f_{oc}$$

Chiou et al (1983) suggested that the linearity of sorption isotherms is evidence that sorption of non-ionic compounds in soils mainly consists of partitioning of organic compounds into the soil organic matter. Thus, the K_{oc} model for organic compounds sorption is also called the "partitioning model".

The K_{oc} partitioning model is perhaps the most widely-used model to describe sorption of organic pollutants to soils. A large part of its appeal is its mathematical simplicity – just a single parameter can be used to predict sorption of a given compound to any soil. Furthermore, K_{oc} values for different compounds have been found to closely correlate with the physicochemical properties of organic solutes. Chiou et al (1979) found a close relationship ($r^2 = 0.988$) between K_{oc} and the solubility (S) of fifteen organic compounds;

$$\log K_{oc} = 4.040 - 0.557 \log S$$

Means et al (1980) reported a highly significant negative correlation between K_{oc} and the log of water solubility (S) for four hydrophobic organic compounds on fourteen different soils.

$$\log K_{oc} = -0.82 \log S + 4.070$$

The same authors also demonstrated a strong linear relationship ($r^2 = 0.980$) between K_{oc} and K_{ow} (the octanol-water partition co-efficient) for the sorption of 22 non-polar organic compounds by different soils and sediments (Means et al. 1982);

$$\log K_{oc} = \log K_{ow} - 0.317$$

Schellenberg et al (1984) found a similarly close correlation ($r^2 = 0.98$) for the sorption of chlorinated phenols by sediments;

$$\log K_{oc} = 0.82 \log K_{ow} + 1.05$$

A number of other studies have proposed different equations to predict K_{oc} (Schwarzenbach et al. 1981; Chin and Weber Jr 1989).

The simplicity of the K_{oc} model is also its short-coming, as it is unable to account for more complex sorption behaviour. This includes the contribution of minerals to sorption, variability of K_{oc} between soils, non-linear sorption isotherms, sorption-desorption hysteresis and slow sorption kinetics. Furthermore, it has been suggested

that even when sorption isotherms are linear, this does not necessarily infer a partitioning mechanism (Spurlock and Bigger 1994).

The strong link between K_d and f_{oc} is only valid for sorbents with organic carbon contents >0.1%. K_d values for organic-poor sorbents (<0.1%), even those with high specific surface area are usually very small (Schwarzenbach and Westall 1981). Schrap and Opperhuizen (1989) have also suggested that organic matter dominates sorption in sediments for f_{oc} > 0.1%. On the other hand, Hundel et al (2001) reported that smectites were able to retain as much phenanthrene as soils with high organic matter content, and so their role in sorption must be considered in soils containing this mineral. Based on results from sorption of benzene, chlorinated benzene isomers, naphthalene and tetrachloroethylene, McCarthy et al (1981) identified a critical level ($f_{oc}*$) of organic matter content below which mineral adsorption is the dominant process;

$$f_{oc}* = (S/200) [(1/ (K_{ow})^{0.84}]$$

where S is the silica-specific surface area (m ^{2}/g).

In another study, Kishi et al (1990) used five soils and five organic compounds to show the contribution of soil minerals to sorption. They plotted K_d against f_{oc}, and identified K_{oc} as the slope of the regression line and the intercept (α) as the fraction of adsorption by the mineral part of soils;

$$K_d = K_{oc} \times f_{oc} + \alpha$$

However, it should be noted that many researchers have reported that the sorption of nonionic compounds by soil and sediments is independent of the amount and type of soil clay minerals (Means et al. 1980).

Aside from the issue of sorption to mineral components, a number of other limitations of the K_{oc} model have been identified. According to the partitioning model, sorption affinity is independent of differences in soil organic matter structure and K_{oc} should be constant for any given compound across a range of different soils when $f_{OC} > 0.001$. However, it has been found that K_{oc} values vary between soils by up to two orders of magnitude (Oepen et al. 1991; Ahmad et al. 2001; Salloum et al. 2001). Also the partition model assumes that sorption is completely reversible or non-hysteretic, but numerous studies have showed hysteresis (Huang and Weber 1997; Yuan and Xing 2001). The partitioning model infers the rate of sorption is fast, but many studies have reported slow rates of sorption (Schwarzenbach et al. 1993; Kohl et al. 2000). Another sorption phenomenon that the partitioning model is not consistent with is competitive sorption, where the sorption of one compound is affected by the presence of one or more other compounds (Schwarzenbach et al. 1993).

4.2 The Langmuir Adsorption Model

The Langmuir model was developed in 1916 to describe the dependence of the surface coverage of an adsorbed gas on the pressure of the gas above the surface at a fixed temperature (Langmuir 1916). Even though the model was developed to predict the sorption of gas molecules on a solid phase, it can be used to predict the sorption of

aqueous compounds to solid surfaces. Regarding the assumptions of the model, it seems inappropriate to describe the sorption of organic compounds in soil and sediments. Briefly, model assumptions are:

- adsorption takes place only at specific sites;

- the adsorbent surface can only be covered by a single layer of molecules;

- the surface of the sorbent is energetically homogeneous;

- there is no interaction between adsorbed molecules; and

- there are no phase transitions.

In mathematical terms, the Langmuir model can be expressed as;

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}$$

where Q^0 is the monolayer adsorption capacity, b is a parameter related to the net enthalpy of adsorption, and q_e and C_e are the equilibrium solid-phase and aqueous-phase solute concentrations, respectively.

4.3 The Freundlich Model

The Freundlich model is one of the empirical sorption models used to describe nonlinear sorption. The model has the following form:

$$q_{sorb} = K_f\,C^{1/n}$$

where q_{sorb} is the sorbed concentration (mg kg^{-1}), C is the solution concentration, K_f is the Freundlich coefficient (mg kg^{-1}) (L mg^{-1})$^{1/n}$ and n is the isotherm nonlinearity. Normally the value of n is less than 1, indicating that sorption affinity decreases with increasing solution concentration. Often experimental data do not fit the linear model but they can be fitted by the empirical Freundlich model. The Freundlich model is generally applicable to most experimentally determined data (Schwarzenbach et al. 1993). Even though this is an empirical model some attempts have been made to interpret the Freundlich model theoretically with the aid of a fugacity approach, with limited success (Wauchope and Koskinen 1983). The Freundlich model is commonly used for sorption isotherms of organic compounds because it produces a better fit of the data (Banerjee et al. 2008; Jeongran et al. 2008).

The Freundlich model can also be rearranged and expressed in a linear form:

$$\log q = 1/n \log C + \log K_f$$

The plot of log q versus log C has a slope equal to 1/n, and an intercept equal to log K_f.

4.4 The Polanyi-Manes Adsorption Model

This model was first used to describe the adsorption of gas molecules on energetically heterogeneous solids (Polanyi 1916), but in 1969 it was extended by Manes and Hofer for using in liquid phase systems and called the Polanyi-Manes theory (Manes and Hofer 1969).

In this theory, for any adsorbate molecule in the presence of an adsorbent surface, there is an adsorption potential (ε) between the molecule and the solid surface. The potential (ε) at any location in the adsorption space is defined as the energy level required to remove the molecule from the location outside the attractive force field of the solid surface. The potential (ε) is dependent on the adsorbent surface and the nature of the sorbate.

$$\varepsilon_{sw} = RT \ln (C_s/ C_e)$$

where ε_{sw} is the adsorption potential (energy required for a volume of solute (s) to displace a volume (l) in the adsorption process), R is the gas constant, T is the absolute temperature, C_s is the solute concentration and C_e is equilibrium concentration.

