Sorption and transport of heterocyclic aromatic compounds in soils

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Sorption and transport of heterocyclic aromatic compounds in soils

Abstract

Nitrogen-, sulphur-, and oxygen-heterocyclic aromatic compounds (NSOs) are common groundwater pollutants at sites contaminated by coal tar; however, they are frequently overlooked. NSOs have also been found at others places. For instance, benzotriazole, a commonly used additive in aircraft de-icing fluids and an anticorrosive agent, has been detected in the groundwater at airports. NSOs are of special interest because they often are strong smelling, toxic, and have high water solubilities. Accurate prediction of NSOs' leaching potential and contamination of groundwater requires improved understanding of the sorption of these compounds. The major goals of this study were to identify the various sorption processes that NSOs undergo in aquifers and to investigate the effect of environmental factors on their sorption processes. In this study, a soil column chromatography (SCC) method was validated and applied to characterize the sorption behavior of a wide variety of NSOs to reference soils (Eurosoils 1-5).

Pyrrole, 1-methylpyrrole and pyrimidine were hardly retarded in any soil. The sorption of *S*- and *O*-heterocyclic compounds (thiophene, benzothiophene, 5-methylbenzo[b]thiophene, benzofuran, 2-methylbenzofuran and 2,3-dimethylbenzofuran) was generally controlled by non-specific interactions (partitioning) with soil organic carbon (OC). There is no significant effect of ionic strength and inorganic chemical composition in the aqueous phase on the sorption of these compounds.

Cation exchange was the dominant mechanism in the overall sorption of ionizable compounds (pyridine, 2-methylpyridine, quinoline, isoquinoline, and quinaldine), even at pH values that allow only for a low fraction of the compound to be protonated in aqueous solution. Soil pH was the most important factor influencing the sorption of these compounds. Increasing Ca^{2+} concentration in aqueous solution reduced their sorption due to competition between Ca^{2+} and organic cationic species for the sorption sites. At the same ionic strength, by changing Ca^{2+} to K^+ in the mobile phase, the sorption of protonated *N*-heterocyclic species was enhanced.

The sorption of NSOs can be described by a conceptual model including partition to soil OC, cation exchange, and an additional sorption process (most probably surface complexation of the neutral species), i.e., $K_d = K_{d,part} + K_{d,BH^+} + K_{d,B}$. A fairly precise assessment of sorption

can be expected based on this equation for most *N*-, *S*-, and *O*-heterocyclic compounds and soils without considering additional soil specific properties (e.g., accessible surface, charge density, etc.). Based on this conceptual model, K_d of quinoline and isoquinoline was described accurately in all of the five soil samples, which differed largely in their composition. Sorption of quinaldine, 2-methylpyridine and pyridine was explained by the model in all soils within a factor of 2, except in Eurosoil 1.

Ternary surface complexation involving Ca^{2+} is suggested to be an important mechanism in the sorption of benzotriazole.

Transport of quinoline, quinaldine, and benzotriazole in the column packed with Eurosoil 4 were simulated with a one-site first order model. It shows that the degree of nonequilibrium resulting from intraparticle diffusion is negligible in the column experiments designed here. The tailing of breakthrough curves was primarily caused by nonlinear sorption, although modeled exponents of the Freundlich isotherms were not less than 0.7 for the investigated compounds.

Overall, considering the sorption in a three-dimensional approach (compound-soil-water properties) gives an improved understanding of the fate of polar organic compounds in the subsurface. Further work on specific sorption mechanisms (e.g., surface complexation) for certain NSOs should be carried out in order to quantify the sorption of such compounds more precisely.

Sorptions- und Transportverhalten von heterozyklischen aromatischen Verbindungen in Böden

Kurzfassung

Stickstoff-, schwefel- und sauerstoffhaltige aromatische Verbindungen (NSO-Heteroaromaten) treten häufig im Grundwasser an Standorten mit Kohlenteerverschmutzungen auf, finden jedoch kaum Beachtung. Es gibt mehrere weitere Quellen für NSO-Heteroaromaten, so konnte z.B. Benzotriazol, das als Zusatz in Flugzeugenteisungsmitteln und als Korrosionsinhibitor eingesetzt wird, auch im Grundwasser mehrerer Flughäfen nachgewiesen werden. Da es sich hierbei um giftige, olfaktorisch unangenehme Verbindungen mit hoher Wasserlöslichkeit handelt, sind NSO-Heteroaromaten von besonderem Interesse. Eine genaue Vorhersage über ihr Sickerungsverhalten und das Grundwasserkontaminationspotential erfordert ein sehr gutes Verständnis des Sorptionsverhaltens dieser Verbindungen. Hauptziel der Studie war die Identifizierung der verschiedenen Sorptionsprozesse, denen NSO-Heteroaromaten im Grundwasserleiter unterliegen und die Untersuchung der darauf wirksamen Umweltfaktoren. In der vorliegenden Studie wurde eine Methode für die Bodensäulenchromatographie evaluiert und angewandt, um das Sorptionsverhalten von NSO-Heteroaromaten in Referenzböden (Eurosoil 1-5) zu charakterisieren.

In den untersuchten Böden wurden Pyrrol, 1-Methylpyrrol und Pyrimidin kaum retardiert. Die Sorption von heterozyklischen *S*- und *O*-Verbindungen (Thiophen, Benzothiophen, 5-Methylbenzo[b]thiophen, Benzofuran, 2-Methylbenzofuran and 2,3-Dimethylbenzofuran) wurde im allgemeinen durch unspezifische Adsorptionsreaktionen an organischen Kohlenstoff beherrscht. Es konnte kein signifikanter Einfluss der Ionenstärke und der anorganischen Bestandteile der wässrigen Phase auf das Sorptionsverhalten dieser Verbindungen festgestellt werden.

Bei der Sorption ionisierbarer Verbindungen (Pyridin, 2-Methylpyridin, Chinolin, Isochinolin, und Chinaldin) war Kationenaustausch der vorherrschende Mechanismus, sogar bei pH-Werten, bei denen nur ein sehr geringer Anteil der Verbindung dissoziiert vorliegt. Die entscheidende Einflussgröße beim Sorptionsverhalten dieser Verbindungen war der pH-Wert des Bodens. Bei zunehmender Ca^{2+}-Konzentration in der wässrigen Lösung wird die Sorption aufgrund der Konkurrenz von Ca^{2+}-Ionen und den positiv geladenen organischen Verbindungen bei der Belegung von Sorptionsplätzen schwächer. Wird Ca^{2+} mit K^+ in der

mobilen Phase ausgetauscht (bei gleicher Ionenstärke), verstärkt sich die Sorption von positiv geladenen heterozyklischen *N*-haltigen Verbindungen.

Das Sorptionsverhalten von NSO-Heteroaromaten kann durch ein konzeptionelles Modell beschrieben werden, das sowohl die Adsorption an organischen Kohlenstoff, als auch den Kationenaustausch und einen zusätzlichen Sorptionsmechanismus (hauptsächlich die Oberflächenkomplexierung ungeladener Verbindungen) umfasst: $K_d = K_{d,part} + K_{d,BH^+} + K_{d,B}$. Aufgrund dieser Gleichung kann die Sorption für die meisten heterozyklischen *N*-, *S*- und *O*-haltigen aromatischen Verbindungen und Böden relativ genau abgeschätzt werden, ohne dass weitere bodenspezifische Eigenschaften (z.B. nutzbare Oberfläche, Ladungsdichte, usw.) einbezogen werden müssen. So konnte der K_d von Chinolin und Isochinolin in jedem der fünf Böden trotz der sehr unterschiedlichen Zusammensetzungen korrekt beschrieben werden. Die Sorption von Chinaldin, 2-Methylpyridin und Pyridin konnte durch das Modell innerhalb eines Faktors 2 in allen Böden, mit Ausnahme von Eurosoil 1, beschrieben werden.

Es wird angenommen, dass ternäre Oberflächenkomplexe unter Beteiligung von Ca^{2+}-Ionen bei der Sorption von Benzotriazol eine entscheidende Rolle spielen.

