

**Association of Organic Compounds to  
Dissolved and Particular Natural  
Organic Matter in Soils**

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## Abstract

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To make proper risk assessments of sites with contaminated soil it's important to understand the biogeochemical processes determining transport and sequestration of the contaminants in soil. Soil organic matter (SOM) is the most important component in soil for adsorption of hydrophobic organic compounds (HOC) and the organic carbon normalized partitioning constant ( $K_{OC}$ ) is used to model partitioning of HOCs between the aqueous phase and SOM. The aqueous solubility of HOCs is low and association to dissolved organic matter (DOM) in soil solution is therefore important for the mobility of HOCs. Similarly, association to the solid phase of SOM, in this thesis denoted particulate organic matter (POM), controls the retention of HOCs in organic rich soils. Few data are reported on the partitioning of HOCs to DOM ( $K_{DOC}$ ) and to POM ( $K_{POC}$ ) determined in the same equilibrium system.

In short-term adsorption experiments with controlled equilibrium systems, adsorption to DOM and POM was best described by linear isotherms for chlorophenols (CPs) and nitrobenzene (NB), indicative of a hydrophobic partitioning mechanism. Adsorption of aniline was best described by the Langmuir isotherm, indicative of a specific interaction to functional groups of DOM and POM. Trinitrotoluene (TNT) adsorption data revealed specific interactions of degradation products to DOM and hydrophobic partitioning of TNT to POM.

As a complement to the short-term adsorption experiments, soils with aged contaminants were investigated. Chlorophenols (CP), phenoxy phenols (PCPP), diphenyl ethers (PCDE), dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) associated to DOM and POM and the free analyte in the aqueous phase were determined. In both the adsorption experiments and the soils with aged contaminants, POM showed a higher binding affinity towards HOCs than DOM, when normalized to organic carbon content. The partitioning towards POM, relative to DOM, increased with increasing hydrophobicity of the classes of compound studied in the order CP<PCDE<PCDF<PCDD. No major differences in carbon chemistry were revealed between DOM and POM (using  $^{13}\text{C}$ -NMR, XPS and elemental analysis), thus it is suggested that some other property is responsible for the difference in binding to POM and DOM. The physical size of hydrophobic structures could be such an important property.

*Key words:* soil organic matter, chlorophenols, TNT, dioxins, partitioning, adsorption,

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# Appendix

## Paper I-IV

This doctoral thesis is based upon the following papers, hereafter referred to by their respective Roman numerals:

- I. Eriksson, J., Frankki, S., Shchukarev, A. and Skyllberg, U. 2004 Binding of 2,4,6-trinitrotoluene, aniline and nitrobenzene to dissolved and particulate soil organic matter. *Environmental Science & Technology*, 38, 3074-3080
- II. Frankki, S. and Skyllberg U. 2006. Chlorophenol binding to dissolved and particulate soil organic matter determined in controlled equilibrium systems. *European journal of soil science*, (In press).
- III. Frankki, S., Persson, Y., Tysklind, M. and Skyllberg U. 2006. Partitioning of CPs, PCDEs and PCDD/Fs between dissolved and particulate natural organic matter in a contaminated soil. Submitted manuscript.
- IV. Frankki, S., Persson, Y., Shchukarev, A., Tysklind, M. and Skyllberg U. 2006. Partitioning of CP, PCPP PCDE and PCDD/F between dissolved and particulate soil organic matter at three industrial sites with chlorophenol preservative contamination. Submitted manuscript.

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## Abbreviations

ADNT	Aminodinitrotoluen	K <sub>POC</sub>	K <sub>OC</sub> normalized to particulate organic carbon (L/ kg POC)
CEC	Cation exchange capacity	K <sub>OW</sub>	Octanol water partitioning constant
CP	Chlorophenols	NB	Nitrobenzene
CP-MAS-NMR	Cross polarization magic angle spinning nuclear magnetic resonance	OM	Organic matter
DANT	Diaminonitrotoluene	PCDE	Polychlorinated diphenyl ethers
DOC	Dissolved organic carbon	PCDD	Polychlorinated dibenzo- <i>p</i> -dioxins
DOM	Dissolved organic matter	PCDF	Polychlorinated dibenzo furans
f <sub>OC</sub>	Fraction of organic carbon in soil	PCPP	Polychlorinated phenoxy phenols
GC-MS	Gas chromatography – Mass spectrometry	POC	Particulate organic carbon
HOC	Hydrophobic organic contaminants	POM	Particulate organic matter
HPLC	High performance liquid chromatography	RP-HPLC	Reversed phase high performance liquid chromatography
K <sub>d</sub>	Soil solution partitioning constant (L/kg)	SOC	Soil organic carbon
K <sub>L</sub>	Langmuir constant of binding strength	SOM	Soil organic matter
K <sub>OC</sub>	Organic carbon normalized soil solution partitioning constant (L/kg OC)	TAT	Triaminotoluene
K <sub>DOC</sub>	K <sub>OC</sub> normalized to dissolved organic carbon (L/kg DOC)	TNT	Trinitrotoluene
		TOC	Total organic carbon
		XPS	X-ray photoelectron spectroscopy
		q <sub>max</sub>	Langmuir maximum adsorption capacity

## Introduction

In this thesis, the association of organic compounds to dissolved (DOM) and particulate soil organic matter (POM) is studied. Both polar and non-polar organic contaminants, which are considered a threat to the environment, have been studied in short-term adsorption experiments as well as in soils with contaminants aged for decades. Association of a compound to DOM may increase its mobility, whereas association to POM may lead to sequestration, and therefore relevant binding affinity constants for DOM and POM are needed when modelling transport processes at contaminated sites.

### Contaminated soils

Soil contamination is a world wide problem that recently gained new interest in Sweden after a change in the legislation regarding responsibility of remediation of contaminated soils. The Swedish Environmental Protection Agency has made an inventory of old industrial sites, 40.000 in Sweden only, and ranked them according to their potential risk (Anon., 2005). There is a wide range of contaminants at these sites. In this thesis, two groups of compounds were studied, trinitrotoluene (TNT) and compounds similar to its degradation products and chlorophenols (CP) and chlorinated compounds found in technical chlorophenol formulations.

Trinitrotoluene, (TNT) is an explosive widely used and produced in millions of tons during World War I and II. TNT degrades in soil, through the reduction of nitro groups to amino groups; forming amino-dinitro-toluene (ADNT), diamino-nitro-toluene (DANT) and triamino-toluene (TAT) (Figure 1). These compounds have amino- and nitro- functional groups that make them relatively water soluble and degradable. Furthermore, the amino groups of the decomposition products (ADNT, DANT, TAT) are much more reactive towards surfaces of soils particles than the nitro groups of the mother compound (TNT).

Chlorophenols have for example been used as fungicides for wood protection during drying of the sawn timber. At industrial sites, where technical chlorophenol formulations have been used, a mixture of chlorinated organic compounds can be found. The chlorophenol formulations were contaminated with several chlorinated by-products such as dibenzo-*p*-dioxins (PCDD), dibenzo furans (PCDF), phenoxy phenols (PCPP) and diphenyl ethers (PCDE) (Figure 1), formed during the production of the preservatives. Different ways of production, i.e. chlorination of phenols or hydroxylation of chlorobenzenes give rise to different by-products. Chlorophenols and PCPPs are more water soluble than PCDEs and PCDD/Fs. Thus, even if much of the CPs may have been leached out, PCDEs and PCDD/Fs can still be found at relatively high concentrations in soil at old industrial sites where chlorophenol formulations have been used (Assmuth & Vartiainen, 1994; Kitunen, Valo & Salkinojasalonen, 1985; Kitunen, Valo & Salkinojasalonen, 1987). Chlorophenols are acutely toxic to some organisms by uncoupling the

oxidative phosphorylation in the ATP production (Escher, Snozzi & Schwarzenbach, 1996). The highly hydrophobic PCDD/Fs are biomagnifying and carcinogenic and therefore listed as high risk compounds in the Stockholm Convention on Persistent Organic Pollutants ([http://www.pops.int/documents/convtext/convtext\\_en.pdf](http://www.pops.int/documents/convtext/convtext_en.pdf); 2-May\_2006). Also PCDEs are persistent, hydrophobic and bioaccumulating (Boer & Denneman, 1998). Structurally, PCDEs are non-planar, as opposed to the planar compounds PCDD/Fs. Steric conformation, of which planarity is an example, is a molecular property important for adsorption and bioavailability of compounds in soils and sediments (Lyytikainen *et al.*, 2003).

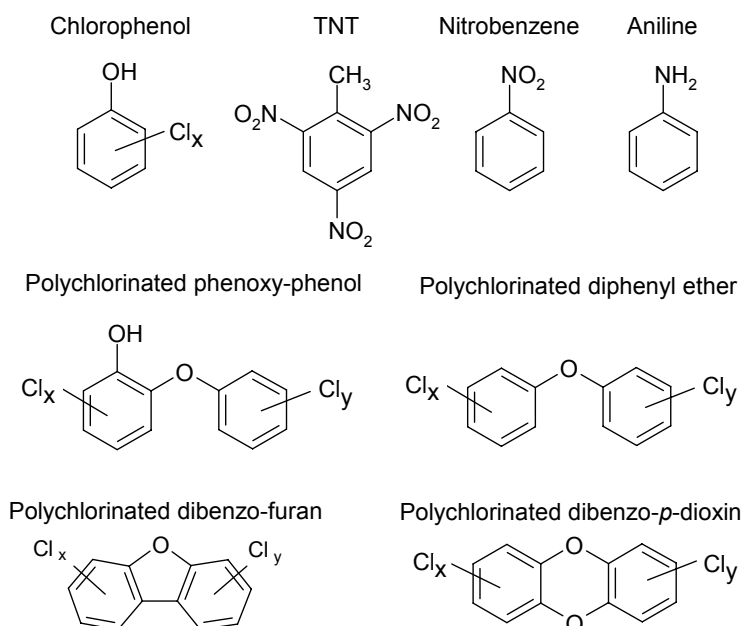


Figure 1. Structure formulas of the compounds studied. The chlorinated compounds may have different number of chlorine atoms (denoted by X and Y). For the PCPPs, one example of the position of the OH-group is shown.

When performing risk assessments for sites with contaminated soil, mobility and transport processes are in focus. Contaminants in soil are transported in the soil solution either in free, dissolved forms or co-transported with dissolved organic matter or other colloids (McCarthy & Zachara, 1989). Co-transport is especially important for compounds with low water solubility. Thus, it is of major importance to define and quantify the active components in the soil and understand how they take part in processes affecting the fate of contaminants in soil.

### Soil organic matter

Soil organic matter (SOM) is widely accepted as being the most important soil component for the retention of hydrophobic organic compounds (HOC) in most



soils and sediments (Chiou, Porter & Schmedding, 1983; Kile *et al.*, 1995; Means *et al.*, 1980; Schwarzenbach & Westall, 1981). A significant correlation between concentrations of HOCs and the fraction of organic carbon per dry mass of soil or sediment ( $f_{OC}$  in %) has been established (Schwarzenbach & Westall, 1981). Soil organic matter is formed by degradation of litter from dead plants and other organisms. The degradation is enhanced by earth worms, microorganisms etc., and parts of SOM is incorporated into more or less stable humic substances (Stevenson, 1994). On a geological time scale, SOM may be further altered under metamorphic conditions to form kerogen, coal and graphite. Soot carbon deposited from industrial activities has quite similar properties as the latter.