This model has been used to describe sorption of organic compounds by soils and sediments in some studies (Xia and Ball 2000; Fuller et al. 2007). It has been reported that sorption of atrazine on carbon nanotubes is nonlinear and based on the correlation coefficient values, the Polanyi-Manes model described the adsorption process better than the Freundlich or Langmuir isotherm models (Yan et al. 2008).

4.5 The Distributed Reactivity Model and Dual SOM Model

One of the main difficulties in modelling sorption in natural systems such as soils and sediments, is that they typically contain multiple sorptive phases. These will not only have different sorption affinities for organic compounds, but may also represent different sorption mechanisms. The explanation of sorption based on a single sorption reaction may therefore be misleading. In light of this, Weber Jr et al (1992) introduced a new concept of sorption, considering different distributions of sorption reactions and mechanisms for different solute-solid combinations. In this model, the overall sorption isotherm is the sum of the sorption isotherms of all active parts;

$$q_{er} = \sum_{i=1}^{m} x_i q_{ei}$$

where q_{er} is total solute sorbed per unit mass, x_i is the mass fraction of soil component i, and q_{ei} is the sorbed phase concentration.

Furthermore, the model assumes there are two types of organic matter: "hard carbon", which has a high sorption capacity and exhibits non-linear isotherms typical of adsorption, and "soft carbon", which is less sorptive and exhibits almost linear

isotherms typical of partitioning sorption behaviour. Therefore, in the distributed reactivity model (DRM), one can consider that the mechanism of sorption in the soft part of SOM is partitioning, and, conversely, the mechanism of sorption on hard carbon SOM is considered as an adsorption process with nonlinear sorption isotherms which can be described by the Freundlich equation. Thus, the model can be shown simply as:

$$q_e = K_D C_e + K_F C^n$$

A related model is the dual sorption model, in which sorption of nonionic organic compounds to SOM is considered as sorption to partitioning domains as well as hole-filling sorption or surface adsorption (Huang and Weber 1997; LeBoeuf et al. 1997; Xing and Pignatello 1997);

$$S = S(D) + S(H) = K_p C + \sum_{i=1}^{n} \frac{S_1^0 b_1 C}{1 + b_1 C}$$

where C is the solute concentration, K_p is a lumped sorption coefficient representing all available dissolution regions, b_i is the affinity constant for each unique site and S_i is the capacity constant for each unique site.

5. Purpose of this study

The purpose of this study is to investigate some of the factors that influence sorption of organic pollutants to soils. The specific aims are:

- to investigate the role of the soil organic matter (SOM) chemistry on the sorption of non-ionic pollutants;

- to investigate the role of interactions between soil minerals and SOM on the sorption affinity of SOM for non-ionic pollutants;

- to investigate the role of soil lipids on the sorption of non-ionic pollutants; and

- to investigate the influence of SOM physical conformation on the sorption affinity of organic matter for non-ionic pollutants.

5.1 Scope of the study

As discussed in the previous sections, there are numerous factors other than those listed above that also influence the sorption of organic pollutants to soils. Furthermore, there are many thousands of organic pollutants and literally an infinite number of different soils. Therefore any investigation in this subject area is limited by practical constraints. In the following sections, the scope of this study is defined and justified, in terms of the choice of factors affecting sorption investigated, target compounds and soils.

5.1.1 Factors affecting sorption investigated – K_{oc} variability. As discussed above, the most widely-used sorption model is the K_{oc} partitioning model. Although this model provides a good approximation of sorption properties in many cases, it is unreasonable to expect such a simple model to accurately describe a process as complex as sorption of organic pollutants to soil. The two main shortcomings of the K_{oc} model are: (i) that it assumes all organic matter is equally sorptive; and (ii) that it implies a partitioning mechanism (linear sorption isotherms, rapid sorption kinetics

and no sorption-desorption hysteresis, competitive sorption etc.). In this study, only the first of these issues – K_{oc} variability – is addressed in detailed. Issues of sorption non-linearity are only touched upon where they potentially impact on the measurement and interpretation of K_{oc} variability.

In particular, this study focuses on four potential causes of K_{oc} variability:

- SOM heterogeneity;

- SOM-mineral interactions;

- the effect of soil lipids; and
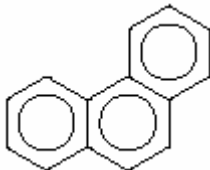
- SOM physical conformation.
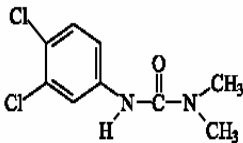
5.1.2 Selected Compounds. Two compounds, phenanthrene and diuron were selected as representative non-ionic organic pollutants. Phenanthrene is a polycyclic aromatic hydrocarbon (PAH), an important class of organic pollutants because of their wide distribution in the environment and their carcinogenic and mutagenic properties (Manoli et al. 2000; Walker 2001). The United States Environmental Protection Agency (USEPA) and the European Union have identified sixteen PAHs as priority pollutants because of their wide distribution in the environment and potential human health risks (Buco et al. 2004). Phenanthrene is the most abundant PAH in the environment and one of the most popular model compounds for studying environmental issues (Cerniglia 1992; Laor et al. 1998).

Diuron, N-(3, 4-dichlorophenyl)-N, N-dimethyl-urea, is one of the phenyl amide family of pesticides and belongs to the subclass of phenyl ureas. Diuron is toxic and slightly hazardous. It is classed as a type III pesticide by the USEPA and is considered

as a priority hazardous substance (PHS) by the European Commission (Malato et al. 2002).

The chemical structure and characteristics of the compounds used are given in Table 1.

Table 1 Structure and characteristics of the compounds studied.

Chemicals	Phenanthrene [a]	Diuron [b]
Structure		
Molecular weight (g/mol)	178.2	233.10
Melting point (^{o}C)	99.5 ^{o}C	158-159 ^{o}C
Vapor pressure (Pa)	0.022 at 20°C	0.0011 at 25°C
Water solubility (S) at 25°C (mg/l)	1.28 mg/l	40 mg/l
Log K_{ow} (unitless)	4.46	2.85
Density (g/cm^3)	1.02	1.48
Henry's law constant (25 ^{o}C) (no units)	0.001	7.04×10^{-6} Pa m^3 mol^{-1}

[a] Data from (Verschueren 1983).

[b] Data from (Tomlin 2000)

The chemical structure and characteristics of the compounds used are given in Table 1.

5.1.3 Selected Soils. About fifty soil samples were collected from a single 2 ha paddock at Flaxley Agriculture Center, Mount Lofty Ranges, SA. The soils are a

series of Ferric, Eutrophic Red Chromosols on the upper to mid-slopes and Mottled Eutrophic Yellow Chromosols on the lower slope. The soils have a neutral to slightly acid pH, are non-saline, and are sodic below 50 cm (Fleming and Cox 1998).

The restriction to soils from a small study site minimizes the possible factors which can cause K_{oc} variability. Uniform parent materials and similar mineralogy (quartz, illite, kaolinite, biotite) across the study site make the influence of these factors diminish, allowing the effect of soil organic matter chemistry and its interaction with soil minerals to be investigated clearly. It has been shown that there is less variability in K_{oc} values at smaller spatial scales (Coquet and Barriuso 2002). Even though K_{oc} variability can reach up 6 orders of magnitude between different study sites, it is limited to around one order of magnitude within a single site (Collins and Worrall 2003).