Der Transport von Chinolin, Chinaldin und Benzotriazol in einer mit Eurosoil 4 gepackten Säule wurde mithilfe eines einseitigen Modells erster Ordnung simuliert. Es zeigte, dass der Grad an Ungleichgewicht, der durch intrapartikuläre Diffusionsprozesse zustande kommt, in den hier durchgeführten Säulenexperimenten vernachlässigbar gering ist. Ein Tailing der Durchbruchskurven wurde hauptsächlich durch nicht-lineare Sorptionsprozesse verursacht, wobei der simulierte Exponent der Freundlich-Isothermen für die untersuchten Substanzen nicht kleiner als 0.7 war.

Zusammenfassend kann gesagt werden, dass die Betrachtung der Sorption mithilfe eines dreidimensionalen Ansatzes (Eigenschaften der Verbindung, des Bodens und der wässrigen Phase) zu einem besseren Verständnis des Verbleibs polarer organischer Verbindungen im Untergrund führt. Weitere Arbeiten zu spezifischen Sorptionsmechanismen (z.B. Oberflächenkomplexierung) einzelner *N*-, *S*- und *O*-Heteroaromaten sind nötig, um künftig die Sorption dieser Verbindungen genauer quantifizieren zu können.

Notation

C_s	sorbed phase concentration [mg/kg]
C_w	aqueous phase concentration [mg/L]
D	hydrodynamic dispersion coefficient [cm^2/min]
D_L	longitudinal dispersion coefficient [cm^2/min]
f_{ion}	fraction of ionic species of organic compounds [-]
f_{oc}	fraction of organic carbon (OC) [-]
K_B	constant for specific interaction process of neutral species [-]
K_{BH^+}	constant for cation exchange process [-]
K_d	sorption distribution coefficient [L/kg]
K_d'	apparent sorption distribution coefficient [L/kg]
$K_{d,B}$	contribution of specific interaction of the neutral organic species [L/kg]
K_{d,BH^+}	contribution of cation exchange of the protonated organic species [L/kg]
$K_{d,part}$	sorption due to partition to soil organic carbon [L/kg]
K_f	Freundlich affinity constant [$mg^{1-n}L^n kg^{-1}$]
K_{oc}	partioning coefficient [L/kg]
K_{ow}	octanol-water distribution coefficient [-]
K_{part}	constant for partition to soil organic carbon [-]
n	exponent [-]
q	flowrate [mL/min]
R	gas constant [8.3145 J/(mol K)]
R_f	retardation factor [-]
t	retention time of target compounds [s], or [pore volume]
t'	traveling time through the injector and connecting capillary between injector and UV detector [s], or [pore volume]
t_F	final point of data collection from column chromatogram [s], or [pore volume]
t_o	dead time (or hold-up time,) of column (i.e., retention time of conservative tracer) [s], or [pore volume]
T	temperature [K]
v	pore water velocity [mm/s]
ΔH	enthalpy change [kJ/mol]
ΔS	entropy change [kJ/(mol K)]
α	mass transfer coefficient [1/s]

α_L	longitudinal dispersivity mass transfer coefficient [mm]
χ^2	weighted least square [-]
ρ_b	bulk density [g/cm^3]
θ	porosity [-]
δ	sensitivity function [-]
μ_1	first moment [min] or [pore volume]

Contents

1. Introduction

1.1 Background

The process in which chemicals become associated with a solid phase is generally referred to as *sorption*. Sorption processes play a major role in determining the environmental fate and impact of organic contaminants. In soils, sorption affects almost all specific fate processes including volatilisation, bioavailability, biodegradability, photolysis, and hydrolysis (Doucette, 2003). Sorption is generally quantified by a distribution coefficient (K_d). In a soil-water system, K_d for a certain organic compound is defined as the ratio of its concentration in the solid phase (C_s) to its concentration in aqueous phase (C_w) at equilibrium (i.e., K_d=C_s/C_w).

*Ab*sorption (partitioning into a bulk phase) and *ad*sorption (partitioning on a surface) are the general terms to describe the sorption processes. Absorptive partitioning describes the process by which a solute is distributed between two bulk phases (e.g., between water and organic matter) and is commonly referred to as just "Partitioning", as it is here, whereas *ad*sorptive partitioning describes the distribution between a bulk phase and a surface. The mechanisms involved in how organic compounds sorb to the various natural solids in soils include (i) a neutral organic compound transferring back and forth from the water and into/onto organic matter (partitioning + *ad*sorption); (ii) the sorbate *adsorbing to a* mineral surface; (iii) a reactive moiety of the sorbate covalently binding to a surface moeitiy (chemosorption); and (iv) a charged sorbate being electrostatically attracted to an oppositely charged surface site (Schwarzenbach et al., 2002). The factors influencing these processes can be depicted in three separate axes: soil, water and organic compound, as is shown in Figure 1-1.

Apolar compounds have been found to readily absorb into the organic material of soils and sediments (Chiou, 2002; Grathwohl, 1998). However, for polar organic compounds, *ad*sorption seems to be the dominating mechanism due to specific interactions (Cox et al., 1997; Farrell et al., 1999; Fesch et al., 1998; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996).

Environmental variables such as temperature (Spurlock, 1995), ionic strength (Alva and Singh, 1991; Rao and Asolekar, 2001), cation type (Dontsova and Bigham, 2005; Haderlein and Schwarzenbach, 1993; Haderlein et al., 1996; Li et al., 2004), and solution pH (Spadotto and Hornsby, 2003; Weber et al., 2003; Zhu et al., 2003a) can affect the sorption of organic compounds, especially polar compounds.

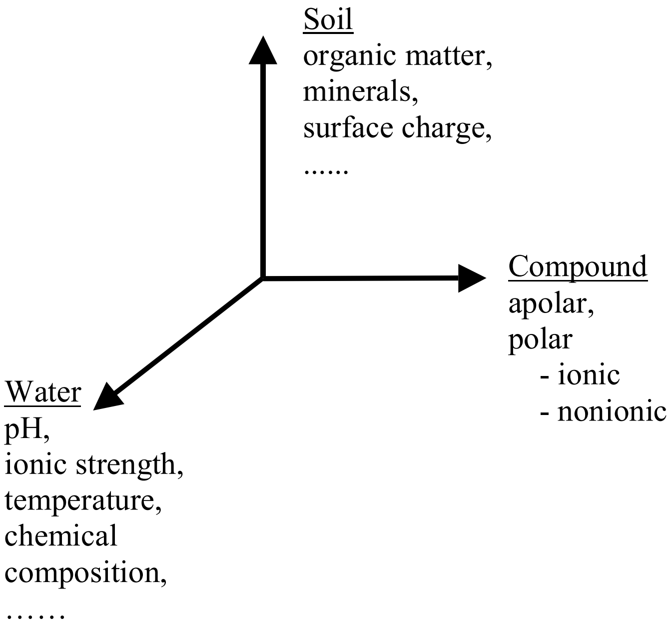


Figure 1-1 Factors influencing K_d demonstrated in a three dimensional system

1.2 Heterocyclic aromatic compounds

Heterocyclic aromatic compounds (NSOs), which contain either a nitrogen, oxygen, or sulfur atom within a carbon based ring-structure, are frequently found in groundwater at the sites contaminated with coal tar, such as in the vicinity of old gasworks and wood treatment facilities (Broholm et al., 1999; Goerlitz et al., 1985; Johansen et al., 1998). NSOs have been shown to exhibit persistence in some cases (Zamfirescu and Grathwohl, 2001). NSOs have also been found at others places. For instance benzotriazole, a commonly used additive in aircraft de-icing fluids and an anticorrosive agent (Hart et al., 2004; Hem et al., 2003), has been detected in the groundwater at several international airports (Cancilla et al., 1998; Hem et al., 2003). NSOs are of special interest because of their strong adverse organoleptic properties, toxicities, and high solubilities (Johansen et al., 1998).