### *Dissolved organic matter (DOM) and particulate organic matter (POM)*

A minor fraction of SOM is dissolved in the soil water, and often referred to as dissolved organic matter (DOM), while SOM pertaining to the solid phase in this thesis is referred to as particulate organic matter (POM). Furthermore, the concentration of DOM released into solution by desorption from POM and mineral surfaces is regulated by pH, ionic strength and the composition of adsorbed major cations (Skylberg & Magnusson, 1995). The DOM fraction has been shown to enhance the total transport of HOCs (Dunnivant *et al.*, 1992; Kim & Osako, 2004). Thus, in soil, HOCs can be sequestered (bound to POM) or bound to and possibly co-transported with DOM (Figure 2). The separation of DOM and POM in experimental setups may be defined by the speed of centrifugation, or by the pore size of a filter e.g. 0.22, 0.45 or 0.70  $\mu\text{m}$ . Microbes are small enough to escape through a 0.70  $\mu\text{m}$  filter, whereas colloidal matter and nano-particles may pass even a 0.22  $\mu\text{m}$  filter. In laboratory studies, DOM may encompass small particles, colloids and living cells in addition to truly dissolved SOM, depending on the experimental setup.

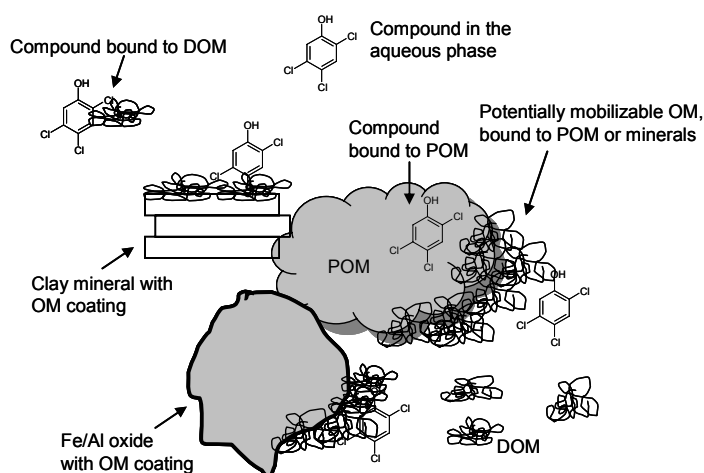


Figure 2. In soil, organic compounds (here exemplified with 2,4,5-trichlorophenol) can be dissolved in the soil solution, bind to dissolved organic matter (DOM) in the soil solution or bind to particulate organic matter (POM) or organic matter (OM) adsorbed to surfaces of minerals and oxides.

### *Chemical characterization of SOM*

The molecular structure of SOM is unknown. To compare SOM with different origins a variety of techniques are used to quantify different fractions of SOM such as wet chemical, elemental analyses and spectroscopic methods. Wet chemical analyses (e.g. acid-base titrations, cation-exchange extractions) are used to determine concentrations of carboxyl and phenol groups, acidity and adsorbed cations. Bulk elemental analysis of the main constituents of organic matter C, H, N and O and the atomic ratios of O/C and H/C give information about the degree of oxidation/reduction of SOM. Cellulose, wood and lignin have high O/C and high H/C; micro-organisms and waxes have high H/C but low O/C; and highly metamorphic kerogens have low H/C and low O/C ratios (Weber *et al.*, 2001).

Organic carbon (OC), altered thermally or by metamorphic conditions, designated soot carbon or black carbon (BC), may be determined using different methods. However, there is yet no standard procedure or general definition of BC, and the different procedures used give very varying results for estimates of BC in soil (Schmidt *et al.*, 2001). Thermal (Gustafsson *et al.*, 1997) or chemical oxidation of non-pyrogenic matter, followed by elemental bulk analysis is one method used for BC determination, mainly for sediments.

Spectroscopic methods such as  $^{13}\text{C}$ -nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) can be used to determine the gross carbon chemistry of SOM. This is useful as the exact molecular structure of SOM not known. The most common spectroscopic technique used to characterize soil organic carbon is cross polarization magic angle spinning (CPMAS)  $^{13}\text{C}$ -NMR. In NMR, the difference in absorption frequencies of C with different chemical environment is detected and expressed in terms of chemical shift with respect to a reference standard. The heterogeneity of the carbon matrix of organic matter in soil makes it difficult to obtain detailed information on the presence of specific carbon groups as the signals overlap. Though, the bulk chemical composition of the sample can be identified by integrating the  $^{13}\text{C}$ -NMR spectrum into regions designated the most tentative chemical groups contributing to the signal e.g. aliphatic C, aromatic C, carboxyl C and carbonyl C, and is used to quantify the relative amounts of different C structures. By using  $^{13}\text{C}$ -labelled compounds,  $^{13}\text{C}$ -NMR can be used for more specific studies on compound organic matter interactions.

X-ray photoelectron spectroscopy (XPS) is a surface sensitive spectroscopic technique that can be used to characterize organic matter. When irradiating the surface with an X-ray beam, photoelectrons are ejected from excited atoms present at the surface. The kinetic energy of these ejected electrons is measured and the electron binding energy of the emitting atom is determined. Chemical forms with different electron density (oxidation state) of elements such as carbon (C-C, C-O, C=O, O=C-O) can be achieved. This technique is limited to the very surface due to the short mean free path of the photoelectron in the matrix. Interestingly enough, the outer 10 nm of the surface of humic substances, probed by XPS, have been shown to give very similar results as CPMAS  $^{13}\text{C}$ -NMR (Bubert, Lambert &

Burba, 2000). This suggests that the average bulk C chemistry in humic substances may be expressed within a volume of only 10 nm thickness. In comparison to NMR, XPS has the advantage of giving information about several other elements during one run.

## **SOM-HOC interactions**

### *Sorption isotherms – studies on SOM-HOC interactions*

The fact that both adsorbate (compound) and adsorbent (SOM) mainly consists of carbon makes the adsorption of organic chemicals to SOM difficult to study using spectroscopic techniques. For this, expensive  $^{13}\text{C}$ - or  $^{14}\text{C}$ -labelled compounds must be used. Therefore, most studies of the adsorption of organic chemicals in soil have been restricted to macroscopic approaches such as the determination of adsorption and desorption isotherms. In isotherm experiments, the relation between the aqueous phase concentration ( $c$ ) of analyte and the concentration of analyte bound to the adsorbent ( $q$ ), is used to describe the interaction, often in batch experiments. Examples of techniques used to separate and quantify the aqueous phase compound from the SOM bound compounds are; reversed phase HPLC (RP-HPLC), solid phase micro extraction (SPME) and dialysis.

There are many different models used to interpret sorption data. Here, three of the most common are discussed. According to the linear isotherm (Figure 3, Eq 1), the relationship between the concentrations of free analyte and sorbed compound is constant and the sorption capacity of the adsorbent (within reasonable concentrations) infinite. A linear isotherm is often found to be the best and most simple model to describe the association of HOCs to SOM. This isotherm is indicative of a hydrophobic partitioning mechanism. This physical partitioning is a non-specific entropy driven process, minimizing the total energy of the system (Chiou, Peters & Freed, 1979).

The Langmuir isotherm (Figure 3, Eq 2) represents a case where the binding of the analyte can be described by a finite number of identical surface sites. It is often assumed that if data follows the Langmuir isotherm, it is indicative of a specific interaction between the compound and a surface. The Langmuir isotherm can be used to determine the maximum adsorption capacity of this specific site,  $q_{\text{max}}$ , and also include a constant related to the binding affinity ( $K_L$ ).

The Freundlich isotherm (Eq 3) is a non-linear model including the distribution coefficient  $K_d$  and a factor  $n$ . The Freundlich isotherm is, in contrast to the Langmuir isotherm, purely empiric and does not give any estimate of an adsorption maximum. By including the factor  $n$ , which describes the deviation from linearity, it is in reality a modification of the linear model. When  $n = 1$ , the Freundlich model becomes equal to the linear model.

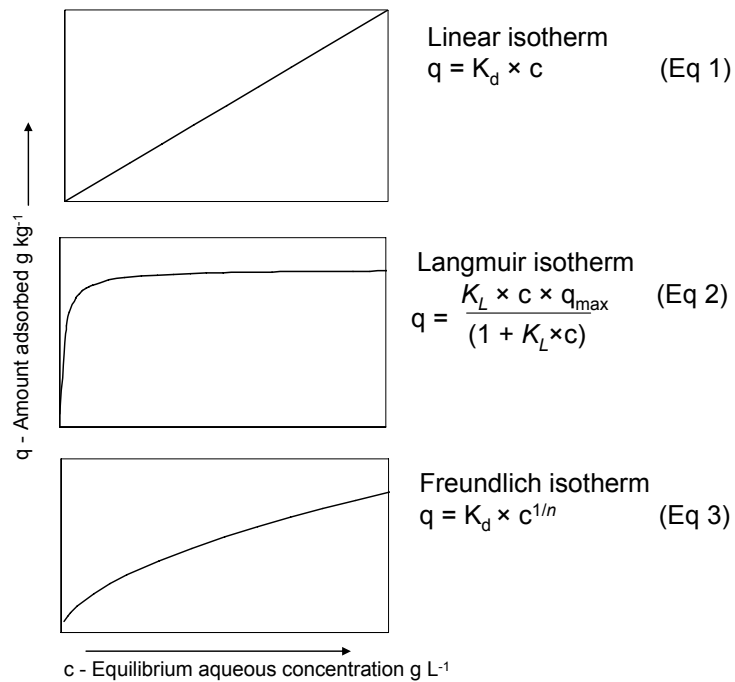


Figure 3. Adsorption isotherms, the amount of a compound adsorbed ( $q$ ) as a function of equilibrium aqueous concentration of the compound ( $c$ ). The linear, Langmuir and Freundlich isotherms are the most commonly discussed adsorption isotherms. For details on the isotherm equations see text.

The partitioning coefficient ( $K_d$ ) in the linear and Freundlich models are often normalized to organic carbon content in the soil (Eq 4), resulting in the organic carbon normalized partitioning coefficient ( $K_{OC}$ ).

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (\text{Eq 4})$$

#### *Adsorption and desorption kinetics*

In order to determine the reaction rate and the time it takes for equilibrium to establish, kinetic experiments are needed. In experiments with HOC adsorption to soil, two kinetic phases of adsorption are often found; an initial fast phase, where most of the compound is bound, and a second slower adsorption phase that may continue for weeks or longer. Most adsorption studies are performed after the first fast adsorption phase when an apparent equilibrium or pseudo-equilibrium has established. Desorption hysteresis, when parameters determined from the desorption deviate from values obtained during adsorption, is common in soil systems. The sorption reaction is said to be irreversible. The longer time allowed for adsorption the less reversible is desorption (Chung & Alexander, 1998), especially when the adsorption process has been going on for years e.g. at industrial estates with soil contamination. This effect is referred to as aging of contaminants in soil. The phenomenon is mainly attributed to intraparticle

diffusion, or possibly by a contribution from covalent bond formation that may increase with time (Pignatello & Xing, 1996). Another theory is that the hysteresis is caused by irreversible changes in the structure of the organic matter matrix upon sorption, known as the “conditioning effect” (Lu & Pignatello, 2002). The hysteresis effect is especially important to consider when parameters determined in laboratory experiments are used to interpret soil processes at industrial estates where contaminants have been aged for years or decades. Ageing of organic compounds in soil reduce the bioavailability as indicated by lower biodegradation rate of e.g. phenanthrene in laboratory experiments with up to about 300 days equilibrium time (Hatzinger & Alexander, 1995).