5.1.4 Selected method for sorption measurement. In this study, sorption experiments were carried out using a batch equilibration technique (OECD 1997). This is a very simple method and can be used for a range of pollutants.

The use of this technique enabled the aqueous phase properties that influence sorption (identified in section 3.3) to be controlled. Salinity was controlled by using a dilute electrolyte (0.01 M $CaCl_2$) solution. This ensured that differences in the concentration and composition of salts coming from the soil had little effect on the composition of the solution phase used in sorption measurements. This electrolyte would also have buffered the solution pH to some extent, although given the two target compounds are neither acidic nor basic, solution pH would not be expected to greatly influence

sorption (see Section 3.3.1). The solid-solution ratio was also held constant, as was the temperature, and no co-solvents were used.

Most of the sorption measurements in this study are single-point measurements; sorption isotherms were only determined in only a few cases. As discussed above, the purpose of this study was not to investigate the linearity of sorption, but rather to investigate the factors that influence sorption affinity of soil organic matter under a given set of fairly tightly-controlled conditions. Therefore, sorption isotherms were only determined across the fairly small range of solution concentrations (generally less than one order of magnitude variation) likely to result from single-point sorption measurements of soils with different K_d values.

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Influences on the sorption affinity
of soil organic matter for non-ionic
organic pollutants

A. G. Ahangar

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CHAPTER 2

CLEAR EFFECTS OF SOIL ORGANIC MATTER CHEMISTRY, AS DETERMINED BY NMR SPECTROSCOPY, ON THE SORPTION OF DIURON

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of soil organic matter for non-ionic
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CLEAR EFFECTS OF SOIL ORGANIC MATTER CHEMISTRY, AS DETERMINED BY NMR SPECTROSCOPY, ON THE SORPTION OF DIURON

Chemosphere 2008; 70 (7): 1153-1160

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Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron

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Abstract

Organic matter has long been recognized as the main sorbent phase in soils for hydrophobic organic compounds (HOCs). In recent times, there has been an increasing realization that not only the amount, but also the chemical composition, of organic matter can influence the sorption properties of a soil. Here, we show that the organic carbon-normalized sorption coefficient (K_{OC}) for diuron is 27–81% higher in 10 A11 horizons than in 10 matching A12 horizons for soils collected from a small (2 ha) field. K_{OC} was generally greater for the deeper (B) horizons, although these values may be inflated by sorption of diuron to clays. Organic matter chemistry of the A11 and A12 horizons was determined using solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. K_{OC} was positively correlated with aryl C ($r^2 = 0.59$, significance level 0.001) and negatively correlated with O-alkyl C ($r^2 = 0.84$, significance level <0.001). This is only the second report of correlations between whole soil K_{OC} and NMR-derived measures of organic matter chemistry. We suggest that this success may be a consequence of limiting this study to a very small area (a single field). There is growing evidence that interactions between organic matter and clay minerals strongly affect K_{OC}. However, because the soil mineralogy varies little across the field, the influence of these interactions is greatly diminished, allowing the effect of organic matter chemistry on K_{OC} to be seen clearly. This study in some way reconciles studies that show strong correlations between K_{OC} and the chemistry of purified organic materials and the general lack of such correlations for whole soils.

Ahangar, A.G., Smernik, R.J. Kookana, R.S. & Chittleborough, D.J. (2008) Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron.
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Influences on the sorption affinity
of soil organic matter for non-ionic
organic pollutants

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CHAPTER 3

SEPARATING THE EFFECTS OF ORGANIC MATTER-MINERAL INTERACTIONS AND ORGANIC MATTER CHEMISTRY ON THE SORPTION OF DIURON AND PHENANTHRENE

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Influences on the sorption affinity   A. G. Ahangar   57
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**SEPARATING THE EFFECTS OF ORGANIC MATTER-
MINERAL INTERACTIONS AND ORGANIC MATTER
CHEMISTRY ON THE SORPTION OF DIURON AND
PHENANTHRENE**

Chemosphere 2008; 72 (6): 886-890

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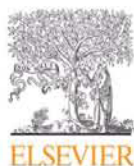Signed   Date

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Separating the effects of organic matter–mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene

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ABSTRACT

Even though it is well established that soil C content is the primary determinant of the sorption affinity of soils for non-ionic compounds, it is also clear that organic carbon-normalized sorption coefficients (K_{OC}) vary considerably between soils. Two factors that may contribute to K_{OC} variability are variations in organic matter chemistry between soils and interactions between organic matter and soil minerals. Here, we quantify these effects for two non-ionic sorbates—diuron and phenanthrene. The effect of organic matter–mineral interactions were evaluated by comparing K_{OC} for demineralized (HF-treated) soils, with K_{OC} for the corresponding whole soils. For diuron and phenanthrene, average ratios of K_{OC} of the HF-treated soils to K_{OC} of the whole soils were 2.5 and 2.3, respectively, indicating a substantial depression of K_{OC} due to the presence of minerals in the whole soils. The effect of organic matter chemistry was determined by correlating K_{OC} against distributions of C types determined using solid-state ^{13}C NMR spectroscopy. For diuron, K_{OC} was positively correlated with aryl C and negatively correlated with O-alkyl C, for both whole and HF-treated soils, whereas for phenanthrene, these correlations were only present for the HF-treated soils. We suggest that the lack of a clear effect of organic matter chemistry on whole soil K_{OC} for phenanthrene is due to an over-riding influence of organic matter–mineral interactions in this case. This hypothesis is supported by a correlation between the increase in K_{OC} on HF-treatment and the soil clay content for phenanthrene, but not for diuron.

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CHAPTER 4

THE EFFECT OF LIPIDS ON THE SORPTION OF DIURON AND PHENANTHRENE IN SOILS

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The effect of lipids on the sorption of diuron and phenanthrene in soils

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ABSTRACT

The influence of lipids on the sorption of diuron and phenanthrene to soils was investigated. Accelerated solvent extraction (ASE) was used to extract lipids from twelve soil horizons. Extractable lipids accounted for 3–13% of organic C. The organic carbon-normalized sorption coefficients (K_{OC}) for diuron and phenanthrene were consistently higher for the lipid-extracted soils than for the whole soils (average of 31% for diuron and 29% for phenanthrene), indicating that lipids compete for or block sorption sites on the organic matter. Sorption experiments on one pair of HF-treated soils indicated that the blocking effects of minerals and lipids are independent, since lipid extraction and HF-treatment combined increased K_{OC} by more than either treatment alone. Lipids extracted from whole and HF-treated soils were very similar in composition, consisting predominantly of long-chain polymethylene structures. K_{OC} of the lipid itself was lower than for any of the whole soils and soil fractions (lipid extracted and HF-treated) for diuron, but higher for phenanthrene. Solid-state ^{13}C NMR spectra of the HF-treated soils before and after lipid extraction indicated that 15–20% of alkyl C was removed by ASE and that no other structures were affected.