Sorption to soils is one of the key processes that determine the fate of NSOs in the subsurface. To date, the sorption of NSOs to soils and minerals has been studied mainly for the organic bases quinoline (Ainsworth et al., 1987; Burgos et al., 2002; Helmy et al., 1983; Thomsen et al., 1999; Zachara et al., 1986; Zachara et al., 1988), pyridine (Zachara et al., 1987; Zachara et al., 1990; Zhu et al., 2003b), and 2-methylpyridine (O'Loughlin et al., 2000). Cation exchange of the ionized form of these compounds proved to be the dominant sorption mechanism, even at pHs when low fractions of the cationic form were present (Ainsworth et al., 1987; Zachara et al., 1986). In many cases, the highest sorption was exhibited at the pH range corresponding to the pK_a of the solutes (Thomsen et al., 1999). The explanation for this is as follows: as the pH is lowered below the pK_a, the fraction of the cationic species increases and the cation exchange surface becomes more positively charged. This causes repulsion between the surface and the cationic species. The sorption of a neutral NOS, benzothiophene, to clay till has been studied, and partitioning into organic carbon was found to be the dominant sorption mechanism (Broholm et al., 1999).

Besides the partitioning of neutral NSOs into organic matter and cation exchange of cationic NSOs on cationic exchange sites, additional specific interactions such as ternary complex formation (Fein, 2002) may also play an important role in the overall sorption of NSOs with specific properties (e.g., benzotriazole). In order to better understand the processes involved in the sorption of NSOs in aquifers, it is necessary to perform a systematic study on the sorption of a large set of NSOs to various soils under different conditions.

1.3 Methods to study sorption

Batch experiments. The conventional approach to investigate the sorption of organic contaminants in water-soil systems is to carry out batch experiments (OECD, 2000). In batch experiments, a given amount of sorbent (i.e., soil) is mixed with a defined volume of an aqueous solution (at a given pH and ionic strength) containing the chemical of interest. The concentrations in both the aqueous and solid phases are then determined as a function of time or after sorption equilibrium has been achieved. The K_d can then be determined, as well as the organic carbon-water partitioning coefficient K_{oc} ($=K_d/f_{oc}$), as long as the fraction of organic carbon in the soil, f_{oc}, is known.

The batch experiment is conceptually simple and reliable although somewhat tedious and time consuming. When the extent of sorption is very low, e.g., due to a low content of soil organic matter (e.g., <0.1%), batch experiments may not yield reliable values, as it is difficult to quantify the solid phase concentration or the difference between the initial and equilibrium aqueous concentrations.

Column Experiments. As an alternative to batch experiments, packed column or miscible displacement techniques are widely used (Brusseau et al., 1989; Buergisser et al., 1993; Das et al., 2004; Fesch et al., 1998; Lee et al., 1991; Mader et al., 1997). In this kind of approach an aqueous solution consisting of the desired pH, ionic strength and concentration of the sorbent, is pumped through a soil column. The concentration of the chemical in the column effluent is monitored over time. A simple algebraic relationship between K_d and retardation factor (R_f) or reactive transport models can be used to calculate K_d values from the obtained breakthrough curves if sorption equilibrium is guaranteed in the experimental set up (Brusseau, 1994; Fesch et al., 1998; Mader et al., 1997).

Soil column experiments have also been used to predict K_{oc} from measured retardation factors (R_f) based on single parameter linear free energy relationships (LFERs of the type $K_{oc} = aR_f + b$ (a and b are fitting parameters)) (Xu et al., 2002; Xu et al., 2001).

Compared with batch experiments, column experiments have several advantages: (i) the solid to solution ratio is closer to that encountered in the natural systems and it better mimics the transport of organic compounds in soil-water system; (ii) it offers the possibility to rapidly determine the parameters affecting sorption without the problems inherent to batch experiments; (iii) it is a preferable experimental approach, especially for the case that sorption is hardly detectable in the batch experiment (e.g., for the highly water soluble organic compounds investigated in this study), because it provides higher soil/water ratio than in batch experiment; (iv) it can provide information both on sorption and desorption processes; and (v) one can directly measure the retardation factor (R_f) for use in transport models (thus no assumptions on relationship between K_d and R_f are needed).

Modeling. Another option to acquire sorption parameters is to simulate the breakthrough curves (BTCs) from column experiments by models considering sorption kinetics (Brusseau, 1994; Brusseau et al., 1990; Fesch et al., 1998; Mader et al., 1997). Both nonlinearity and nonequilibrium conditions for sorption can significantly influence the shape of breakthrough curves (BTCs) in column experiments (Das et al., 2004). Modeling can help one obtain a better understanding of sorption nonequilibrium and sorption nonlinearity. Both simple one-site first order models (Cryer, 2005; Hornsby and Davidson, 1973; Spurlock et al., 1995; Van Genuchten et al., 1974) and two-site (or two-region) first order mass transfer models (Brusseau et al., 1991; van Genuchten et al., 1977) have been successfully used to simulate solute transport.

In many models, it is assumed that the sorption is linear (Ball and Roberts, 1991; Brusseau et al., 1991; Culver et al., 1997; Young and Ball, 1998; Young and Ball, 2000). However, a model based on linear sorption probably cannot provide an accurate simulation of the transformation and transport of nonlinearly sorbing solutes (Brusseau, 1995). Although two-site/region models were successfully applied in several studies, the excellent agreement between experiment and model predictions may just be a consequence of the additional free parameter that is used for “curve fitting” the solution to experimental data (Cryer, 2005), and it needs to be stated that the character of the mass transfer rate coefficients is more or less empirical (Worch, 2004).

1.4 Objectives

Due to the differences in the physiochemical properties of NSO compounds, the effect that various environmental factors have on the sorption processes the NSO compounds undergo in soils may be quite different from one another. Therefore, the first objective of this work was to identify the processes involved in the sorption of NSOs to soils. The second objective was to investigate how the environmental factors (e.g., temperature, ionic strength, and ion type) influence sorption processes of NSOs and to what extent.

To achieve these goals, sorption of 17 NSOs (varying in octanol-water distribution coefficient by 4 log units) to 5 well characterized reference soils (Eurosoils) representing the most widespread soil units in the European Union (Gawlik et al., 1999) has been carried out via soil column chromatography (SCC).

This work is divided into four parts. In chapter 3, optimisation of the soil column chromatography (SCC) method to study the sorption of NSOs is described. Criteria of column dimension, column packing, chromatographic data evaluation, and problems and countermeasures are demonstrated. In chapter 4, the identification of sorption mechanisms is described based on a comprehensive data set. Sorption processes of *N*-heterocyclic compounds are here elucidated in detail. In chapter 5, the effect of environmental factors on the sorption of NSOs is investigated and the sorption mechanisms are further discussed. In chapter 6 the effects of nonequilibrium sorption and nonlinear sorption on the transport of *N*-heterocyclic compounds in soil columns are simulated by first order one-site model by means of the program AQUASIM (Reichert, 1994).

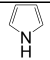
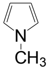
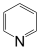
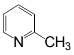
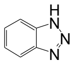
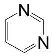
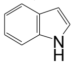
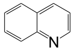
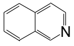
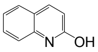
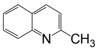
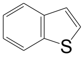
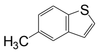
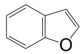
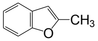
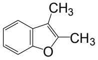
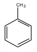
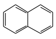
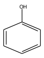
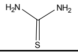
1. Introduction

2. Materials and Methods

2.1 Chemicals and packing materials

Chemicals with the highest purity available were obtained from manufactures (see Table 2-1). Toluene, benzene, and naphthalene were taken as the reference compounds that would not undergo any specific interaction. Stock solutions were prepared in methanol (≥99%, Merck), and all solutions were diluted with MilliQ water and stored at 4°C.