## **Conceptual models and characteristics of soil organic matter**

### *The theory of condensed – expanded domains*

An organic carbon concept used to understand sorption processes between organic chemicals and OM in soils and sediments is the “soft/rubbery/expanded” and “hard/glassy/condensed” domain theory that has been proposed by several research groups (Pignatello & Xing, 1996; Weber, Mcginley & Katz, 1992). The proposed OM domains have different diagenetic histories and different sorption properties. Kerogen, shale, coal and soot are examples of condensed carbon, all diagenetically and/or thermally altered organic carbon, and sometimes denoted BC. Sorption isotherms for HOC to these types of sorbents are typically nonlinear and the relative fast adsorption and slow desorption result in a hysteresis effect (Leboeuf & Weber, 2000). Young and relatively non-altered OM such as peat and humic acids are categorized as expanded carbon. For this type of carbon, adsorption isotherms are in general linear and adsorption reversible (Leboeuf & Weber, 2000). SOM is assumed to be a mixture of the two types of domains. This heterogeneity of SOM complicates the studies of HOC – SOM interactions. As an example, increased sorption capacity (Naes *et al.*, 1998) and nonlinearity in isotherms for phenanthrene binding to sediment OM is attributed to a small but important fraction of condensed soot carbon mixed with the rest of the OM (Cornelissen & Gustafsson, 2004). Planar molecules have been shown to bind stronger in soil than non-planar compounds (Krauss, Wilcke & Zech, 2000) possibly owing to relatively strong  $\pi$ - $\pi$  interactions with soot carbon structures (Cornelissen *et al.*, 2004) or with other aromatic moieties (Zhu *et al.*, 2004).

### *The concept of the humic micelle*

Traditionally, humic substances are operationally separated into three classes; humic acids (HA), fulvic acids (FA) and humin (Stevenson, 1994). Fulvic acids are soluble in both dilute acid and dilute base solutions, humic acids are soluble in dilute base but precipitates in dilute acid (<pH 2) and humins are insoluble in both acid and base. High molecular weight and/or complexation with mineral substances are believed to explain the low solubility of humin (Hatcher & Spiker, 1983). Fulvic acids are less aromatic, have more oxygen functional groups (greater O/C ratio) and smaller molecular weight than humic acids.

Humic substances are amphiphilic and may in solution form macromolecules, micelles, with interior hydrophobic structures and exterior hydrophilic surfaces (Wershaw, 1993). The inner volume of these macromolecules is thought of as a hydrophobic phase held together by hydrogen bonds, into which hydrophobic molecules may partition (Wershaw, 1993). Khan and Schnitzer (1972) proposed that sorption of HOCs take place at external surfaces or in internal voids of HA extracted from soil. Ionic or polar compounds can bind to functional groups at the outer hydrophilic surface (Chiou *et al.*, 2000). Adsorption of phenolic compounds, like chlorophenols, to humic substances is pH dependent. The adsorption increases at lower pH, higher ionic strength and in presence of polyvalent cations due to a formation of coiled, more condensed structure of the humic substances (Fingler, Drevenkar & Frobe, 2005; Lafrance *et al.*, 1994). The size and conformation of the humic macromolecules affects the HOC binding capacity and is influenced by pH and cations in the soil solution (Jota & Hassett, 1991; Schlautman & Morgan, 1993; vonWandruszka, Ragle & Engebretson, 1997). Polyvalent cations can dissociate the protons of functional groups of organic matter and bind to several smaller molecules creating larger humic compounds and also change the three dimensional structure. Polyvalent cations are used as a method to flocculate DOM (Laor & Rebhun, 1997).

#### *Molecular size of humus*

Molecular size of dissolved humic substances is positively correlated to adsorption of HOC (Engebretson & Von Wandruszka, 1997; Kopinke, Georgi & MacKenzie, 2001; Ragle, Engebretson & vonWandruszka, 1997). The increased adsorption affinity of larger hydrophobic molecules is attributed to the formation of larger hydrophobic intramolecular volumes with increasing molecular size (Hur & Schlautman, 2004). Furthermore, Khalaf *et al.* (2003) demonstrated that humic acid macromolecules larger than 100 000 Daltons were primarily aliphatic in character, and macromolecules smaller than 30 000 Daltons were primarily aromatic in character. Thus, it can be concluded that the size distribution of macromolecules in SOM may play a major role in hydrophobic partitioning processes of HOCs. The molecular size of POM can not be determined with available methods.

#### *Aliphatic and aromatic structures*

As  $K_{OC}$  for a certain compound can differ greatly between OM of different origins characteristics of SOM have been used to model the  $K_{OC}$ . Hydrophobic organic compounds like polycyclic aromatic hydrocarbons (PAHs) have been shown to preferentially associate to fractions of aromatic C structures in humic substances (Chin, Aiken & Danielsen, 1997; Uhle *et al.*, 1999). Such an association may be explained by  $\pi$ - $\pi$  interactions. More recently, however, several studies have shown that aliphatic C structures may be more important than aromatic for the adsorption of PAHs (Chefetz *et al.*, 2000; Kang & Xing, 2005). Other studies have failed to find any significant link between any of these two major structures and adsorption of HOCs (Mao *et al.*, 2002; Simpson, Chefetz & Hatcher, 2003). Bassmann-Schnitzler and Sequaris (2005) used polymers to model the binding of pyrene to SOM and found a linear relationship between  $\log K_{OC}$  and alkyl chain C content. The polymers were indicated to form hydrophobic micelle-like structures with

increased binding of pyrene at decreased pH. The partitioning behaviour of HOC in hydrophobic, micelle-like structures of SOM could be modelled. In another study, the fraction of poly-methylene rich amorphous aliphatic domains in SOM of nanometre diameter size correlated positively with  $K_{OC}$  of phenanthrene in different humic materials (Mao, *et al.*, 2002). Kang and Xing (2005) found a positive correlation between extent of adsorption and aliphaticity of SOM. Increasing concentration of aliphatic C gave rise to increasing linearity of isotherms, indicative of a hydrophobic partitioning mechanism to an expanded C-structure. Even if it is discussed whether aromatic or aliphatic structures are most important, it is a consensus that HOCs are mainly associated to either aliphatic or aromatic hydrophobic structures in SOM. In line with this a negative correlation is observed between polarity and  $K_{OC}$  for HOCs (Kile, Wershaw & Chiou, 1999; Tanaka *et al.*, 2005).

### **Determinations of $K_{OC}$**

Compound properties such as water solubility, octanol-water partitioning constants ( $K_{OW}$ ), ionisability etc have been used to model variations in  $K_{OC}$  for different compounds. With this approach differences in SOM properties is not considered. Values on  $K_{OC}$  calculated from relationships with compound properties such as water solubility and  $K_{OW}$  are available in the literature for most organic compounds, but regarding the above discussion on differences in adsorption to different SOM, these modelled  $K_{OC}$  values can only be seen as estimates. For chlorophenols, literature  $K_{OC}$  values differ up to one order of magnitude,  $K_{DOC}$  being generally lower than  $K_{POC}$  (Paper II). Most  $K_{OC}$  values for PCDDs are calculated from  $K_{OW}$  and only a few experimentally determined values are available. Literature log  $K_{OC}$  values differ substantially as a result of OM of different origins but also from different methods used (RP-HPLC, fluorescence quenching, equilibrium dialysis etc.). As an example log  $K_{OC}$  values for 2,3,7,8-TCDD show a range of 3.1-7.6, and the range for OCDD is 5.9-7.9 (Mackay, Shiu & Ma, 1992). For PCDFs, no experimentally determined  $K_{OC}$  values were found and values calculated from relationships with  $K_{OW}$  differed by more than two orders of magnitude (Mackay, Shiu & Ma, 1992).

An important assumption made when using calculated  $K_{OC}$  from relationships with  $K_{OW}$ , or when using experimentally values on  $K_{OC}$  from the literature, is that all organic carbon in the soil or sediment matrix has the same binding affinity and capacity for the compound. Results of  $K_{OC}$  determinations for a specific compound vary widely, both for different kinds of organic matter and for different analytical methods. Furthermore, there is a lack of studies on the association of organic compounds to DOM and POM in the same system, either in laboratory experiments or *in situ* / *ex situ* experiments of contaminated soils.

In this thesis, the focus is to describe and quantify the association of HOCs to DOM and POM in soil systems.

## **Research objectives**

The following research objectives were addressed in this thesis:

- 1) To determine the association of TNT, nitrobenzene and aniline to dissolved and particulate soil organic matter in controlled adsorption experiments (Paper I).
  
- 2) To determine the association of 2,4-dichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol to dissolved and particulate soil organic matter in controlled adsorption experiments (Paper II).
  
- 3) To determine the concentration of CP, PCPP, PCDE and PCDD/F associated with dissolved and particulate soil organic matter in aged, contaminated soils (Paper III and IV).



## Experiments and results

The experiments within the thesis focus on sorption of the studied compounds to DOM, POM and the concentration in the aqueous phase. The separation of these three fractions was somewhat different in the different experiments and is therefore described first. In the following section, the methods used for determination of the studied compounds are briefly described. The many different analytical techniques used for the experiments conducted within this thesis are fully described within respective paper (Paper I-IV). Here, a short description and comparison between the different experiments follow.

Paper I: Adsorption of TNT, aniline and nitrobenzene to DOM and POM in controlled equilibrium systems. Nitrobenzene (NB) and aniline were used as model compounds for TNT degradation products and the SOM systems were saturated with Na or Al to investigate differences of present cations on adsorption processes.

Paper II: Adsorption of 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP) and pentachlorophenol (PCP) to DOM and POM. The values of  $K_{DOC}$  and  $K_{POC}$  for the compounds were determined in controlled equilibrium systems.

In paper III and IV: Soil was collected from three contaminated sites and the concentrations of CPs, PCDEs, PCPPs and PCDD/Fs associated to POM, DOM and in the aqueous phase were determined. In paper III, extraction of DOM was performed at different pH to evaluate the method. Firstly to extract different amounts of DOM to evaluate differences in concentration of bound compounds normalized to DOC and secondly to evaluate an eventual pH effect on desorption of the compounds, especially the phenolic compounds. In paper IV, concentrations of the determined compounds in DOM, POM and the aqueous phase were compared between the three soils.

### Soils - sampling, characterization and pre-treatment

#### *Soils*

For the adsorption experiments (Paper I and II), the organic horizon of two spodosols outside Umeå in northern Sweden were used (Table 1). The soil was passed through a 4 mm cutting sieve, homogenized and stored at 4°C until further use.