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CHAPTER 5

THE EFFECT OF SOLVENT CONDITIONING ON SOIL ORGANIC MATTER SORPTION AFFINITY FOR DIURON AND PHENANTHRENE

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Influences on the sorption affinity   A. G. Ahangar   73
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Chemosphere 2009; Submitted paper

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The effect of solvent conditioning on soil organic matter sorption affinity for diuron and phenanthrene

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ABSTRACT:

The effect of solvent-conditioning on the sorption of diuron and phenanthrene was investigated. The organic carbon-normalized sorption coefficients (K_{OC}) for diuron and phenanthrene were consistently higher following solvent-conditioning of a whole soil with five organic solvents (acetonitrile, acetone, methanol, chloroform and dichloromethane). The relative increase in K_{OC} was inversely related to the polarity of the conditioning solvent (i.e. greater increases in K_{OC} were observed for the least polar solvents: chloroform and dichloromethane). The effect of solvent-conditioning

on the sorption properties of the same soil that had been lipid-extracted using accelerated solvent extraction (ASE) was also investigated. Since lipid extraction involves treatment with a non-polar solvent (95:5 dichloromethane:methanol) one may have expected no further increase in K_{OC} on solvent-conditioning. On the contrary, the lipid-extracted soil exhibited very similar increases in K_{OC} as the whole soil. This demonstrated that lipid removal and solvent-conditioning, which both increased K_{OC} for this soil, are quite separate phenomena.

Introduction

The fate and behaviour of non-ionic organic compounds in the environment are largely controlled by their sorption to soil organic matter (SOM) (Wauchope et al. 2002). The simplest and most widely-used model to describe and predict the sorption affinity of soils for such molecules is partitioning between soil solution and SOM. The C-normalized partition coefficient (K_{OC}) quantifies the sorption interaction in this model (Chiou 1989). Although the K_{OC} model is appealing in its simplicity, it cannot be said to provide a full description of soil sorption properties. In particular, the implicit assumption that SOM in all soils is equally sorptive is a serious over-simplification, as K_{OC} values commonly vary by a factor of 3-10 amongst soils (Wauchope et al. 2002). Furthermore, sorption of non-ionic organic compounds often exhibits non-partitioning behaviour such as non-linear sorption isotherms, desorption hysteresis and competitive sorption (Allen-King et al. 2002; Wauchope et al. 2002).

K_{OC} variability for different organic matter types (e.g. plant residues, SOM, peat, coal, kerogen) has been shown by many researchers (Chen et al. 1996; Chefetz et al. 2000; Salloum et al. 2002). It is also well-documented that different humic fractions from the same soil can have different K_{OC} values (Chen et al. 1996; Chefetz et al. 2000; Salloum et al. 2001; Mao et al. 2002; Gunasekara and Xing 2003; Kang and Xing 2005). Some studies have reported correlations between K_{OC} and particular C types, especially aromatic C (Xing 1997; Ahmad et al. 2001; Abelman et al. 2005; Golding et al. 2005) and alkyl C (Chefetz et al. 2000; Salloum et al. 2002; Chen et al. 2007). Alternative causes of K_{OC} variability are sorption by soil minerals (Teppen et al. 2006) and blocking of sorption sites by minerals (Celis et al. 2006) or by the lipid fraction of SOM (Kohl and Rice 1999; Chilom et al. 2005; Tremblay et al. 2005; Drori et al. 2006).

In a series of recent papers (Ahangar et al. 2008a; Ahangar et al. 2008b; Ahangar et al. in press), we have investigated the causes of K_{OC} variability for a set of soils collected from a single paddock at the Flaxley Agricultural Centre, Mount Lofty Ranges, South Australia. We have studied the influence of organic matter chemistry on sorption affinity (Ahangar et al. 2008a; Ahangar et al. 2008b), organic matter-mineral interactions that block organic matter sorption sites (Ahangar et al. 2008b) and the influence of lipid removal on sorption affinity (Ahangar et al. in press). In the last of these studies (Ahangar et al. in press), we found that removal of the soil lipid fraction using accelerated solvent extraction (ASE) increased K_{OC} of whole soils for diuron and phenanthrene by approximately 30%. We suggested that K_{OC} for the whole soils was lower because the lipids blocked sorption sites on the remainder of the SOM, however, we could not rule out the possibility that ASE altered the physical conformation of the SOM, making it more sorptive. This has been called the "conditioning effect".

The term "conditioning effect" was introduced to soil sorption studies by Xia and Pignatello (2001), and has its origins in the sorption of gases to synthetic polymers, where it is a well-established phenomenon. Exposure of "glassy" polymers to high pressures of gases such as CO_2 result in changes to their physical conformation, including swelling, that remain after the gas is removed (Kamiya et al. 1998; Wang et al. 1998). As a result of these changes, the polymer is more sortive of the gas in subsequent exposures. Xia and Pignatello (2001) reported a similar effect for sorption of trichloromethane to a peat soil: following exposure to high concentrations of trichloromethane, the soil was more sorptive in subsequent exposures. They interpreted this as evidence that some SOM components are "glassy".

Further investigations of the conditioning effect were carried out by Lu and Pignatello (2002), who reported increased sorption affinity of a peat soil toward trichloromethane following conditioning with dichloromethane, and increased sorption affinity of a mineral soil toward chlorobenzenes following conditioning with benzene. In all cases, K_{OC} increased by around 40% (Lu and Pignatello 2002). They found that the memory of the conditioning effect persisted for more than 96 days at 21 ^{o}C but vanished after heating to 100 ^{o}C (Lu and Pignatello 2002). Weber et al. (2002) also attributed the enhanced sorption of phenanthrene in the presence of much larger concentrations of trichloroethylene or dichlorobenzene to a conditioning effect.

More recently, Sander et al. (2006) carried out detailed studies on the conditioning effect of trichloroethylene on two polymers, a peat and a humic acid. They confirmed that the conditioning effect occurred for a glassy polymer, but not a rubbery polymer. They found solvent conditioning increased sorption of the peat and the humic acid by a factor of up to two. Furthermore, they studied the reversibility of the conditioning effect on heating the samples (annealing) and concluded that it is unlikely to occur at ambient environmental temperatures. Finally, Wang and Xing (2007) investigated the effect of acetone conditioning on the sorption properties of a peat and its humic fractions. They found that acetone-conditioning increased K_{OC} for phenanthrene, but not for 1-naphthol.

In this paper, we investigate the effect of conditioning of a whole soil and a lipid-extracted soil with a range of solvents of different polarities on the subsequent sorption of diuron and phenanthrene. In particular, we aim to determine whether the increased sorption of the lipid-extracted soil over the whole soil may be due to an inadvertent conditioning effect occurring during lipid extraction.

Materials and Methods

Soil and chemicals

The sorption studies were carried out on a surface soil (0-5 cm) collected from Flaxley Agriculture Center, Mount Lofty Ranges, South Australia. The soil is a Mollic Haploxeralf (Soil Survey Staff 1999), the dominant characteristic of which is a very strong texture contrast between the E and B horizons. The soil was identified as 27A11 in our previous study (Ahangar et al. in press).

Diuron and phenanthrene (>99% purity) were purchased from Sigma-Aldrich (Sydney, Australia). Analytical grade solvents and calcium chloride were obtained from Sigma-Aldrich (Sydney, Australia). Stock solutions of 1000 mg L^{-1} diuron and phenanthrene were prepared in methanol.

HF-treatment

Soils were HF-treated prior to solid-state ^{13}C NMR analysis using the procedure of Skjemstad et al. (1994). Briefly, approximately 3 g aliquots of soil was shaken end-over-end with 50 ml of HF for 5×1 h, 3×16 h and 1×64 h. Following each treatment, the samples were centrifuged at 1300 g for 20 min. After the final extraction, the residue was washed three times with deionized Millipore water and freeze-dried.

Lipid extraction

For the extraction of soil lipids, an accelerated solvent extractor (Dionex ASE 300) was used with a heating phase of 5 min and a static extraction time of 20 min (Wiesenberg et al. 2004). Approximately 30 g of soil was placed in a stainless-steel sample cell (34 mL volume) and free lipids were extracted with

dichloromethane/methanol (95/5, v/v) at 5×10^6 Pa and a temperature of 75 °C. Lipid-extracted soil was heated at 30 °C for 10 days to ensure complete removal of DCM and methanol (Kohl and Rice 1999).