Table 2-1 Information on the investigated chemicals

Compound (Abbreviation)	CAS Number	Structure	Log K_{ow} 1)	pK_a 1)	Purity	Manufacturer
Pyrrole (PR)	109-97-7		0.75	17.5	99%	Acros Organics
1-Methylpyrrole (1MPR)	96-54-8		1.21	-3.15*	98%	Fluka
Pyridine (PY)	110-86-1		0.65	5.23 *	99%	Aldrich
2-Methylpyridine (2-Picoline) (2MPY)	109-06-8		1.11	6.00 *	99%	Aldrich
Benzotriazole (BTA)	95-14-7		1.44	1.6 * 8.6 2)	99%	Aldrich
Pyrimidine (PM)	289-95-2		-0.40	1.23 * (20°C)	99%	Aldrich
Indole (IND)	120-72-9		2.14	-2.40*	99%	Acros Organics
Quinoline (QUI)	91-22-5		2.03	4.90 * (20°C)	98%	Aldrich
Isoquinoline (IQUI)	119-65-3		2.08	5.42 * (20°C)	97%	Aldrich
2-Hydroxyquinoline (2QUI)	59-31-4		1.26	11.76(NH) -0.31(OH) 3)	98%	Aldrich
Quinaldine (2MQUI)	91-63-4		2.59	5.71 *	97%	Fluka
Thiophene (THIO)	110-02-1		1.81	-	99%	Acros Organics
1-Benzothiophene (BT)	95-15-8		3.12	-	99%	Aldrich
5-Methyl benzo[b]thiophene (5MBT)	14315-14-1		3.54	-	98%	ABCR
Benzofuran (BF)	271-89-6		2.67	-	99%	Aldrich
2-Methylbenzofuran (2MBF)	4265-25-2		3.22	-	96%	Aldrich
2,3-Dimethylbenzofuran (DMBF)	3782-00-1		3.63	-	≥95%	Fluka
Benzene (Benz)	71-43-2		2.13	-	≥99%	Aldrich
Toluene (Tol)	108-88-3		2.73	-	99+%	Acros Organics
Naphthalene) (Naph)	91-20-3		3.30	-	99%	Aldrich
Phenol (Phen)	108-95-2		1.46	9.99	≥99%	Aldrich
Thiourea (THS)	62-56-6		-1.08	2.03 *	99%	Fluka

1): data from database SRC (http://www.syrres.com/esc) except logK_{ow} values of DMBF and 5MBT were calculated with the SRC-KowWin (http://www.syrres.com/esc/kowdemo.htm); 2): data from ref. (Albert et al., 1948); 3): data from ref. (Vasudevan et al., 2001); *: pK_a is valid for a corresponding cation.

The packing materials in the column experiments include reference soils (Eurosoils 1-5 from IRMM, Belgium) and soil minerals (Alumina, Aldrich; Quartz, Merck). Lepidocrocite and goethite used in batch experiments were purchased as pigment-grade powders from Lanxess, Germany. The properties of tested soils are shown in Table 2-2.

Table 2-2 Properties of the column packing materials*

Sample		Eurosoil 1	Eurosoil 2	Eurosoil 3	Eurosoil 4	Eurosoil 5
Pedological characterization	OC wt.%	1.30	3.70	3.45	1.55	9.25
	CEC mequiv/100g	29.9	28.3	18.3	17.5	32.7
	pH (0.01M$CaCl_2$)	5.10	7.40	5.20	6.50	3.20
	pH (water) **	5.90	8.00	5.80	7.00	4.60
	SiO_2 wt.%	56.2	21.6	68.5	68.6	71.6
	Al_2O_3 wt.%	23.9	8.66	11.9	12.1	11.6
	Fe_2O_3 wt.%	10.8	1.66	4.14	2.71	<0.05
Grain size	Sand wt.%	3.3	13.4	46.4	4.1	81.6
	Silt wt.%	21.9	64.1	36.8	75.7	12.6
	Clay wt.%	75.0	22.6	17.0	20.3	6.0

*: Data compiled from ref. (Gawlik et al., 1999); **: own measurements.

2.2 Column experiments

2.2.1 Soil Column Chromatography

Soil column chromatography (SCC) utilizes a standard high performance liquid chromatography (HPLC) system (Bischoff Analysentechnik und -geräte GmbH, Germany) equipped with a soil column. It is suggested that the column length should be at least 4 times that of the column's inner diameter in order to overcome the possible reduction of the effective porosity by high velocities of the mobile phase (Relyea, 1982). A sketch of the set-up can be found in reference (Fesch et al., 1998). The detection cell volume was 10 µL. The data interface was LC-CaDI 2214. The temperature in the column oven is regulated in the range of 5 to 90 °C. A Dirac type input of sample was done by an injection-loop-valve (5 µL). The inner diameter of stainless steel capillaries was 0.13 mm, and its length between injector, column, and UV detector was kept as short as possible. A UV-vis spectrophotometer (Varian, Cary 50 Bio, Germany) was used to measure some compounds in the mass recovery experiments.

As in many other batch and column experiments, 0.005 M $CaCl_2$ was kept in the eluent to simulate the background electrolyte. The eluent was degassed by an online degasser (Degasys, DG-120, Germany). The pH of the post column eluent was monitored by a micro pH electrode (pH Elektrode 9803, Thermo Orion, USA; pH-Einstabmesskette ScienceLine N 6003 Mikro, Schott, Germany) in a custom-made micro-flow-through cell.

2.2.2 Column Packing

Reproducible column packing is a prerequisite for the SCC. Firstly, soils and minerals were ground manually by a pestle and mortar. Sieving the grounded materials indicated that they were less than 0.063 mm. Secondly, a stainless steel column (5.3-cm long, 0.3-cm internal diameter, Bischoff, Germany; 6.0-cm and 25-cm long, 0.3-cm internal diameter, CS-Chromatography Service GmbH, Germany) was connected to a 6-cm long pre-column. Thirdly, the dry packing material was carefully added into the column with the help of a stand, a vibrator, a 2-mL glass pipette as funnel, and a spatula. During the addition of soil, a small screwdriver was used to slightly tap the column wall in order to make the material packing denser. Fourthly, after encasing the column, it was connected to the HPLC pump. At the beginning, a slow flowrate (e.g., 10 µL/min) was applied in order to saturate the column with water and to get rid of entrapped air. Then, the flowrate was increased gradually until a high backpressure (e.g., 45 MPa) was reached. This is done in order to compress the packing material so that it will not be compressed further during later column experiments (when the back pressure was several times lower). If the clay or silt content of soil is low then the backpressure is usually low. In this case, the maximal flowrate of the HPLC pump (here 0.99 mL/min) can be selected. The flow can be stopped after the backpressure is stable for 30 minutes or longer. After the compressing by HPLC pump, the precolumn should be removed, and the column can be encased to finish the packing procedure. If the backpressure is found to be too high (e.g., > 30 MPa at a flow rate of 0.1 mL/min), this is indicative of column-clogging. In this case, it is necessary to dilute the soil with inert material (e.g., quartz, see chapter 3).

2.2.3 Retardation Factor

The dead time (or hold-up time, t_o) of SCC is determined by the breakthrough curve of a conservative (non-sorbing) tracer. In the calculation of the retardation factor (R_f), the traveling time (t') through the injector and connecting capillary between the injector and UV detector should be subtracted from the measured retention time (t) (Equation 2-1). A general expression for the retardation factor is shown in Equation 2-2 (Zheng and Bennett, 1997). When the Freundlich isotherm (Equation 2-3) is assumed, R_f can be represented by Equation 2-4. Based on at least two breakthrough curves obtained from different aqueous concentrations of a given compound C_w (mg/L), the Freundlich constant K_f ($\mathrm{mg}^{1-n}\mathrm{L}^n\mathrm{kg}^{-1}$) and the Freundlich exponent *n* can be elucidated by software (e.g., OriginPro 7.0). Plugging these values into Equation 2-3 allows for the determination of the solid phase concentration, C_s (mg/kg). The distribution coefficient, K_d, can then be calculated. If the sorption isotherm is linear, R_f and K_d are proportional to each other (Equation 2-5).

$$R_f = \frac{t - t'}{t_o - t'} \tag{2-1}$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot \frac{\partial C_s}{\partial C_w} \tag{2-2}$$

$$C_s = K_f \cdot C_w^n \tag{2-3}$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot K_f \cdot n \cdot C_w^{n-1} \tag{2-4}$$

$$R_f = 1 + \frac{\rho_b}{\theta} \cdot K_d \tag{2-5}$$

where ρ_b and θ are the bulk density and porosity of the soil, respectively.