The soils used in paper III and IV were collected at known “hot spots” (with detected chlorophenols and PCDD/Fs) at three old industrial sites at which technical chlorophenol formulations has been used. The objective was to determine the amount of contaminants normalized to organic carbon in DOM and POM. Beside the presence of contaminants, the three sites were chosen because of their relatively high amount of soil organic matter (LOI 10-42%). Because of human activities for decades, the soils are difficult to describe with conventional

classification systems e.g. Soil Taxonomy (Staff, 1999). In addition to disturbance, residues of wood fibre have been incorporated into the soil. At the Öbacka site, the contaminated soil contained a large fraction of wood fibre and was covered with organic rich top-soil (on average a 30 cm thick layer) with a grass cover. On the two other sites (Sikeå and Hillringsberg) there were no vegetation and the soil was contaminated at the surface. On each of the three sites, one bulk sample was taken at a known contaminated spot. The soil was collected by hand with a spade at the depths at which the contaminants had been detected in previous investigations; Hillringsberg 0-10cm, Sikeå 5-30 cm and Öbacka 40-50 cm. No roots were found in the sampled layer in any of the soils. All samples were sieved (2mm mesh size) and stored at -20°C until further use. Data for the soil is presented in table 1.

Table 1. Properties of the five soils used within the thesis; location, soil description, pH, total cation exchange capacity ( $CEC_{tot}$ ), loss on ignition (LOI), total organic carbon (TOC), black carbon (BC).

Soil	V bäcken	Renberget	Sikeå	Öbacka	Hillringsberg
Used in paper	I	II	III & IV	IV	IV
Location	64°10'N, 19°46'E	64°10'N, 19°46'E	64°9'N, 20°58'E	63°83'N, 20°27'E	59°32'N, 12°37'E
Soil description	Organic horizon of a podsol	Organic horizon of a podsol	Organic rich mineral soil	Organic rich mineral soil	Organic rich mineral soil
pH	3.2	3.0	5.8	5.5	6.8
$CEC_{tot}$ (mmolc /kg)	2110	2170	-	-	-
LOI (%)	-	-	14	42	10
TOC (%)	46	55	4.8	21.3	3.0
BC (% of TOC)	-	-	0.68	0.10	1.16
C/N (POM / DOM)	-	-	32 / 13	202 / 6	17 / 4

### *Separation of DOM and POM*

The distinction between DOM and POM is a major issue in this thesis. The practical separation of DOM from POM has been somewhat different in the different studies, especially when comparing the adsorption studies with the study on contaminated soils (Figure 3). In the adsorption experiments, the DOM-POM systems were equilibrated for at least a week before addition of the contaminants, while in the soils from contaminated sites DOM, POM and aqueous phase were separated 48h after addition of alkaline solution (NaOH).

In paper I, DOM was extracted using a cation exchange resin (Chelex®) and POM was H-saturated with HCl to remove metals. The DOM stock solution and POM were thereafter equilibrated with NaCl or  $AlCl_3$  and NaOH to achieve a pH of 5.1. These new equilibrium systems were thereafter separated using centrifugation. For the kinetic and equilibrium experiments, DOM and POM were mixed and the slurry was spiked with TNT, aniline and nitrobenzene, respectively. Because TNT can degrade within hours in soil, parallel experiments with sterilized

soil (gamma irradiation) was performed to evaluate the effect of degradation on adsorption.

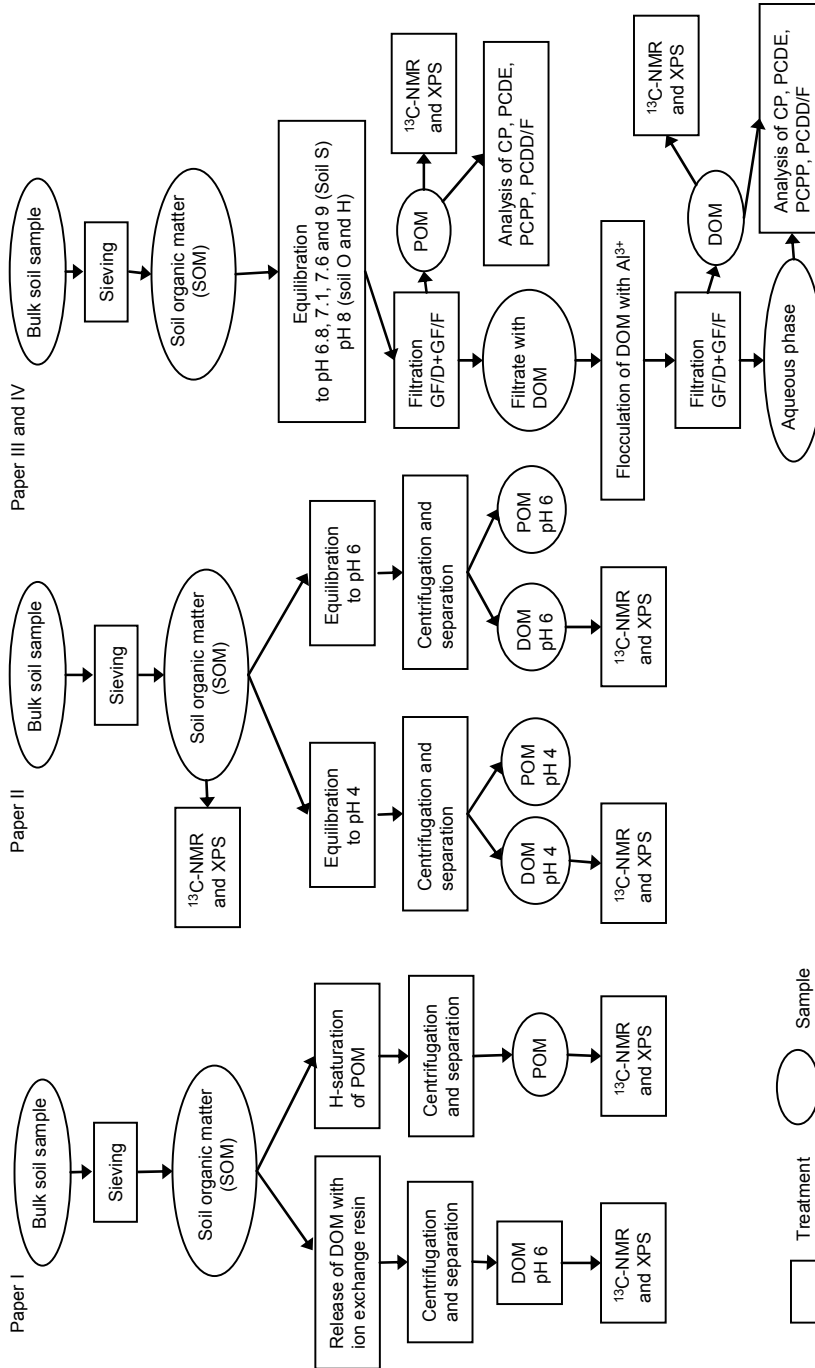


Figure 4. Flowchart over pre-treatment of soil samples and separation into DOM and POM in the various experiments (for details see text and respective paper).

In paper II, the soil was equilibrated with 10 mM NaCl and NaOH to adjust pH to 4 and 6, respectively (for PCP only pH 4). To separate DOM and POM, the soil slurry was centrifuged and the supernatant including DOM decanted. For the adsorption experiments POM, DOM and 10 mM NaCl was mixed (250 mg DOC L<sup>-1</sup>) and spiked with chlorophenols. For details, see paper II.

In the experiments with field contaminated soils (Paper III and IV), DOM was extracted by mixing the soil with 10 mM NaCl and NaOH to raise pH. In paper III, soil from Sikeå was extracted at several pH (6.8, 7.1, 9.1 and three replicates at 7.7) to evaluate a possible pH effect on the extraction of the phenolic compounds, but also to evaluate different sorption properties of the DOM fractions released at different pH. In paper IV, DOM from the two additional soils (Hillringsberg and Öbacka) was extracted at pH 8 only. After NaOH addition, the soil slurries were equilibrated for 48 hours on a horizontal shaker, enough for pH to stabilize and the DOM-POM equilibrium to establish. The soil slurries were filtered (0.7 µm glass fibre filter GF/F, Whatman) and the soil on the filter was rinsed with MilliQ® water until the filtrate was colourless (by visual inspection). A sub-sample was taken from the filtrate for TOC analysis. Al(NO<sub>3</sub>)<sub>3</sub> and Na(OH) were added to flocculate DOM, which was thereafter captured on a GF/F filter. This procedure resulted in three “phases”; POM, DOM and the aqueous phase, which were analysed for CPs, PCDEs, PCPPs and PCDD/Fs. For details, see papers III and IV. The DOC concentrations in all experiments (Paper I – IV) were determined with a TOC analyser (TOC-5000, Shimadzu, Japan).

Studies have revealed lower K<sub>OC</sub> for phenanthrene (Jones & Tiller, 1999) and pyrene (Hur & Schlautman, 2004) for humic acids adsorbed to mineral surfaces, as compared to dissolved humic acids in solution. If these results can be applied to the studied soils, the release of DOM from the solid soil phase in the experiments should not increase the aqueous phase concentrations of free analyte by release of adsorbed analyte.

#### *Organic carbon characterization of DOM and POM*

XPS was used to characterize the gross carbon chemistry of the soil organic matter fractions (POM and DOM) from all soils (Paper I-IV). Four components were identified and quantified from the C 1s spectra: binding energy 285 eV (C-C and C-H bonds), 286.5 eV (C-OH, C-N and C-O-C bonds), 288.0 eV (C=O and N-C=O bonds) and 289.3 eV (O-C=O bonds). The precision for each component was approximately ± 2 atomic %.

Freeze-dried SOM, DOM<sub>pH 4.0</sub> and DOM<sub>pH 6.0</sub> used in the chlorophenol adsorption experiments (Paper I), as well as DOM and POM from the TNT experiments (Paper II) were characterized using CP-MAS <sup>13</sup>C-NMR. Spectra were integrated into four major chemical shift regions; -10 to 45 ppm: alkyl-C, 45-110 ppm: O- and N-alkyl-C, 110-160 ppm: aryl- C and 160-220 ppm: C=O, N-C=O and O-C=O functional groups. The precision of each energy region was ± 2%.

As discussed earlier, XPS and CP-MAS  $^{13}\text{C}$ -NMR have been shown to give similar results for extracted humic substances (Bubert, Lambert & Burba, 2000). Thus, the XPS data should reflect the gross C chemistry fairly well in the soils of paper III and IV.

To determine the amount of black carbon (BC) in the soils from Sikeå, Hillringsberg and Öbacka, TOC was determined in POM and DOM samples, after treatment with 1.0 M HCl, before and after heating at 375 °C. The latter procedure removes non-pyrogenic OC and gives an estimate of black carbon (BC), following the procedure for muffle furnace of Gustafsson et al., (1997).