Solvent conditioning

The whole soil and lipid-extracted soil were conditioned with six different solvents (water, acetonitrile, acetone, methanol, chloroform and dichloromethane) at a solid-to-liquid ratio of 1:20 for 5 days, after which the suspensions were centrifuged at 1300 g for 30 min and the conditioned solids were separated and air-dried for 5 days, then oven-dried for 5 days at 50 °C to evaporate the remaining solvent.

Sorption Experiments

Sorption experiments were carried out using a batch equilibration technique at 25 °C, as described previously (Ahangar et al. 2008a). To minimize changes in ionic strength and to avoid dispersion, 0.01 M $CaCl_2$ was used as a background solution and 200 mg L^{-1} $HgCl_2$ was used as a microbial growth inhibitor (Wolf et al. 1989; Trevors 1996). Soil (1 g) and diuron solution (1.5 mg L^{-1}, 10 mL) or soil (0.5 g) and phenanthrene solution (0.8 mg L^{-1}, 100 mL) were shaken end-over-end for 24 h (diuron) or 16 h (phenanthrene). The equilibration times were chosen based on preliminary experiments in which equilibration times were varied up to 96 h.

At the end of the equilibration period, suspensions were centrifuged at 1300 g for 20 minutes and 1 mL aliquots of the supernatant were passed through 0.45 μm Teflon filters and analysed. Sorption on filters was tested before the main experiment and was found to be negligible. Diuron and phenanthrene concentrations were determined using an Agilent 1100 series high performance liquid chromatograph (HPLC)

equipped with diode array detector and C18 column (250 mm × 4.6 mm internal diameter, 5 μm particle size). The mobile phase was 70% acetonitrile and 30% water, and the flow rate was 1 mL per minute. Diuron was detected at a UV wavelength of 210 nm and phenanthrene at a UV wavelength of 254 nm. The retention times under these conditions were 4.48 and 15.70 minutes for diuron and phenanthrene, respectively. The detection limit was 0.05 mg L^{-1} for both compounds. Blanks without diuron and phenanthrene and without soil were analysed and appropriate corrections were applied. Sorbed concentrations were calculated from the difference between the initial solution concentration and equilibrium solution concentration.

NMR analysis

Solid-state ^{13}C cross polarization (CP) NMR spectra were acquired with magic angle spinning (MAS) at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000±100 Hz in a Doty Scientific MAS probe. A 1-ms contact time and a 1-s recycle delay were used, and 4000 transients were collected for each spectrum. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero-filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Results and Discussion

Separate aliquots of the whole soil and the lipid-extracted soil were conditioned by shaking for five days with six separate solvents (water, acetonitrile, acetone, methanol, chloroform and dichloromethane) at a soil:solvent ratio of 1:20 (see Materials and Methods for a detailed description of the conditioning procedure). The C content of the solvent-conditioned whole soils varied between 50.1 and 60.1 mg g^{-1}, whilst that of the solvent-conditioned lipid-extracted soils varied between 46.1 and 51.3 mg g^{-1} (Table 1). Based on the NMR analyses (see below), we believe these variations were probably due to variations in the C contents of the soil aliquots, rather than removal of soil carbon by the conditioning solvent.

Table 1. Polarity index of conditioning solvents and soil C contents before and after solvent conditioning. Standard deviations of replicate analyses are shown in parentheses.

Conditioning solvent	Polarity Index	C content(mg C (g soil)$^{-1}$)	
		Whole soils	Lipid-extracted soils
Untreated		56.0 (1.4)	51.7 (2.2)
Water	9.0	54.1 (0.8)	51.3 (3.5)
Acetonitrile	5.8	60.1 (1.0)	50.4 (2.0)
Acetone	5.1	52.7 (1.8)	48.5 (0.7)
Methanol	5.1	51.7 (0.3)	47.3 (0.8)
Chloroform	4.1	50.1 (0.6)	48.3 (1.8)
Dichloromethane	3.1	53.9 (2.1)	46.1 (1.9)

The solid-state ^{13}C cross polarization (CP) NMR spectra (Figure 1) are very similar amongst the solvent-conditioned whole soils and amongst the solvent-conditioned lipid-extracted soils. On the other hand, there are clear differences between ^{13}C CP NMR spectra of the whole soils and the lipid-extracted soils (Figure 1), with the latter containing less alkyl signal at 30-33 ppm (Ahangar et al. in press). This indicates that whilst treatment with dichloromethane/methanol under accelerated solvent extraction (ASE) conditions does remove a substantial portion of the soil organic matter, namely the lipid fraction (Ahangar et al. in press), treatment with solvents (including neat dichloromethane and neat methanol) under gentler conditions (but for much longer periods) does not remove a substantial portion of the soil organic matter.

These results contrast with those of Wang and Xing (2007), who reported that acetone-conditioning resulted in large changes in the distribution of C types in a peat soil as determined by solid-state ^{13}C NMR, including an almost doubling of alkyl C.

Organic carbon-normalized partitioning coefficients (K_{OC}) for diuron and phenanthrene, for solvent-conditioned whole soil and lipid-extracted soil, are presented in Table 2. K_{OC} values for diuron and phenanthrene were consistently higher for the solvent-conditioned soils than for the untreated soils. Water was included amongst the conditioning solvents as a control treatment. Soils are in constant contact with water, and batch sorption is carried out in aqueous solution, so "water-conditioning" should not affect sorption affinity. This was the case for diuron sorption, in that there was no significant difference between K_{OC} for diuron between untreated and water-treated soils (Table 2). However, there was a significant increase in K_{OC} for phenanthrene on water-treatment (though generally smaller than for the other solvents) and this indicates that some factor other than solvent-conditioning is

operating (Table 2). One possibility is that the extended period of shaking causes some physical disruption that opens up otherwise inaccessible sorption sites.
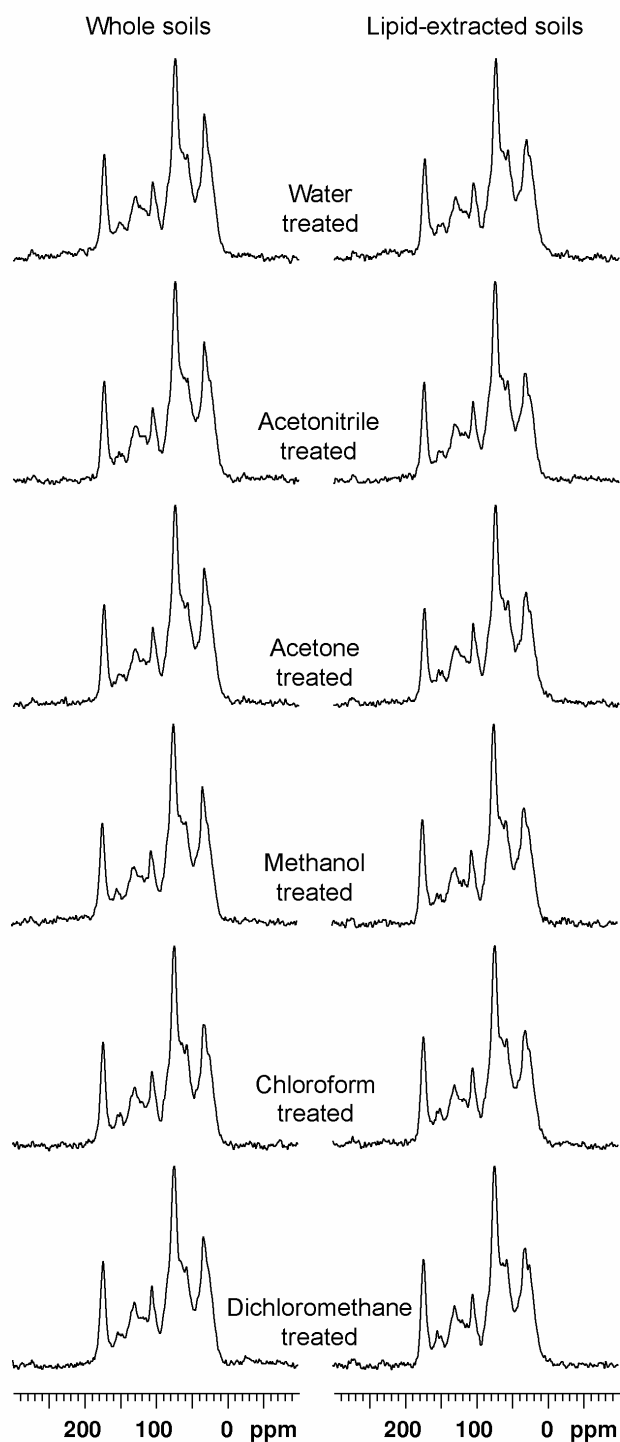