2.2.4 Column experiment design

Experiments for the identification of sorption processes. In the experimental investigation of sorption mechanisms of NSOs to soils, the flow velocity and temperature were kept at 1.42 cm/min (100 µL/min) and 25 °C, respectively. The mobile phase was a 0.005 M $CaCl_2$ solution. The pH of the eluent after column was continuously monitored.

The injection volume was 5 µL. The concentration of the injected solution was varied from low to high concentrations, until a descent signal could be detected. The concentration was then further increased so that the K_d could be determined. The injected concentration range of NSOs was 130 to 180 mg/L, except for 5MBT (53 to 57 mg/L), BTA (147 to 338 mg/L), IND (211 to 292 mg/L) and IQUI (75 to 351 mg/L). The concentrations of the investigate aromatic hydrocarbons Benz, Tol, Naph and Phen were 880, 299, 27.3 and 46.2 mg/L, respectively. In the investigated concentration range the resulting isotherms were almost all linear. Only the N-heterocyclic compounds exhibited nonlinearity; however, the resulting Freundlich exponents were no less than 0.7 (see chapter 6). Therefore, K_d was calculated from their retardation factors by using Equation 2-5. If the measured R_f was less than 1.05, a reliable evaluation of K_d was not possible, and its value was set to zero, due to the experimental difficulty in a reliable quantification of such low R_f values.

Measuring the influence of environmental factors. The effects of temperature, ionic strength, and cation type on the sorption of NSOs were studied via the experiments depicted (Table 2-3).

Table 2-3 Column experiments to investigate environmental factors influencing sorption

Factors	Experimental conditions
Temperature	Column: E4b*; flowrate: 100 µL/min; mobile phase: 0.005 M $CaCl_2$; four different concentrations of each analyte were injected at temperatures of 5, 25 and 40 °C.
Ionic strength	columns: E4Q-3 and E4Q-1*; flowrate: 100 µL/min; temperature: 25 °C; mobile phasses: 0.00, 0.005, 0.05 M $CaCl_2$; the concentration of each analyte was kept constant for each mobile phase
Cation type	column: E4Q-1*; flowrate: 100 µL/min; temperature: 25 °C, mobile phases: 0.005 M $CaCl_2$ and 0.015 M KCl in mobile phase; the concentration of each analyte was kept constant for each mobile phase

*: Column information see Table 3-2.

Experiments designed for transport modeling. A column packed with a mixture of Eurosoil 4 and quartz was used (see information on column E4Q-1 in Table 3-2 in chapter 3). The sample was introduced to the column via a Dirac pulse injection conducted by an injection-loop-valve (5 µL). The system temperature was 25°C. Thiourea was used as conservative tracer.

To investigate influence of flow velocity and concentration on the sorption of compounds, experiments under the various conditions listed in Table 2-4 were conducted. The gravimetric method (i.e., to calculate the flow velocity according to the weight of eluent pumping through the system in a certain time period) was performed to check the pore water velocity. During the whole experiment period, the measured pore water velocity and the set value in the HPLC pump was within 1 to 4% of each other.

Table 2-4 Injection concentrations and pore water velocities for investigated compounds

Compounds	Injection concentrations (mg/L)	Pore water velocity (mm/s)
Thiourea	25, 40, 100, 200, 400, 800	1.06, 0.530, 0.265, 0.106
Toluene	42.7*, 84.9, 209.3, 408.6	
BTA	82.6, 164.36, 404.9, 790.5	
QUI	54.4, 108.2, 520.8	
2MQUI**	103.8*, 258.3, 407.3	

*: Indicated concentrations were not applied in transport modeling due to high background noise in measured data; **: experiments with pore water velocity of 0.106 mm/s were not conducted.

2.3 Batch experiments

2.3.1 Sorption to minerals

The sorption of target compounds to alumina, goethite and Lepidocrocite were determined with batch experiments. The sorbents adjusted to pH 7 by adding the appropriate amount of 0.1N HCl and 0.05N NaOH solutions to the sorbent sludge. The sludge was then dried in the oven (105°C) for 24 hours. Eppendorf (plastic) vials proved to be not suitable for the experiment as sorption to the walls of the vials led to a pronounced decrease in the concentration of the controls (e.g., 90% of 5MBT) after one hour. The 0.2-μm polycarbonate membrane filter could not be used for the separation of solid and solution in batch experiments due to the strong sorption of compounds (e.g., BTA and 5MBT) to it.

In the kinetic experiments, 1.5 mL solution of each compound was spiked into the vials (1.5-mL borosilicate glass vials with Teflon septa) which contained a specified amount of sorbent (see Table 2-5). Controls and triplicate sets of samples were prepared for each compound. Initial concentrations for the compounds (in mg/L) are 5MBT 6.52, BTA 4.12 and 6.64 (repeated), QUI 5.465, 2QUI 5.16, 2MQUI 5.295, IQUI 4.6, BF 5.36 and Tol 4.29 mg/L. The solutions (in 0.005M $CaCl_2.2H_2O$) were prepared from the stock solutions in methanol of the following concentrations: 1630 mg/L, 20600 and 16600 mg/L, 10930 mg/L, 7940 mg/L, 10590 mg/L, 4600 mg/L and 10720 mg/L respectively. The solution of $CaCl_2.2H_2O$ was prepared with the use of millipore water (ionic strength of 1.5 x 10^{-2}M). Toluene in concentration of 4.29 mg/l (stock solution in methanol – 8.58 g/L) was considered as a reference compound as it does not undergo specific interaction with sorbents.

Table 2-5 Sorbents used in the batch experiments

Sorbent	Amount per vial, g	Compounds sorbed
Quartz	0.20	5MBT, BTA, Tol
Alumina (Al_2O_3)	0.20 / 0.10	5MBT, BTA, Tol / QUI, 2MQUI, IQUI
Goethite (α-FeO(OH))	0.10	all compounds
Lepidocrocite (γ-FeOOH)	0.15 0.10	5MBT, BTA, Tol QUI, 2QUI, 2MQUI, IQUI, BTA (repeated), BF

After preparation, samples were shaken on an end-to-end shaker (Heidolph REA×2, speed set to 3). Sorbent and solution were separated by a centrifuge (Hermle Z320) at 3900 rpm (maximum). The centrifugation times were 25 minutes for the quartz and 60 minutes for other sorbents. The concentration of supernatant solutions was measured using a UV-vis spectrophotometer (Varian, Cary 50 Bio, Germany) with wavelengths of 230 nm (5MBT), 260 nm (BTA), 210 nm (toluene), 225 nm (QUI), 228 nm (2QUI), 230 nm (2MQUI), and 216 nm (IQUI). The compound concentration in the controls was taken as the initial concentration.

In batch experiments, there was no observable sorption of the investigated compounds to the selected minerals. Therefore, this is not further discussed in the later chapter.

2.3.2 Sorption to Eurosoil 4

Sorption of toluene, BTA, QUI, and 2MQUI to Eurosoil 4 was performed in batch experiments in order to compare results with those from the column experiments. After weighing 0.10 g of a 2:1 mixture of Eurosoil 4 to Quartz in a 1.5-mL borosilicate glass vial, 1.5 mL of solution was spiked into separate vials and sealed with Teflon septum screw caps. The vials with suspensions were shaken on a shaker (IKA, HS501) with speed of 185 Mot/min for one week at temperature of 22±1°C. The samples were then centrifuged (Hermle, Z320) at 3900 rpm for 45 min. Duplicated samples were prepared for each concentration. Controls without soil were prepared in the same way.

QUI, 2MQUI and toluene were analysed with an HPLC equipped with an analytical column (125*4.0 mm, Prontosil Eurobond C18, 5.0 µm, Bischoff) and a mobile phase consisting of 70% methanol and 30% 0.01M phosphate buffer at pH 7.02. The mobile phase for TBA analysis was 55% methanol and 45% 0.01 M phosphate solution at pH 7.02. The column oven temperature was set to 25 °C.