## **Adsorption experiments with DOM – POM – aqueous phase systems**

Adsorption experiments were performed in two steps. First, kinetic studies were performed for all compounds and soil, followed by equilibrium experiments used for isotherms. In the kinetic studies, the interaction between the compounds and DOM and POM respectively were studied. The compounds studied in adsorption experiments were in paper I; TNT, aniline and nitrobenzene and in paper II; 2,4-dichlorophenol, 2,4,5-trichlorophenol and pentachlorophenol.

### **Kinetic experiments**

For TNT,  $^{14}\text{C}$ -labelled TNT was used and concentrations of both DOM and POM bound analyte were determined. For the rest of the compounds, only the free analyte in the water phase was determined and the total amount bound to SOM (DOM and POM) was calculated as the difference between amount of added compound and amount free analyte. Slurries consisting of soil and 10 mM NaCl solution were pre-equilibrated and checked for pH and DOM concentration. Thereafter the compound of interest was added and the slurry was incubated on an end-over-end shaker for different time periods. The DOM and POM fractions were separated by centrifugation and the supernatant analysed for pH, DOC and the analyte of interest with reversed phase high performance liquid chromatography (RP-HPLC). More detailed descriptions of the analytical methods used can be found in paper I (TNT) and II (chlorophenols). External standard curves were used for quantification. To determine the concentration bound to DOC in the TNT experiment, the HPLC fractions with DOM and free analyte were collected, mixed with scintillation cocktail, and analysed for  $^{14}\text{C}$ -activity by liquid scintillation. The detected  $^{14}\text{C}$ -activity in the TNT experiments represents the sum of TNT and its degradation products, further denoted TNT\*. To evaluate the effect of degradation on adsorption kinetics for TNT\*, the same experiments were performed on irradiated equilibrium systems to study the kinetics in sterile environments.

In the irradiated TNT-system, the adsorption was initially fast and reached equilibrium within approximately one day (Figure 5). As seen from the kinetic study on TNT\*, the soil slurry was not complete sterile as the DOM bound  $^{14}\text{C}$ -activity started to increase after five days, probably due to biological degradation of TNT. In the non-irradiated system, adsorption to POM also reached equilibrium within one day, similar to the irradiated system, suggesting the same adsorption processes to POM. Adsorption to DOM continued to increase, attributed to biological degradation of TNT to its amino-derivatives with higher reactivity towards DOM than non-degraded TNT. Nitrobenzene adsorbed rapidly, within hours, similar to the fast adsorption in the irradiated TNT system, suggesting similar mechanisms in the two systems. Aniline had a fast initial adsorption followed by a slower adsorption continuing still after 3 days. For aniline and nitrobenzene there were no differences between the sterile and non-treated systems.

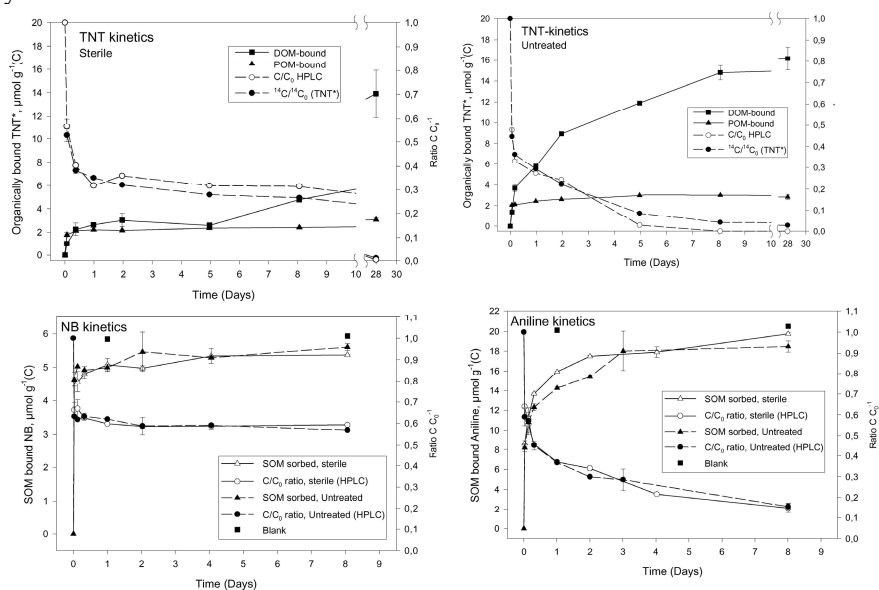


Figure 5. Kinetics of the adsorption of trinitrotoluene (TNT) to dissolved (DOM) and particulate organic matter (POM), and the adsorption of nitrobenzene (NB) and aniline to soil organic matter (SOM). The pH was 5.1 and the ionic strength 50 mM.

In summary, under non-sterile conditions the kinetics of TNT adsorption to POM was in fair agreement with the adsorption of nitrobenzene to SOM and the kinetics of TNT adsorption to DOM was in fair agreement with aniline adsorption to SOM. The sterilization had a strong effect on the adsorption of TNT\* to DOM but not particularly to POM.

In the chlorophenol experiments, adsorption was relatively fast and comparable to nitrobenzene, equilibrium was reached within 2 days for all compounds (Figure 6). Adsorption increased with degree of chlorination of the chlorophenols. Generally, in all experiments, the hydrophobic chemicals nitrobenzene and the

chlorophenols had a fast adsorption phase while aniline and TNT\* adsorption to DOM exhibited a first fast phase followed by a slower phase.

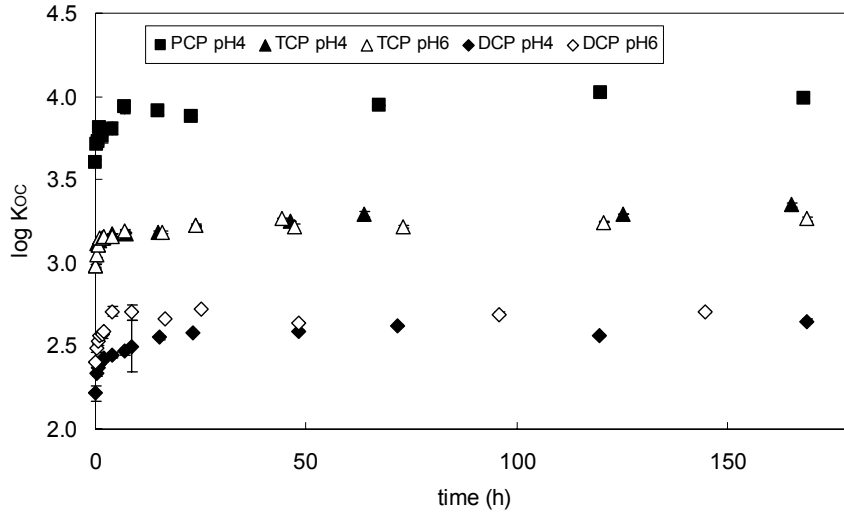


Figure 6. Kinetics of the adsorption of 2,4-dichlorophenol (DCP), 2,4,5-trichlorophenol (TCP) and pentachlorophenol (PCP) to soil organic matter at pH 4 and 6.

### Equilibrium experiments

<sup>14</sup>C-labelled compounds were used in the equilibrium studies to enable detection of compounds bound to DOM. Soil slurries were prepared in the same way as in the kinetic experiments and at the time of equilibrium, as determined in the kinetic experiments, DOM and POM were separated by centrifugation. Equilibrium times used were 22 hours for TNT and nitrobenzene, 72 hours for aniline and 48 hours for the CPs. As in the kinetic experiments, the soil slurries were analysed for pH, DOC, free analyte by RP- HPLC and DOM-bound analyte by liquid scintillation of RP-HPLC fractions.

Linear (Eq 1), Langmuir (Eq 2), Freundlich (Eq 3) and linear + Langmuir (Eq 5) isotherms were used to model adsorption data from the equilibrium experiments. The simplest model with the best fit was chosen for each compound.

$$q = \frac{K_p \times c + K_L \times c \times q_{\max}}{1 + K_L \times c} \quad (\text{Eq 5})$$

Association of NB to DOM and POM were best described by a linear isotherm.  $K_{\text{POC}}$  was greater than  $K_{\text{DOC}}$  indicating greater binding affinity in POM than in DOM (Figure 6).

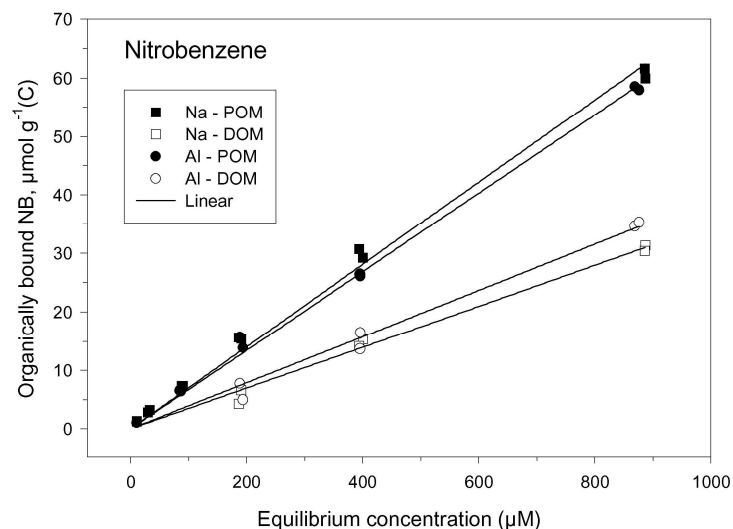


Figure 7. Experimental data and fitted linear isotherms for the adsorption of nitrobenzene to DOM and POM.

The amino-group in aniline is known to form specific bonds with carbonyl functional groups. In line with this, aniline adsorption to DOM and POM could be modelled with the Langmuir isotherm (Figure 8). The binding strength ( $K_L$ ) was similar to DOM and POM while  $q_{max}$  was slightly higher for DOM. The concentration of carbonyl C, as determined with  $^{13}\text{C}$ -NMR and XPS, were similar in DOM and POM. Taking all oxygen containing functional groups into account, the concentration in DOM was 1.4 times higher than POM, about the same relation as in  $q_{max}$  for DOM relative to POM.

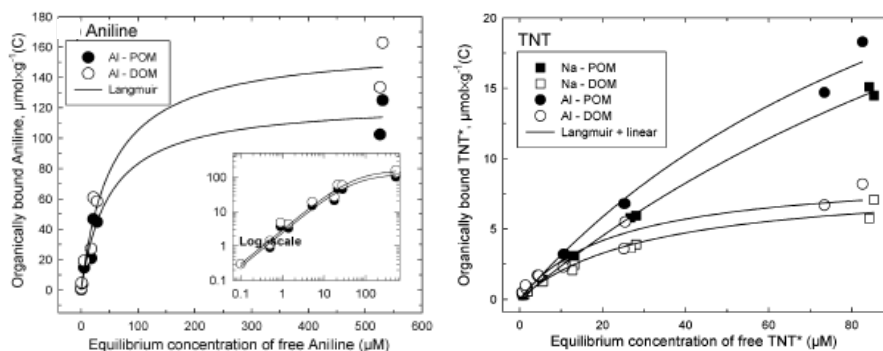


Figure 8. Experimental data and fitted isotherms for the adsorption of aniline and TNT to dissolved (DOM) and particulate soil organic matter (POM). Ionic strength 50mM and pH was 5.1 (aniline) and 4.9 (TNT).