Figure 1. Solid-state ^{13}C CP NMR spectra of solvent-conditioned whole soils and lipid-extracted soils.

Table 2. Organic carbon-normalized partitioning coefficients (K_{OC}) (L (kg C)$^{-1}$) of solvent-conditioned soils for diuron and phenanthrene before and after lipid extraction. Standard deviations of replicate analyses are shown in parentheses.

| Conditioning solvent | K_{OC} (L (kg C)$^{-1}$) | | | |
| | Whole soils | | Lipid-extracted soils | |
	Diuron	Phenanthrene	Diuron	Phenanthrene
Untreated	541 (20)	26300 (1200)	721 (62)	32000 (900)
Water	550 (5)	30200 (600)	635 (56)	35800 (3000)
Acetonitrile	589 (14)	28200 (1900)	840 (46)	39100 (1800)
Acetone	688 (47)	29800 (1000)	841 (22)	33300 (1100)
Methanol	683 (7)	38000 (700)	820 (6)	42600 (700)
Chloroform	860 (16)	40900 (1800)	978 (31)	44900 (2500)
Dichloromethane	695 (29)	40200 (2700)	1020 (40)	56000 (2900)

The increase in K_{OC} on solvent-conditioning was closely related to solvent polarity (Figure 2). The greatest increases in K_{OC} (29-75%, average 49%, Table 2) were for the least polar solvents (chloroform and dichloromethane, polarity indices 4.1 and 3.1, respectively, Table 1). This was true for both whole soils and for lipid-extracted soils and for both diuron and phenanthrene. More moderate increases in K_{OC} (4-45%, average 20%, Table 2) were recorded for the more polar conditioning solvents (acetonitrile, acetone and methanol, polarity indices 5.8, 5.1 and 5.1, respectively, Table 1).

The increase in K_{OC} on solvent-conditioning was only slightly higher for phenanthrene (average 35% increase for the five solvents other than water) than for
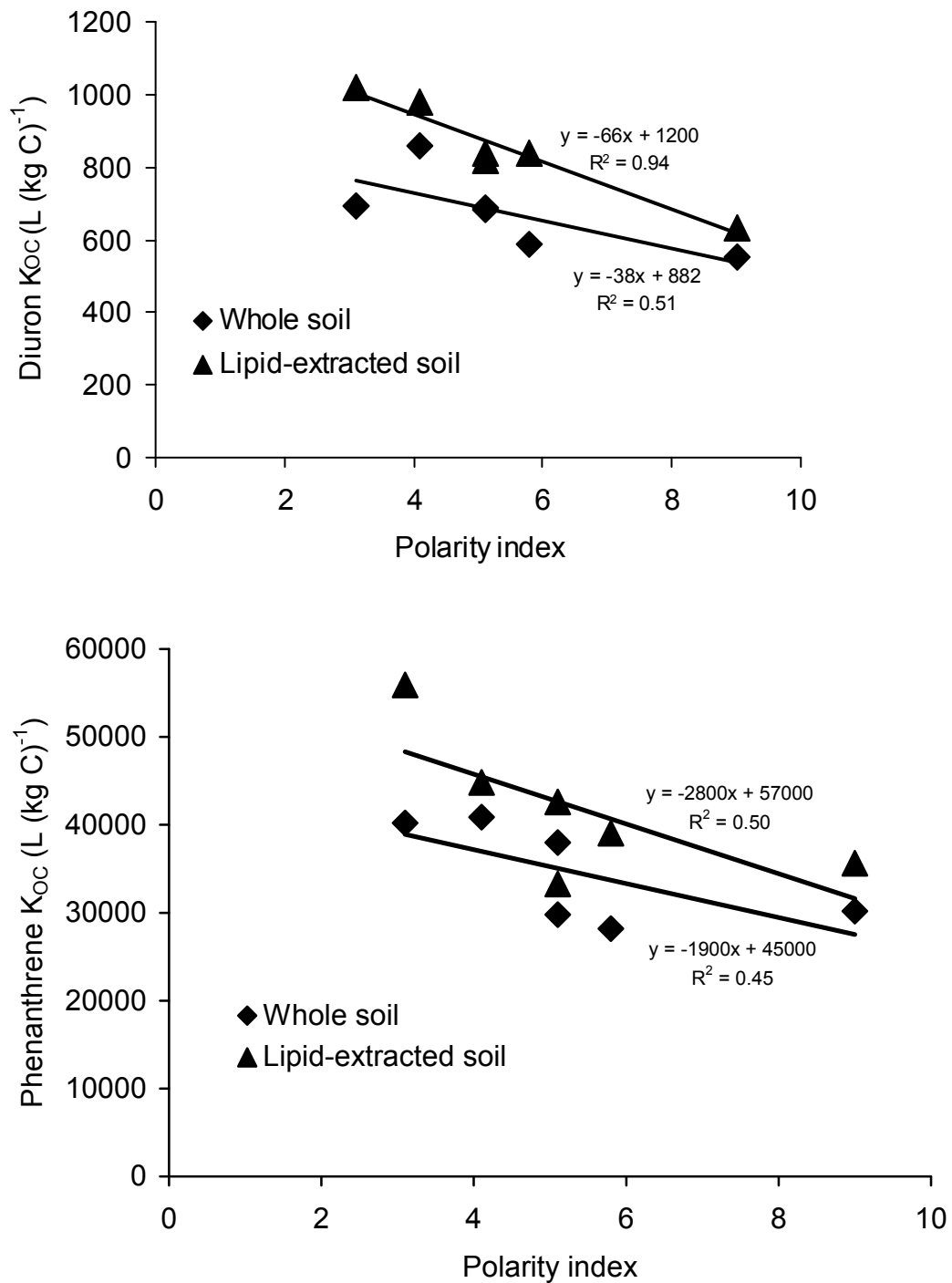
Figure 2. Plots of organic carbon-normalized partitioning coefficients (K_{OC}) (L (kg C)$^{-1}$) versus polarity index for whole soils and lipid-extracted soils.

diuron (average 27% increase). Again, this contrasts with the findings of Wang and Xing (2007), who reported that acetone-conditioning had a large effect on the sorption

of phenanthrene, but little effect on the sorption of 1-naphthol (which has a similar polarity to diuron).