In order to reduce the loss of toluene during the batch experiment, samples for headspace GC-FID analysis were also prepared. Two ml of toluene solution (42.69 mg/L) was added into 8-mL crimped headspace vials (real volume 8.4 mL) which contained either 0.2 g or 0.5 g of Eurosoil 4. Controls without soils were prepared as well. Kinetic experiment of toluene shows that equilibrium can be achieved in 30 minutes. All samples were shaken on the shaker (IKA, HS501) in a 20°C room with an intensity of 185 Mot/min before the analysis.

2.4 Modeling

2.4.1 Transport of solutes in porous media

For one-dimensional steady state flow in homogeneous and isotropic porous media, the conservative solute transport is governed by the advection and dispersion equation (ADE).

$$\frac{\partial C_w}{\partial t} = -v\frac{\partial C_w}{\partial x} + D\frac{\partial^2 C_w}{\partial x^2} \qquad (2\text{-}6)$$

For a reactive solute, the solute transport can be described as:

$$\frac{\partial C_w}{\partial t} = -v\frac{\partial C_w}{\partial x} + D\frac{\partial^2 C_w}{\partial x^2} - \frac{\rho_b}{\theta}\frac{\partial C_S}{\partial t} \tag{2-7}$$

where v is the average pore-water velocity [mm/s]; t is time [s]; D is the hydrodynamic dispersion coefficient [mm^2/s]; and x is the distance along the column [mm].

2.4.2 One-site first order model

For the one-site first order model the Freundlich isotherm (Equation 2-3) was used to describe the sorption. One-site first order model assumes that the sorption is controlled by diffusion limitations and the sorption kinetics is represented by first order mass transfer rate α [s^{-1}] (Equation 7).

$$\frac{\partial C_S}{\partial t} = \alpha\left(K_f C_w^n - C_S\right) \tag{2-8}$$

The solute transport can be determined by equations (2-7) and (2-8). With the help of AQUASIM, the values of three parameters (a, K_f and n) can be obtained by fitting measured data.

2.4.3 AQUASIM

The analytical solutions are not available for transport equations of nonlinearly sorbing solutes. Therefore, a simulation and data analysis program AQUASIM (Reichert, 1994; Reichert, 1995) was used. In AQUASIM, any type of processes such as linear and/or nonlinear sorption can be set up by the user. However, the computational time and the burden on the processor required by AQUASIM is quite high because of its use of a numerical integration technique. A sensitivity function (Equation 2-9) is applied by AQUASIM to estimate the sensitivity and uncertainty of the parameters. It measures the absolute change in y for a 100% change in parameter p.

$$\delta_{y,p}^{a,r} = p\frac{\partial y}{\partial p} \tag{2-9}$$

AQUASIM uses the weighted least square method (minimized χ^2) to estimate the values of parameters from measured data.

$$\chi^2(p) = \sum_{i=1}^{m}\left(\frac{y_{meas,i} - y_i(p)}{\sigma_{meas,i}}\right)^2 \tag{2-10}$$

where $y_{meas,i}$ is the i-th measurement, $y_i(p)$ is the calculated value of the model variable corresponding to the i-th measurement and evaluated at the time and location of this measurement, $\sigma_{meas,i}$, is its standard deviation, $p = (p_1,..., p_m)$ are the model parameters and m

is the number of data points. In this study, χ^2/m was used to check the fitting quality under different conditions.

3. Validation of Soil Column Chromatography Method

Determination of small sorption coefficients K_d (corresponding to retardation factors R_f of 1.1 in column experiments) by batch experiments might be inaccurate due to the low solid to solution ratio. Furthermore, for systematic investigations of the effects of environmental factors (e.g., temperature, ionic strength, exchangeable cations, etc.) on the sorption of a large set of compounds to a given sorbent, batch experiments are probably too tedious and time consuming. As an alternative to batch experiments, column studies can be used (Brusseau et al., 1989; Buergisser et al., 1993; Das et al., 2004; Fesch et al., 1998; Lee et al., 1991; Mader et al., 1997). Once the column approach is validated, it is easy to operate the system and to rapidly generate highly precise sorption data. Furthermore, sorption data from column chromatography consider both *ad*- and de- sorption processes, i.e., they take into account the reversibility of the sorption process.

In this chapter, a soil column chromatography (SCC) approach was validated and optimized to determine K_d values of NSOs. Reference soils (Eurosoils 1-5) and model sorbents (quartz and alumina) were chosen as packing materials. Criteria in SCC application were addressed. The problems and countermeasures were elucidated. An easy and reproducible column packing method was introduced and the evaluation of chromatographic data was discussed in detail.

3.1 Column preparation

3.1.1 Column dimension and sample injection volume

As a part of the dead volume, the volume V' of connecting capillaries, fittings and detection cell may lead to artifacts. For a good isocratic instrument, V' should (i) not exceed the detection cell volume by more than 5 – 6 times, and (ii) be about 1/6 of the pore volume of the column (Kromidas, 2000). V' was measured at 15 μL by the injection of 5 μL thiourea solution (30 mg/L) as the nonsorbing tracer. The main contributors to V', therefore, are the UV detection cell (10 μL) and injection loop (5 μL). The contribution of the capillaries to V' are negligible. A capillary of an inner diameter of 0.13 mm and a length of 20 cm corresponds to a volume of 0.66 μL. This meets the first requirement, i. e., $V' < 60$ μL (= 6 times of the detection cell volume). To meet the second requirement, the pore volume of soil column should not be less than 90 μL ($= 6 \times V'$). In our case, columns with lengths 53 – 60 mm and inner diameter 3 mm were used, which results in pore volumes of around 180 – 210 μL. Thus, if a shorter column was used, such as a 1-cm long column, this would result in a pore volume of 35 µL, which would not meet the above stated criteria. Relyea suggested that the column length should be at least 4 times of the column's inner diameter in order to overcome the possible reduction in the effective porosity of a column caused by high eluent velocities (Relyea, 1982). Since the injection volume contributes to the dead volume, the injection volume should be minimized. As a rule of thumb, the largest tolerable injection volume should be 10% of the column volume (Kromidas, 2000).

3.1.2 Column packing

Homogenization of packing material. The occurrence of channeling (or formation of preferential flow paths) in the column may be minimized by making sure that the column diameter is at least 30 times the maximum particle size found in the column packing (Relyea, 1982). Therefore, in order to make the particle size smaller as well as to make the material more homogeneous, the packing materials were ground. In columns where a dilution material was used, it was also ground. Sieving results show that the particle size after grinding is less than 63 µm. BET data show that the grinding does not change the specific area of the material significantly (Table 3-1). This process also helps to reduce the intraparticle diffusion distance, which reduces the influence of diffusion on sorption kinetics.

Table 3-1 Specific surface area (m^2/g) of the packing materials

Name	Original sample	Samples after grinding**
Eurosoil1	47.0 *	50.0
Eurosoil4	4.3 *	6.95
Quartz	0.39**	0.53

*: Data from Ref. (Kuhnt et al., 1994); **: own measurements.

Packing procedure. Sorption studies with SCC require a reliable method for reproducible packing of soil. A commonly used method for packing is to tap small increments of soil into the column. This method is tedious, usually results in layering of the soil and is not reproducible. The column packing method described by Yaron et al. needs a special device (Yaron et al., 1966), which restricts its wide application. To use the HPLC pump as a packing device, as described in Chapter 2, makes packing much easier. This method resulted in good uniformity and reproducibility of soil column packing.