Adsorption of TNT\* to DOM and POM was best described by a combined model of linear and Langmuir isotherms (eq 4) (Figure 8). The  $q_{max}$  and  $K_L$  from the Langmuir part of the model was greater for DOM than for POM. The linear part of the isotherm showed a 3 times higher binding capacity for POM than for



DOM. An interpretation of the TNT\* isotherms in light of the nitrobenzene and aniline isotherms, suggests that the linear part of the TNT\* isotherm is attributed to hydrophobic partitioning of mainly TNT into DOM and POM, and the non-linear part of the TNT\* isotherm is attributed to specific bonding of TNTs amino-derivatives to functional groups in DOM and POM. The TNT degradation products ADNT, DANT and TAT are known to form covalent bonds with soil humic acids (Thorn & Kennedy, 2002). These interpretations are also supported by the results from the kinetic study.

Adsorption of 2,4-DCP, 2,4,5-TCP and PCP to DOM and POM could be described by linear isotherms (Figure 9). Together with the fast adsorption observed in the kinetic experiments, linear isotherms suggest that hydrophobic partitioning is the likely binding mechanism. For DCP,  $K_{DOC}$  and  $K_{POC}$  were similar in magnitude but for TCP and PCP, POM had a greater binding affinity than DOM. The difference between  $K_{DOC}$  and  $K_{POC}$  increased with hydrophobicity (as expressed by  $K_{OW}$ ) of the chlorophenols.

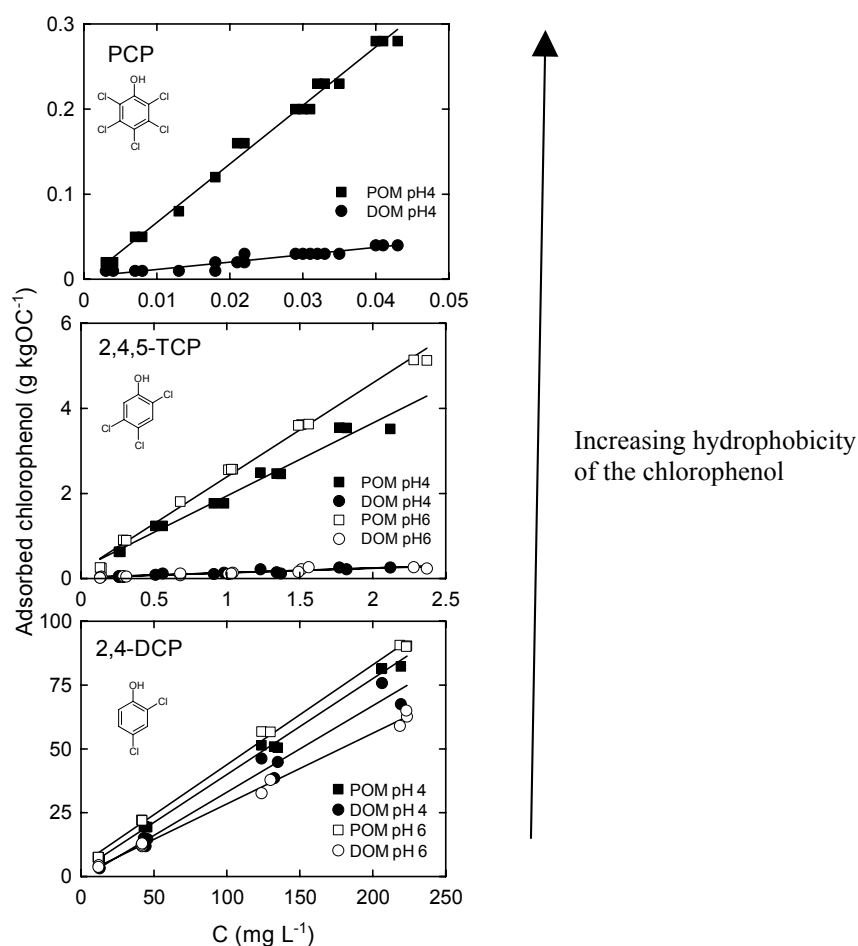


Figure 9. Linear isotherms of the adsorption of chlorophenols to dissolved (DOM) and particulate soil organic matter (POM) at pH 4 and 6.

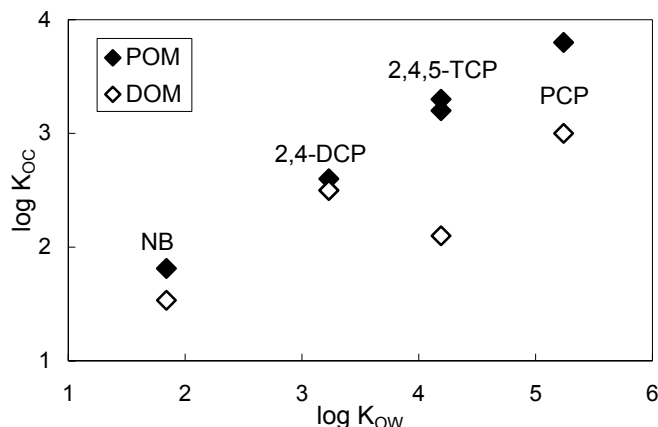


Figure 10. Experimental data on nitrobenzene, 2,4-DCP, 2,4,5-TCP and PCP adsorption to dissolved (DOM) and particulate organic matter (POM) as compared to the relationship (hatched line) between  $\log K_{OW}$  and  $\log K_{OC}$  for phenolic compounds from Schellenberg (1984). Data on  $\log K_{OW}$  from Schellenberg (1984).

$\log K_{POC}$  was linearly correlated with  $\log K_{OW}$  while  $\log K_{DOC}$  was not (Figure 10). The correlation between  $K_{OW}$  and  $K_{POC}$  was similar to the correlation for phenolic compounds reported by Schellenberg (1984). Similarly, Naes et al. (1998) report  $K_{OC}$  for the adsorption of PAHs to particulate organic carbon in sea water to correlate positively with  $K_{OW}$  while  $K_{DOC}$  did not. The difference in partitioning between DOM and POM in both paper I and II could not be explained by differences in carbon structures on the basis of the  $^{13}C$ -NMR or XPS characterization.

## Soils with aged contaminants

Soils with aged contaminants were studied for comparison with the adsorption studies. In these soils the contaminants had been aged for more than 30 years, while in the adsorption studies a few days equilibrium time was used. No previous studies were found in the literature on amounts of chlorophenols, and related organohalogen compounds, in DOM and POM in industrially contaminated soils. Concentrations of CPs, PCPPs, PCDEs and PCDD/Fs were determined in DOM, POM and the aqueous phase of three soils contaminated with chlorophenol formulations. The three soils used in the experiments (Hillringsberg, Sikeå and Öbacka) were sampled, characterized and pre-treated as described above (Section Soils – sampling, characterization and pre-treatment).

The three phases; DOM, POM and aqueous phase, were analysed for CPs, PCPPs, PCDEs and PCDD/Fs. The aqueous phase was extracted with liquid – liquid extraction with dichloromethane. The POM and DOM samples were extracted with toluene using Soxhlet-Dean-Stark equipment. For DOM, the whole

filter with captured DOM was extracted, while for POM, a sub-sample was taken. To enhance the extraction of phenolic compounds, and to dissolve  $\text{Al}(\text{OH})_3$  formed during the DOM flocculation, the samples were acidified with acetic acid before the solvent extractions.

The isotope dilution technique was used in the analysis procedure to correct for losses of analytes during clean-up. Internal standards (IS) were added prior to extraction of the aqueous phase, but after Soxhlet extraction of DOM and POM. Phenolic compounds were separated from neutral compounds with liquid-liquid extraction, using 0.5 M LiOH (Paper III) or 0.5M KOH (Paper IV). The CPs and PCPPs were acetylated and analyzed with gas chromatography coupled to mass spectrometry (GC-MS) according to Liljelind et al. (2003). Clean-up and instrumental analysis of PCDEs and PCDD/Fs followed in general the procedure of Liljelind et al. (2003) except for the use of a carbon column containing AX21 active carbon mixed with Celite® from which the PCDEs were eluted using dichloromethane/hexane (1:1) and the PCDD/Fs were back-eluted with toluene. PCDEs and PCDD/Fs were determined with high resolution GC/ high resolution MS (HRGC/HRMS). Details of standards, clean-up and instrumental analysis is further described in paper III and IV.

The concentrations of compounds bound to DOM and POM were normalized to organic carbon content. Values of  $K_{\text{DOC}}$  and  $K_{\text{POC}}$  were calculated for the compounds determined in the aqueous phase and DOM and/or POM (Eq 6), assuming equilibrium and hydrophobic partitioning. No distinction between dissociated and protonated forms of the phenolic compounds were made in the calculations of  $K_{\text{OC}}$  or concentrations in the different phases.

$$K_{\text{OC}} = \frac{\text{ng}/(\text{kgOC})}{\text{ng}/L} \quad (\text{Eq 6})$$

Determined  $K_{\text{DOC}}$  and  $K_{\text{POC}}$  were compared with relationships between  $K_{\text{OW}}$  and  $K_{\text{OC}}$  reported for dissolved humic substances by Burkhard (2000) (Eq 7) and for soils and sediments by Seth (1999) (Eq 8), respectively. These two models were combined into a third (Eq 9), used for comparison in plots where  $K_{\text{DOC}}$  and  $K_{\text{POC}}$  were plotted, and similarly for the reported 95% confidence intervals of respective model.

$$K_{\text{DOC}} = K_{\text{OW}} \times 0.08 \quad (\text{Eq 7})$$

$$K_{\text{OC}} = K_{\text{OW}} \times 0.33 \quad (\text{Eq 8})$$

$$K_{\text{DOC}} = K_{\text{OC}} \times 0.24 \quad (\text{Eq 9})$$

In Paper III, the effect of pH on contaminant concentrations in the different phases was tested. No correlation between pH and contaminant concentrations in DOM, POM or the aqueous phase was found in the Sikeå soil, and therefore all six samples were treated as replicates. Based on these results from paper III, a single pH of 8 was used for DOM extraction of the Hillringsberg and Öbacka soils (Paper IV). Here, the two studies will be discussed together. The incubation time

used in the experiment in paper III and IV (48h) is enough to reach a constant concentration of DOM in solution (Skylberg & Magnusson, 1995). But the time is most likely too short for a true equilibrium to establish for the partitioning of contaminants between the aqueous phase and DOM or POM in these soils where the contaminants have been aged for decades. The difference in concentrations in DOM and POM is not affected (as the aqueous concentrations are so low) but determined  $K_{OC}$  values could be overestimated.

### Soil properties in Hillringsberg, Sikeå and Öbacka

Degradation of SOM is generally reflected by a decrease in C/N ratio (Stevenson, 1994). The C/N ratio was lower for DOM than for POM in all soils possibly indicating different degrees of humification or degradation, especially in Öbacka (Table 1). This is also explained by the predominance of poorly degraded wood fibres in the Öbacka soil.