Importantly, increases in K_{OC} on solvent-conditioning were similar for whole soils and lipid-extracted soils (average 32% and 30% increases, respectively, for the five solvents other than water). A key objective of this study was to determine whether the increase in K_{OC} on lipid extraction using ASE may be due to a solvent-conditioning effect, rather than lipid removal, as we had previously proposed (Ahangar et al. in press). The results here support our original assertion, since solvent-conditioning effects were observed for the lipid-extracted soils, and were of the same magnitude as for the whole soils. If lipid extraction (ASE) had caused a solvent-conditioning effect, then there should have been no further increases in K_{OC} on solvent-treatment.

The question then arises as to why lipid extraction did not cause a solvent-conditioning effect, despite the fact that it involved treatment with 95% dichloromethane, a solvent shown here to cause a strong conditioning effect. We believe the most likely explanation is that ASE involved only a short exposure to dichloromethane; the ASE procedure was carried out for only 20 minutes, after which the bulk of the solvent was decanted off, and the remaining solvent removed by evaporation. Although the total exposure time to dichloromethane during ASE was therefore greater than 20 minutes, for most of the time the solvent would have been present at low concentrations. By contrast, the solvent-conditioning procedure involved shaking the soil in the solvent for five days.

Conclusions

Solvent conditioning increased the affinity of both whole soils and lipid-extracted soils for diuron and phenanthrene. The increase in K_{OC} was on average slightly

greater for phenanthrene than for diuron. There was a strong relationship between K_{OC} increase and conditioning solvent polarity, with the less polar solvents (chloroform and dichloromethane) having a stronger effect than the more polar solvents (acetonitrile, acetone and methanol). The increase in K_{OC} was similar for lipid-extracted soils as for whole soils, and showed the same relationship with solvent polarity. This shows that the removal of soil lipids using accelerated solvent extraction (ASE) did not have a conditioning effect on the organic matrix and supports our previous assertion that ASE increases K_{OC} through the removal of lipids that block sorption sites and thereby reduce the sorption affinity of the whole soils.

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CHAPTER 6

SUMMARY AND CONCLUSION

1. Implications of research findings

For a long time it has been recognized that SOM is the most important sorption phase for non-ionic organic pollutants (Chiou et al. 1979; 1983; Chiou 1989; Lambert et al. 1965). On the basis of the correlation between sorption affinity and organic carbon content, Chiou (1989) developed the K_{oc} model for sorption of non-ionic compounds. In this model, sorption is described as a partitioning of organic molecules between the solution phase and an implicitly homogeneous organic matter phase. However, there are lots of examples where the simple K_{oc} model does not provide an adequate description of sorption to soils. First these include situations where the sorption affinity of organic matter in different soils varies considerably for a single organic compound, i.e. K_{oc} is variable (Wauchope et al. 2002), and also where non-partitioning behaviour is observed. However; other factors such as where sorption affinity is concentration dependent i.e. where sorption isotherms are non-linear, where sorption is not reversible, where there is competition between compounds, and where sorption kinetics are very slow, may contribute to K_{oc} variability (Schwarzenbach et al. 1993). This study addresses the first of these issues: the variability of K_{oc} between soils.

It has been suggested that about half of the variation in K_{oc} is due to experimental error and the remainder is due to differences in soil organic matter chemistry (Wauchope et al. 2002). Most studies on K_{oc} variability have focused on variability of

organic matter chemistry. However, there is no general consensus on the link between SOM chemistry and K_{oc} variability.

Several studies have sought correlations between sorption properties and the chemistry of organic matter. Gauthier et al (1987), Chin et al (1997) and Perminova et al. (1999) all reported that the sorption affinity of humic and fulvic acids increased with increasing aromacity. Similar findings have been reported for soils (Abelmann et al. 2005; Ahmad et al. 2001) and also for sediments (Golding et al. 2005). On the other hand, several other studies have found a relationship between aliphatic domains of organic matter and sorption affinity (Chefetz et al. 2000; Salloum et al. 2002; Mao et al. 2002). A negative correlation between sorption affinity and organic matter polarity has also been reported in several instances (Grathwohl 1990; Rutherford et al. 1992; Chen et al. 1996; Kile et al. 1999).

The first part of this study addresses the influence of SOM chemistry on sorption affinity of diuron and phenanthrene. Restricting the soils used to a small locality provided the best chance to see this relationship (Collins and Worrall 2003). In the case of diuron, K_{oc} was positively correlated with aryl C (r^2=0.59, significance level 0.001). In other words about 60% of K_{oc} variability was explained by this aspect of soil organic matter chemistry. This finding is consistent with the findings of others (Chin et al. 1997; Perminova et al. 1999; Ahmad et al. 2001; Abelmann et al. 2005; Golding et al. 2005). An even stronger negative correlation was found between sorption affinity and O-alkyl C (r^2=0.84, significance level 0.001), which is consistent with decreasing sorption affinity with increasing polarity (Grathwohl 1990; Rutherford et al. 1992; Chen et al. 1996; Kile et al. 1999). In contrast to the results for

diuron, there was no correlation between SOM chemistry and sorption affinity for phenanthrene.

Not all aspects of organic matter composition are contained in NMR spectra. Thus, it is not surprising that not all the K_{oc} variability is explained. More sophisticated SOM analysis may provide even stronger relationships, but rather than pursuing this line of investigation, a different approach was taken. In the next set of experiments (detailed in chapter 3), sorption measurement were carried out on HF-treated soils to test whether stronger relationships could be found by isolating the organic matter from soil minerals.

It had been shown previously that K_{oc} values can be greater for isolated humic and humin fractions than for the corresponding whole soils, and that greatest differences are for the mineral soils (Bonin and Simpson 2007). This suggests that interactions between SOM and clay minerals reduce the availability of sorption sites on SOM. This hypothesis has credence because addition of clays to isolated humic fractions lowers K_{oc} values (Jones and Tiller 1999).

As detailed in chapter 3, K_{oc} values for HF-treated soils were higher than for the corresponding whole soils by an average factor of 2.5 and 2.3 for diuron and phenanthrene, respectively, confirming that in these soils, the organo- mineral interactions decrease the sorption affinity for non-ionic compounds.

More importantly, after removing minerals from organic matter, a positive relationship between aryl C and sorption affinity (r^2=0.52) and a negative correlation with O-alkyl C (r^2=0.38) were observed for phenanthrene. No such relationships were

evident for the whole soils. It can be concluded that removal of minerals not only increased sorption affinity for phenanthrene, but also made the effect of organic matter chemistry clearer than that for whole soils. This shows that the blocking effect of minerals can be substantial and organo-mineral interactions can mask the effect of organic matter chemistry on K_{oc}. This could be the reason why there is no clear and consistent relationship between organic matter chemistry and sorption affinity for whole soils in general. Until now this factor has been largely ignored.

It is not only interactions with minerals that may block sorption sites on organic matter but also organic compounds such as lipids may cover the sorption sites. In the next set of the experiments (chapter 4), another possible contribution to K_{oc} variability – the blocking of active sorption sites on SOM by lipids – was investigated by comparing sorption properties of both whole and HF-treated soils before and after lipid extraction.