A not-well-packed column can lead to many problems. For example, radial heterogeneity of the packing density of a column is a cause for peak tailing (Miyabe and Guiochon, 1999), and a changing retention time would result from a change in packing density (Kromidas, 2000). The information about the packed columns used is listed in Table 3-2. Results of repeated injections of the conservative tracer show that the column packing in this study is rather homogenous and stable (Figure 3-1). For column E4-9, packed with Eurosoil4, the backpressure increased to about 30 MPa after a short period at a flowrate of 50 µL/min. This indicates that dilution of Eurosoil4 with inert material (i.e., quartz) is necessary. For the well-

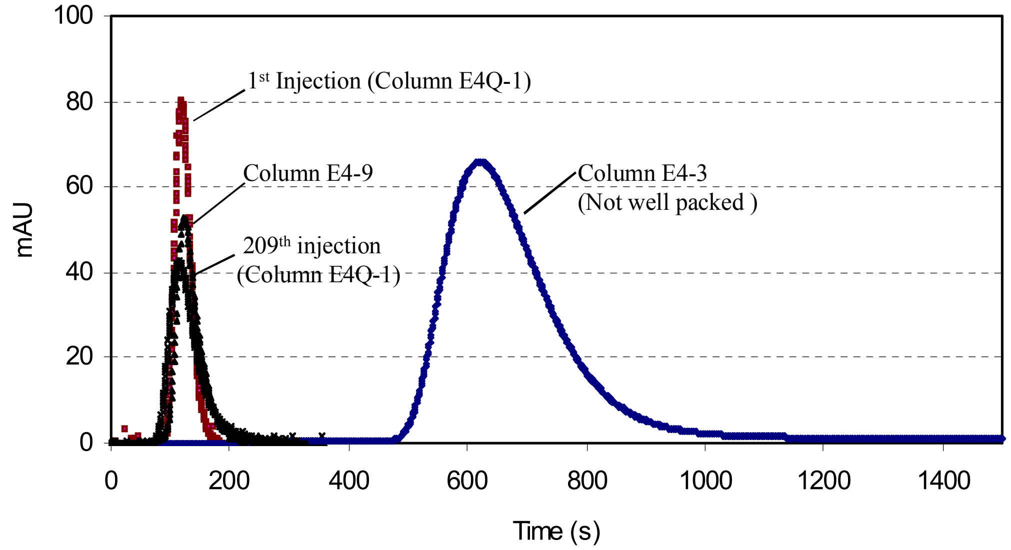


Figure 3-1 Breakthrough curves of the conservative tracer in columns (60mm*3mm) packed by different materials and methods (flowrate 100 µL/min; temperature 25 °C).

Table 3-2 Packed columns with reference materials

Column	L mm * ID mm	Packing material [3]	OC (%)	Porosity [4]	Density (g/cm^3) [5]
Q-6	250 * 3	Quartz	-	0.409	2.65
Q-5	53 * 3	Quartz	-	0.393	2.65
Al-1	250 * 3	Alumina	-	0.565	3.5 [6]
E4-3 [1]	60 * 3	Eurosoil4	1.55	0.880	2.72
E4-9	53 * 3	Eurosoil4	1.55	0.539	2.72
E4Q-1	60 * 3	Eurosoil4 : Quartz = 1:0.5	1.03	0.444	2.69
E1Q-2	60 * 3	Eurosoil1 : Quartz = 1:3	0.325	0.388	2.68
E2Q-3	60 * 3	Eurosoil2 : Quartz = 1:1	1.85	0.413	2.69
E3Q-1	60 * 3	Eurosoil3 : Quartz = 1:1	1.725	0.545	2.68
E4b [2]	53 * 3	Eurosoil4	1.55	0.476	2.72
E5Q-4	60 * 3	Eurosoil5 : Quartz = 1:9	0.925	0.437	2.65

[1]: Packed without compressing by HPLC pump; [2]: Packed by Bischoff Company; [3]: Weight ratio is given for soils with mixed packing material; [4]: Porosity was determined by traveling time of THS; [5]: Solid density was estimated from the material composition and specific gravity data (quartz: 2.65; silt: 2.70; and clay: 2.80); [6]: Data from http://www.reade.com.

packed column E4Q-1, there is no significant shift of the retention time of the conservative tracer after more than 200 injections. The different peak heights in Figure 3-1 are due to different injected concentrations of conservative tracer. Such changes of the conservative tracer concentration did not result in changes of the retention time. After the experiments were completed, there was no observable sinking of the packing material at the inlet part of the column. However, for the column E4-3 packed by only vibrating the column wall (without compressing by HPLC pump), a highly retarded and broad peak was formed, which indicates an increased dead volume resulting from the void at the column inlet. This void is caused by the compression of packing material, due to the backpressure in experiments.

Packing material dilution. In the SCC approach, clogging is often a problem due to clay and silt particles in the soil. To avoid clogging, various measures can be taken. Sieving out smaller is one option (Culver et al., 2000). However, this treatment will also change the soil properties, especially the content of organic matter, which might be heterogeneously distributed among various particle size fractions. Another choice is to dilute the whole soil with a certain proportion of inert material (e.g., quartz or glass beads) (Das et al., 2004). Of course, the retardation of the target compounds should be checked in a column packed with the dilution material. The retention caused by the diluting material should be subtracted from that of both the quartz and diluted soil to determine the retention by the diluted soil alone.

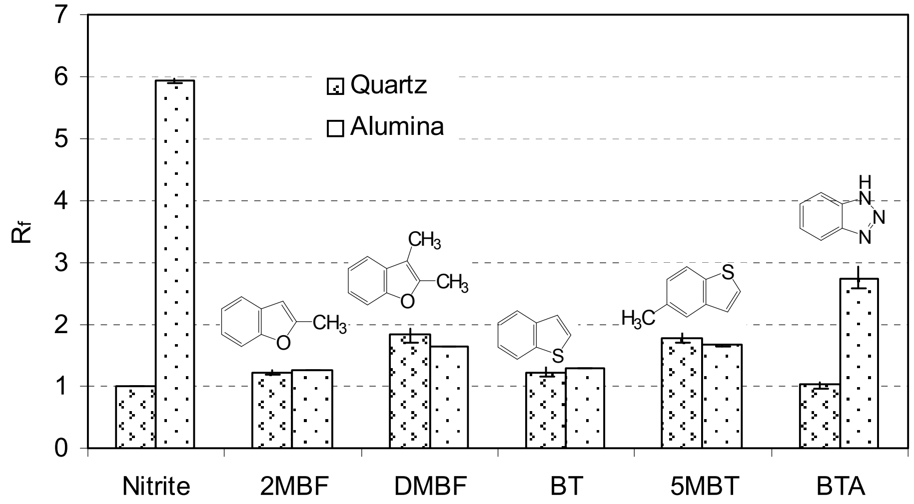


Figure 3-2 Retardation of compounds in the quartz column Q-5 and alumina column Al-1 (25 °C; injection volume 5 µL; injected concentrations: Nitrite 20 mg/L, 2MBF 151 mg/L, BT 127 mg/L, 5MBT 57 mg/L, and BTA 174 mg/L; flowrates were 100 µL/min and 500 µL/min in Q-5 and Al-1, respectively).

As shown in Figure 3-2 (the data of non-retarded compounds not shown), only some investigated compounds, which are highly retarded in the soil columns, were slightly retarded in quartz column. However, alumina exhibited higher retardation for some compounds (e.g., BTA). In our study, quartz was chosen as the dilution material. The dilution method might also be adopted in experiments with large K_d to reduce the solute retardation factor, thus allowing the experiments to be completed in a reasonable time period (Das et al., 2004).

3.2 Method verification and data analysis

3.2.1 Conservative tracer and mass recovery

The selection of a suitable conservative tracer is a critical point, because this will affect the final calculation result (see Equation 2-1). Different tracers were used in column experiments, for instance, thiourea (Bucheli and Gustafsson, 2000; Fesch et al., 1998), tritiated water (Brusseau et al., 1990; Culver et al., 2000); nitrite (Guo et al., 2004b; Xu et al., 2001), bromide (Das et al., 2004), and fluorescent tracers such as fluoresceine and eosine (Ptak et al., 2004). An ideal conservative tracer should meet two requirements: it is detectable and it undergoes no (or negligible) interaction with the column stationary phase. Tritiated water is theoretically the optimal conservative tracer, because there is no reaction with the sorbent. However, it is not UV detectable. Thiourea is considered as a good tracer due to its hydrophilic properties and the possibility of convenient on-line UV detection (Fesch et al., 1998). Compared with UV-active ionic tracers (e.g, NO_2^-), neutral thiourea does not undergo any significant ion exchange or charge repulsion/attraction when the pH is above 4 (the pK_a of $THS\text{-}H^+$ is 2.03). Note that in soil, due to negatively charged clay particles, anion exclusion may result in a faster transport of anions than bulk water molecules. Anions may also be retarded. We observed that nitrite was highly retarded (Figure 3-2) in the alumina column due to ion exchange. This shows that a high content of soil alumina can significantly affect the transport of nitrite and possibly other anions.