The organic carbon chemistry was different between the three soils studied. Hillringsberg had the highest fraction of oxidized functional groups followed by Sikeå and Öbacka, as determined with XPS (Figure 11). No significant differences in the carbon chemistry were revealed between DOM and POM at either Hillringsberg or Sikeå, while the carbon chemistry of DOM and POM differed substantially at Öbacka. The main explanation for this difference was the high content of wood fibre in the soil. The high fraction of C-C carbon and low fraction of oxidized functional groups in Öbacka POM is similar to XPS data for pine wood from Shen et al. (1998).

At the Öbacka site, the contaminated soil was covered with non-contaminated organic rich soil, and probably DOM was transported from this layer downwards to the contaminated layer.

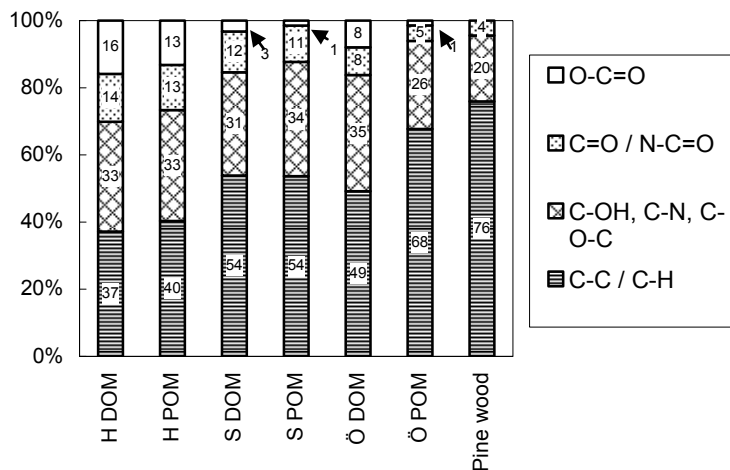


Figure 11. Relative composition of organic carbon structures in dissolved (DOM) and particulate organic matter (POM) from soils at Hillringsberg (H), Sikeå (S) and Öbacka (Ö). Included are XPS data for pine wood reported by (Shen, Mikkola & Rosenholm, 1998).

### *Mass balances of contaminants in DOM, POM and aqueous phase*

The percent of homologues detected in respective phase was calculated. Mass balance calculations of the percentage of compound homologues in the three phases showed differences between the three soils respectively (Table 2 and Paper IV). For the phenolic compounds, the relative amount determined in the aqueous phase and bound to DOM was highest at Öbacka and lowest at Hillringsberg. Of the PCDEs and PCDD/Fs approximately 99% were detected in POM, <1% in DOM and <0.001% in the aqueous phase in all three soils.

Table 2. Relative composition of HOCs in the aqueous phase and associated to DOM and POM in soils at Hillringsberg (H), Sikeå (S) and Öbacka (Ö). The ranges reported correspond to the range of different homologues within respective class of compounds. For PCDE aqueous phase concentrations were below detection limit and reported as not detected (ND).

Compound	Soil	Aqueous phase (%)	DOM (%)	POM (%)
CP	H	0.04-6	0.5-0.6	94.0-99.4
	S	2-11	5-6	83-93
	Ö	8-27	12-17	60-75
PCDE	H	ND	0.4-1	99.0-99.6
	S	ND	1.4-2.6	97.5-98.6
	Ö	ND	0.1-0.7	99.3-99.9
PCDF	H	<0.001	0.5-0.8	99.2-99.5
	S	<0.001	0.4-2.5	97.5-99.6
	Ö	<0.001	0.09-0.23	99.8-99.9
PCDD	H	<0.001	0.21-0.35	99.7-99.8
	S	<0.001	0.03-0.4	99.6-99.9
	Ö	<0.001	0.08-0.42	99.6-99.9

Öbacka had the highest concentration of contaminants of the three soils on a dry mass basis (Paper IV). Because Öbacka also had the highest TOC due to the wood fibres (Table 1), concentrations of contaminants normalised to organic carbon were not always the highest.

### *CP and PCPP*

Tetrachlorophenol was the compound found at Sikeå in highest concentrations, and pentachlorophenol at Hillringsberg and Öbacka. At Hillringsberg, concentrations of CPs normalised to organic carbon was higher in POM than in DOM. At Sikeå and Öbacka, concentrations of CPs associated to DOM and POM were not significantly different. One of the aqueous phase replicates in each soil had to be omitted due to low recoveries.  $K_{\text{DOC}}$  versus  $K_{\text{POC}}$  were therefore plotted for two replicates at Hillringsberg and Öbacka and five replicates at Sikeå (Figure 12a). The  $K_{\text{DOC}}$  and  $K_{\text{POC}}$  in Hillringsberg were significantly higher compared to the other soils, as seen e.g. for PCP.

In the PCPP analysis, recoveries were very low for the Sikeå samples (<20%) and these were excluded from further calculations. For Hillringsberg and Öbacka, recoveries were good (>50%), but different PCPP congeners were found in the different phases. Therefore only samples from Öbacka and Hillringsberg in which the same congeners were detected in all three phases are presented (Figure 12b). At Hillringsberg and Öbacka,  $K_{DOC}$  and  $K_{POC}$  increase with degree of chlorination for CP and PCPP, but not at Sikeå (Figure 12a and b).

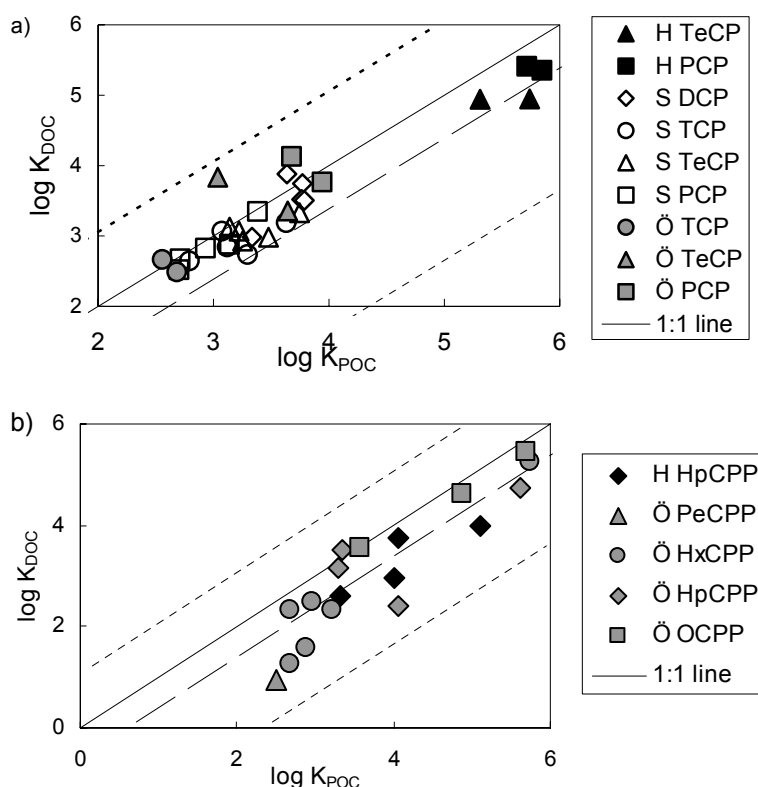


Figure 12. Organic carbon partitioning coefficients for the association of a) di-chlorophenols (DCP), tri-chlorophenols (TCP, tetra-chlorophenols (TeCP) and pentachlorophenol (PCP), and b) penta- (PeCPP), hexa- (HxCPP), hepta- (HpCPP) and octachlorinated (OCPP) phenoxy phenols (right) to dissolved organic matter ( $\log K_{DOC}$ ) and to particulate soil organic matter ( $\log K_{POC}$ ) determined in three soils with chlorophenol contamination; Sikeå (S), Hillringsberg (H) and Öbacka (Ö). The hatched line represents the average relative partitioning between DOM and POM calculated from relationships between KOW and  $K_{DOC}$  reported by Burkhard et al. (1999) and between KOW and KOC reported by Seth et al. (2000). The dotted lines are the 95% confidence interval of the two models.

#### PCDE, PCDF and PCDD

The neutral compounds, PCDEs and PCDD/Fs, were detected in higher concentrations in POM than in DOM. The relative partitioning to POM increased with hydrophobicity of the compound group in the order  $PCDE < PCDF < PCDD$ .

The PCDE homolog profiles were different in the three soils, but similar in DOM and POM of the respective soil for Hillringsberg and Sikeå. At Hillringsberg, OCDE and NoCDE homologues dominated both in POM and in DOM. At Sikeå, HpCDE and OCDE dominated. Öbacka had a more even distribution in POM with highest concentrations of HxCDE, HpCDE and OCDE, while OCDE dominated in DOM. Concentrations of PCDEs were higher in POM than in DOM with the exception of OCDE and NoCDE in Öbacka, which were found in the same concentrations in the two phases (the grey squares found on the 1:1 line in figure 13). Higher concentrations were found in POM in all soils and the relative concentrations in DOM and POM were similar in all soils (Figure 13). The relative concentrations in DOM and POM did not change with degree of chlorination among the PCDEs. Aqueous phase concentrations were below detection limit and no  $K_{OC}$  values could therefore be calculated.

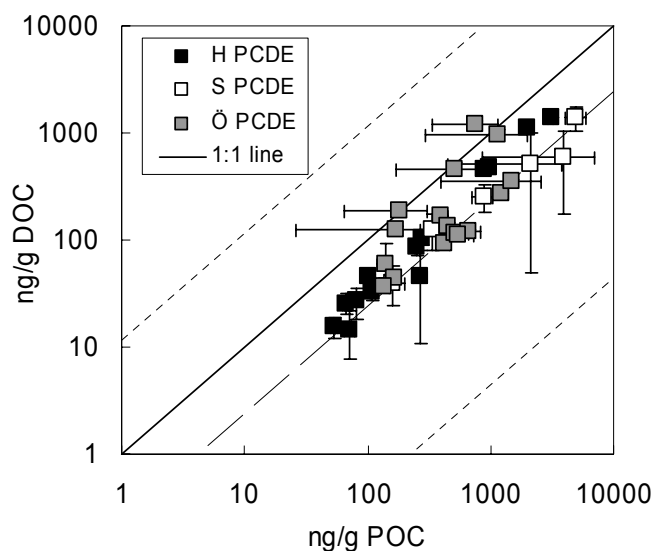


Figure 13. Concentrations of polychlorinated diphenyl ethers (PCDE) in dissolved organic matter and particulate organic matter normalized to organic carbon, in three soils with chlorophenol contamination; Hillringsberg (H), Sikeå (S) and Öbacka (Ö). The hatched line represents the average relative partitioning between DOM and POM calculated from relationships between  $K_{OW}$  and  $K_{DOC}$  reported by Burkhard et al. (1999) and between  $K_{OW}$  and  $K_{POC}$  reported Seth et al. (2000). The dotted lines are the 95% confidence interval of the two models.