The removal of lipids has been shown to increase the sorption affinity of soils (Kohl and Rice1999; Chilom et al. 2005; Drori et al. 2006), sediments (Chilom et al. 2005; (Tremblay et al., 2005) and humic fractions (Tremblay et al., 2005; Wang and Xing, 2007). This increase in sorption affinity can be up to one order of magnitude (Kohl and Rice 1999; Tremblay et al. 2005).

Lipid extraction of the soils in this study increased K_{oc} by an average of 31% and 29% for diuron and phenanthrene, respectively. Soil lipids were also extracted from soils following HF-treatment. The increase in K_{oc} was even greater for the HF-treated soils than for the whole soils, reaching up to a factor of 4.3 for phenanthrene. Not only do

lipids block sorption sites on SOM, but also the blocking effects of minerals and lipids are independent.

Another finding of this experiment was that K_{oc} of the isolated lipid for diuron was much lower than for any of the whole or HF-treated soils. Removal of this poorly sorptive fraction would therefore contribute to the increase in K_{oc} on lipid removal. Because lipids only represented about 5% of organic carbon, this effect would be minor. In the case of phenanthrene, K_{oc} of the isolated lipid was much higher than for any of the whole or HF-treated soils, so its removal may have been expected to decrease, not increase, K_{oc} on lipid extraction. The very different affinities of lipids relative to non-lipid organic matter for diuron and phenanthrene may in part explain why the relationship between K_{oc} and alkyl carbon appears to be so unpredictable.

The final experiments in this study (detailed in chapter 5) were performed, in part, to test an alternative explanation for the increase in sorption affinity on lipid extraction. Several studies have shown that exposure of soils to organic solvents can increase sorption affinity (Xia and Pignatello 2001; Lu and Pignatello 2002; Sander et al. 2006; Wang and Xing 2007). Because lipid extraction involved exposure to organic solvents (specifically 95% dichloromethane / 5% methanol), it was possible that the increase in sorption affinity on lipid removal was due to changes in the physical structure of the residual organic matter, rather than the removal of lipids that block sorption sites.

The so-called "solvent conditioning effect" is believed to increase sorption affinity through irreversible expansion and creation of holes in the SOM matrix. This effect

and mechanism have been proven for glassy polymers (Wang et al. 1997; Kamiya et al. 1998), and the observation of a conditioning effect for soils has been taken as evidence for the glassy nature of SOM.

In this study, aliquots of a whole soil and a lipid-extracted soil were conditioned by shaking with for five days with five organic solvents (acetonitrile, acetone, methanol, chloroform and dichloromethane). Solvent conditioning increased K_{oc} for both diuron and phenanthrene in every case. The magnitude of the increase in K_{oc} was closely related to solvent polarity, with the least polar solvents (dichloromethane and chloroform) having the greatest effect.

Most importantly, the increase in K_{oc} on solvent conditioning was similar for the whole soil and the lipid-extracted soil (an average of 32% and 30%, respectively). This strongly suggests that the increase in K_{oc} on lipid extraction is not due to the solvent conditioning effect (otherwise there would have been no increase in K_{oc} on solvent conditioning the lipid-extracted soil). Finally, ^{13}C NMR spectra of the solvent-treated soils show that there were no significant changes in the alkyl region of SOM after solvent conditioning, i.e. solvent conditioning did not result in lipid removal. Taken together, these lines of evidence indicate that the effect of lipids on masking active sorption sites on organic matter and the effect of solvent conditioning on the structure of organic matter can be considered as two different phenomena that independently affect sorption.

This dissertation represents a significant advance in the fundamental understanding of the role of SOM in sorption because of the approach taken via four key factors that

may have an influence on sorption – soil organic chemistry, mineralogy, lipid chemistry and solvent conditioning – were studied and quantified on the one set of soils. Most previous studies in this area have focussed solely on the effect of SOM chemistry on the sorption of non-ionic compounds. Much less attention has been paid to the interactions between SOM and the mineral phase and lipid components, or to SOM physical conformation, and no single previous study has investigated all four aspects on a set of soils in close geographic proximity and with very similar soil forming factors, especially that of parent material. The role of SOM chemistry on sorption of non-ionic compounds has been over-emphasized .Other factors, identified above, can alter the sorption properties of SOM to a degree that the effect of SOM chemistry is masked.

2. Recommendations for future work

To address some of the issues raised in this study, the following areas for further research are recommended:

1) In this research, the study site was very small (about 2 ha) in order to minimize the impact of soil mineralogy on the sorption of target compounds. Whereas this approach can be considered successful in enabling four separate effects on K_{oc} to be identified and quantified, the downside is that these results only truly reflect the conditions for the soils at this particular location. It is likely that the factors affecting K_{oc} are important for soils more generally, but their relative importance is likely to vary. Therefore, soils from other areas with different factors of formation - especially those relating to parent material characteristics such as texture and mineralogy - should be investigated in order to quantify the contribution of SOM-mineral interactions to sorption. To do

this, soil samples with different mineralogy should be chosen and K_{oc} for target compounds should be measured before and after HF-treatment. At the same time ^{13}C NMR can be employed to investigate the SOM chemistry. Changes in K_{oc} before and after HF-treatment for soils with almost similar SOM chemistry but different mineralogy can be considered as a first step to quantify the contribution of soil mineral phase to SOM-minerals interactions and its impact on organic matter affinity for sorption of non-ionic compounds.

2) The same argument can be made with regards to the effect of soil lipids on K_{oc}. The soils in this study all contained similar quantities of lipids. A better understanding of the role of lipids in affecting sorption requires similar measurements be taken for a broad range of soils with different quantities and compositions of lipids. Extractable lipids in this study represented 3.2-13.4% of soil C, with an average value of 6.6%. This is higher than the 1.2-6.3% of soil C suggested as typical by Stevenson (1982), and the 4-8% suggested by Dinel et al. (1990), although this may be partly explained by the greater efficiency of accelerated solvent extraction used in this study (Jansen et al. 2006) compared to traditional Soxhlet extraction. The composition and amount of free lipids in SOM is dependent on the biotic and parent material factors governing soil development,. Hence, the type of overlying vegetation and the physico-chemistry of the soils (Kogel-Knabner et al. 1992; 2000) should govern the choice of soils for such a study. Non-wetting sands would be of particular interest. Water-repellency in these soils is caused by high amounts of lipid (hydrophobic waxes) that coat the surfaces of soil particles in sandy surface soils (Franco et al. 2000). The high proportion of soil lipids in

non-wetting sands may have a larger effect on sorption site availability. Bigger differences before and after lipid extraction may be expected in non-wetting sands.

3) In this study, only the impact of free lipids was investigated. Free lipids are those that can be extracted with organic solvents. It was shown in chapter 4, using solid-state ^{13}C NMR, that lipid extraction removed only 15-20% of alkyl C. Thus free lipids contribute only about 20% of whole alkyl C and at least some part of the remainder is likely to be bound lipids. Bound lipids, which are not extractable with organic solvents, can be separated from soil with the aid of chemical methods such as alkaline hydrolysis (Howard et al. 1998 but these methods will affect the physical structure of SOM because a portion will be solubilised. Therefore it would be harder to differentiate between the effect of bound lipid removal and effect of changes in SOM physical structure.

4) This study showed that changes in the physical conformation of organic matter alter sorption properties for non-ionic pollutants in the soil matrix, but these experiments were only carried out on whole soils. This could be extended to investigate the effect of solvent conditioning on organic matter separated from whole soil by HF-treatment. Such an approach would remove the interaction of soil minerals and in this condition the effect of solvent treatment on the structural changes of SOM may be seen more clearly.

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