The PCDD/Fs were detected in all three phases in all soils. The homolog profiles differed between the soils but were similar in the three phases within a soil. At Hillringsberg, HpCDF and OCDD were the dominating homologues, and at Sikeå, HpCDF and HpCDD dominated. At Öbacka, HpCDF was the dominating PCDF. The Öbacka PCDD concentrations differed considerably in the POM samples, the sum of all PCDD varied from 26 to 235  $\mu\text{g/gOC}$ . Though looking at each replicate the concentration of OCDD was slightly higher than HxCDD and HpCDD. PCDD concentrations in Öbacka DOM and aqueous phase did not vary

between the replicates. The different compositions of PCDEs and PCDD/Fs in the three soils are probably the result of the original contamination of these compounds in the chlorophenol preservatives used at the different sites and not the result of chemical or biological processes in the soil.

In all soils, PCDF and PCDD were found in higher concentrations in POM than in DOM, the difference between DOM and POM being greater for PCDDs than for PCDFs.

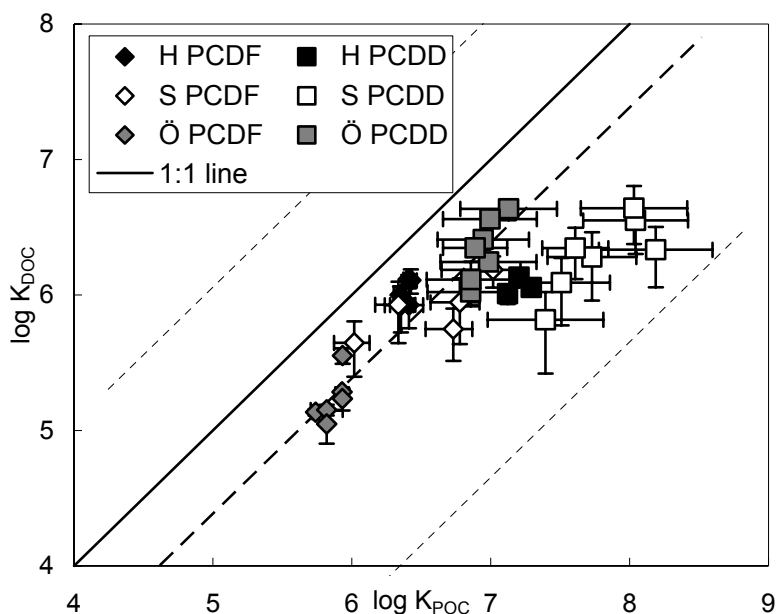


Figure 14. Association of PCDD/Fs to dissolved- (DOM) and particulate soil organic matter (POM) in three soils with chlorophenol contamination; Hillringsberg (H) and Öbacka (Ö) expressed as organic carbon normalized partitioning coefficients for the association of PCDD/Fs to DOM ( $K_{DOC}$ ) and to POM ( $K_{POC}$ ). The hatched line represents the average relative partitioning to DOM and POM calculated from relationships between  $K_{OW}$  and  $K_{DOC}$  reported by Burkhard et al. (1999) and between  $K_{OW}$  and  $K_{POC}$  reported Seth et al. (2000). The dotted lines are the 95% confidence interval of the two models.

Interesting to note is that  $\log K_{DOC}$  for PCDDs covered the same range in all soils while for PCDFs  $\log K_{DOC}$  was lower in the soil at Öbacka than at Sikeå and Hillringsberg (Figure 14). For PCDDs, there is a trend in  $\log K_{POC}$  following the order Ö<H<S and for PCDFs Ö<H=S. The relatively lower sorption capacity (normalised to OC) at Öbacka may be explained by the high fraction wood fibre in the soil constituting most of the OC, as also seen in the XPS analysis. Though, wood fibre is often present in the soil at former wood preserving industries and therefore important to consider in risk assessments of these sites.

The DOM fraction at the Öbacka site is, as discussed above, probably a mixture of DOM from the wood fibres and DOM released from the soil overlaying the contaminated wood fibers. This DOM can potentially enhance the mobility of



contaminants in the contaminated layer. Ground water samples taken at Öbacka with high DOC levels (around 100 mg L<sup>-1</sup>) and high contaminant concentrations (unpublished data, Persson, 2006) indicate that DOM is transported through the soil in layers that adsorb neither DOM nor contaminants. Concentrations of PCDEs and PCDD/Fs in these ground water samples were only detected on particles captured on filters, while CP and PCPP were found in the aqueous phase too.

## Differences in DOM and POM sorption of HOC

The main mechanism of interaction between HOC and SOM was hydrophobic partitioning, as indicated by the determined linear isotherms for the adsorption of CPs and NB to DOM and POM in paper I and II. In Paper III and IV, no isotherm or kinetic experiments were performed and we can only assume hydrophobic partitioning as the main HOC-SOM interaction. Hydrophobic partitioning is mainly a physical process driven by an entropy change when the hydrophobic molecule migrates from the polar aqueous phase to a hydrophobic surface or matrix such as SOM.

An increasing partitioning in favour of POM over DOM with increasing hydrophobicity of organic compounds were found both in the adsorption studies with CPs (Paper II) and NB (Paper I) and in the soils with aged contaminants (Paper III and IV). This difference could not be explained by the methods used to characterize SOM. Neither spectroscopic (<sup>13</sup>C-NMR and XPS), nor bulk chemical analyses could reveal chemical differences large enough to explain the shift in partitioning in favour of POM over DOM. The C/N ratio did differ between DOM and POM in all soils, most probably reflecting greater degree of degradation of DOM relative POM. Small amounts of soot carbon has been shown to explain extremely high adsorption affinities of HOCs to sediment organic matter (Bucheli & Gustafsson, 2000), but the BC concentrations determined in the soils within this thesis were not enough to explain the difference in adsorption. Obviously other properties not measured in this study must be important.

The DOM fraction extracted from the soils in paper III and IV represents a potentially mobile fraction of SOM consisting of truly dissolved DOM, as well as particles and colloids passing the 0.7µm filter. The DOM and POM fractions in paper I and II were separated by centrifugation and these DOM fractions also include colloids. Even though DOM was partly a mobilized fraction of SOM, the contaminant concentration normalized to organic carbon was much lower in DOM than in POM. Mineral bound humic acids adsorb less PAHs than humic acids in solution (Hur & Schlautman, 2004; Jones & Tiller, 1999). If this stronger association of contaminants to DOM in solution, as compared to when bound to POM or mineral phases, is valid for these compounds, the release of DOM should not increase the aqueous phase concentration. It also implies that contaminants in the potentially mobile SOM fraction does not contribute to the observed higher

binding capacity of POM and that POM in average has fundamentally different properties (stronger binding affinity towards HOCs) as compared to DOM.

As no difference in organic carbon chemistry was observed between DOM and POM in all soils but Öbacka, the main reason for DOM to stay in solution, should be its smaller molecular size as compared to POM. Increasing molecular size of dissolved humic substances has in several studies been shown to increase the binding affinity of PAHs (Engebretson & Von Wandruszka, 1997; Ragle, Engebretson & vonWandruszka, 1997; vonWandruszka, Ragle & Engebretson, 1997). On the basis of these findings, it is plausible that the greater partitioning of HOCs to POM than to DOM may be explained by larger hydrophobic structures in POM than in DOM. This hypothesis still needs to be confirmed. For particulate soil organic matter, there is to my knowledge no straightforward way of determining the molecular size or hydrophobic moieties.

## **Environmental implications and future research needs**

Risk assessment of contaminated sites includes estimates of the mobility of contaminants in soil and transport from soil to surface waters. These estimates are often based on geochemical modelling. A prerequisite for an appropriate model is correctly determined  $K_{DOC}$  and  $K_{POC}$  values, relevant for the soil at the site. On the basis of the findings in this thesis, data on  $K_{DOC}$  and  $K_{POC}$  should be explicitly determined and not calculated from relationships between for example  $K_{OW}$  and  $K_{OC}$ . Models estimating  $K_{OC}$  from  $K_{OW}$ , do not take differences in SOM into account and can only be used as a very rough tool for comparing compound classes of very different hydrophobicities.

The relative partitioning between DOM and POM can be very different for different groups of compounds. For compounds with reactive functional groups, in this thesis exemplified by aniline and degradation products of TNT, specific bonds to functional groups of SOM are formed, resulting in similar binding affinities and capacities for DOM and POM for the soil studied. In contrast, the binding affinity of HOCs was greater to POM than to DOM. As reported in paper IV,  $K_{DOC}$  and  $K_{POC}$  for the same compound can differ by orders of magnitude among different soils. Partitioning constants used for modelling needs to be carefully chosen based on the properties of both the compound and the soil.

Release of DOM, from top soils with high organic matter content, covering contaminated soil layers, could increase the mobility of HOCs. The Öbacka site is an example where DOM is probably transported from the topsoil to the soil layer with chlorophenol contamination. The wood fibre in the soil is not likely to contribute significantly to the overall release of DOM. High DOC and contaminant concentrations were found in ground water at the Öbacka site (Unpublished data, Persson et al 2006), indicating transport of DOM and associated compounds through soil layers unable to retain and sequester DOM.

The hydrology on the specific site is of great importance when estimating the mobility of the HOC-DOM complexes. Soil layers with Al and Fe oxides would efficiently bind DOM, decreasing the mobility of HOC-DOM complexes.

To generalize the findings about the adsorption of organic chemicals to DOM and POM in different soil types, more research is needed to identify and quantify the important properties of SOM controlling adsorption of HOCs. As discussed above, the size of hydrophobic moieties is one interesting property likely differing between DOM and POM. Furthermore, factors affecting the rate of release of DOM and associated compounds, such as climate, plants and the soil microbial community, need to be investigated.

## Major conclusions

- Adsorption of aniline was best described by the Langmuir isotherm, supporting previous findings of a specific interaction between amino groups of aniline and carbonyl groups of SOM. The adsorption capacity was similar in POM and DOM, indicating similar concentrations of the active sites in POM and DOM.
- Adsorption of nitrobenzene to DOM and POM was best described by linear isotherms, indicating hydrophobic partitioning to be the likely binding mechanism.  $K_{POC}$  was twice as high as  $K_{DOC}$ , indicating greater binding affinity for NB in POM than in DOM.
- Adsorption of TNT to POM and DOM was best described with a combined model of linear and Langmuir isotherms. The greater partitioning to POM is in agreement with the hydrophobic partitioning of NB to POM. The more specific adsorption to DOM is explained by degradation of the nitro-groups TNT to amino-groups with similar binding properties as aniline.
- In all adsorption experiments resulting in linear isotherms, adsorption to POM was greater than to DOM.
- The difference in partitioning of HOCs to POM relative DOM, determined in controlled equilibrium systems, increased with hydrophobicity of the organic compounds  $NB < 2,4\text{-DCP} < 2,4,5\text{-TCP} < PCP$ .
- In the three contaminated soils, higher concentrations of neutral contaminants (normalized to organic carbon) were determined in POM than in DOM.
- Partitioning of HOCs to POM relative to DOM in the contaminated soils increased with hydrophobicity of the compound in the order,  $CP < PCDE < PCDF < PCDD$ .
- Other properties of SOM than carbon chemistry, as determined by XPS or  $^{13}\text{C}$ -NMR should be responsible for the difference in adsorption capacity of DOM and POM.

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