The solute recovery was carried out by comparing the breakthrough curve area of a soil column with that of a quartz column, and/or directly by measuring the compound concentration in the effluent. The mass recovery results from column E4Q-1 are listed in Table 3-3. Most of compounds were recovered with a very good yield. Recoveries greater than 100%, as determined by the comparison with quartz breakthrough curves, are likely resulting from long tailing and baseline noise. Low recovery yields are likely due to measuring error, i.e., the concentration of the effluent was too close to the detection limit of the UV-vis Spectrophotometer.

Table 3-3 Mass recovery percentages from column E4Q-1

Compounds	THS	Toluene	BTA	QUI	BT	BF	2MPY	IND	IQUI	QUI	2MQUI	2MBF	5MBT
Mass recovery (%)	98	104	109	113	89	97	73* ~ 154	98* ~138	86	102	120* ~132	99	41 ~85*

* Measurements by UV spectrophotometer.

3.2.2 Determining the retention time from the breakthrough curve

A breakthrough curve will be symmetrical if (i) the injection technique is good; (ii) the injection volume and dimensions of the column meet the requirements discussed above; (iii) the amount of solute is not large enough to overload the column or detector; (iv) the residence time of the solute in the stationary phase is long enough to achieve dynamic equilibrium; (v) the solute sorption isotherm is linear. One common problem in using column studies to measure K_d values is that the breakthrough curves are asymmetric. Nonequilibrium and nonlinear sorption/desorption lead to pronounced tailing of the breakthrough curves. This is more problematic for polar solutes with HPLC (Kromidas, 2000), due to the more significant nonlinear sorption processes.

In various modeling studies, it was shown that the first moment approach (Equation 3-1, for the Dirac input) is appropriate to determine the mean breakthrough time (Valocchi, 1985; Young and Ball, 2000). However, moments are susceptible to noise and are severely affected by baseline drift, inaccurate determination of the peak limits, tailing, incomplete resolution, and insufficient sampling frequency. Peak moments higher than zero are too sensitive for routine use (Dyson, 1998; TorresLapasio et al., 1997). For the case of a Dirac input, the column experiment is terminated when the quantification limit of the target compound is reached. Due to the sensitive effect of tailing on the moment analysis, breakthrough curves may lack much of the tail data required for calculating the first moment, even though most of the solute has actually been recovered (Altfelder et al., 2001). Another approach to determine R_f is the curve-fitting approach, i.e., using a model to fit the breakthrough curve (Maraqa et al., 1998).

$$\mu_1 = \frac{\int_0^{t_F} tC_w dt}{\int_0^{t_F} C_w dt} \tag{3-1}$$

Where: μ_1 - first moment of residence time; t – in units of time or pore volume; t_F – final point of data collection in time or pore volume units.

In our study the half mass point, which is the point at which the peak area (integration of sorption unit over time) can be divided into two equal parts, was used as the mean retention time (t_i) (Stoob, 2000; Thomson et al., 1999).

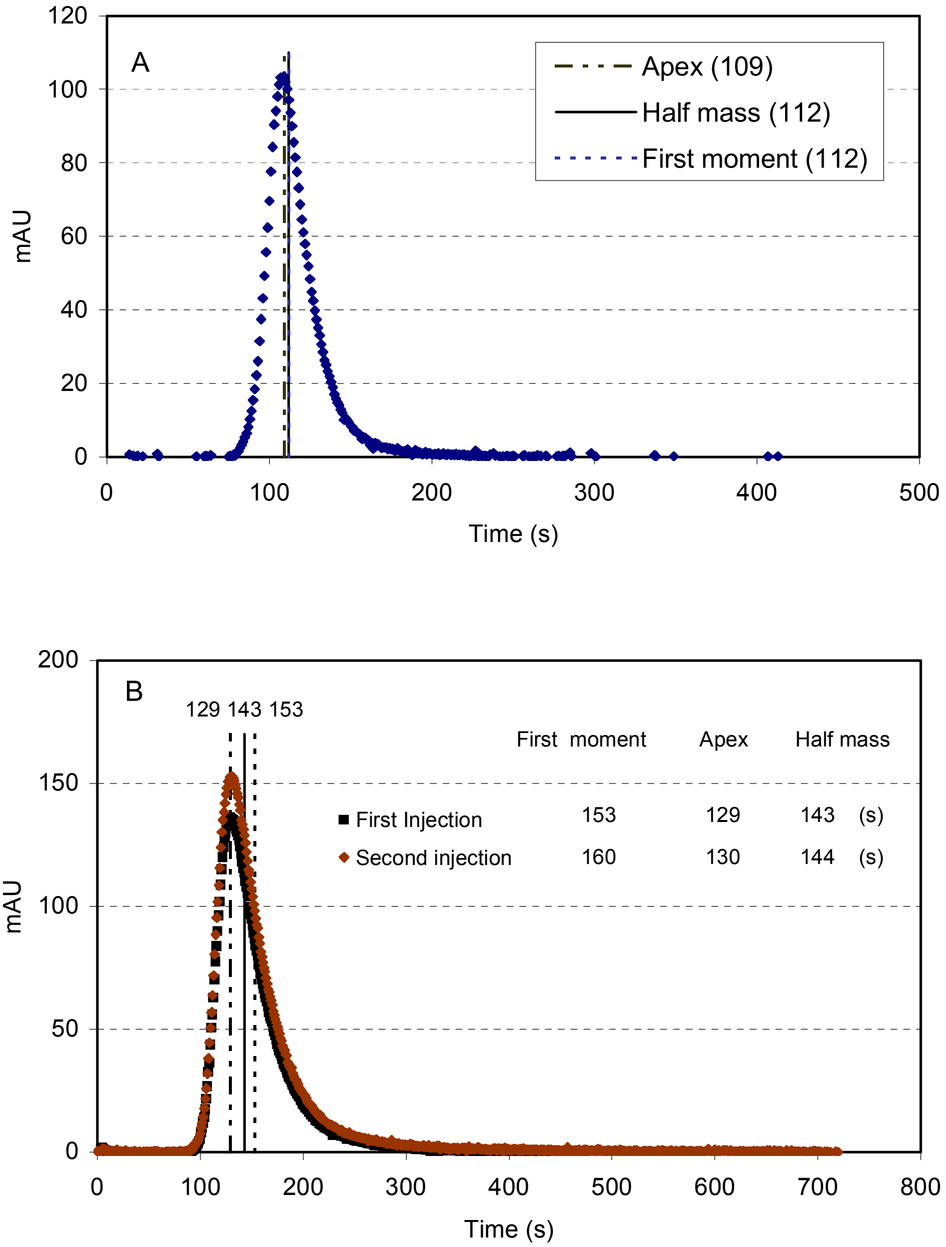


Figure 3-3 Retention time determination by various methods for thiourea (A) and 1-benzothiophene (B) in column Q5 (25°C, flowrate 100 µL/min, injection volume 5 µL, sample concentrations BT 127 mg/L and THS 30 mg/L)

As shown in Figure 3-3 (A), for the relatively symmetric peak of the conservative tracer, the retention times obtained by peak apex, half mass, and first moment are very close. However, for the asymmetric peak in Figure 3-3 (B), the retention time obtained from first moment was affected by the slight drift of baseline. In of work of Maraqa et al., uncertainty associated with the values of R_f determined by moment analysis was discussed (Maraqa et al., 1998) and it was shown that the result from half mass method is relatively stable.

Generally speaking, the lower the flowrate in the column experiments, the more likely the occurrence of equilibrium sorption. In Figure 3-4, it is shown that the retention time calculated by the first moment method cannot eliminate the artifact due to nonequilibrium sorption. Maraqa et al. also found the values of R_f determined by first moment were dependent on eluent velocity (Maraqa et al., 1998). The values of R_f differ by 17 % for BT. Relatively, the R_f values calculated by half mass method are more stable at varying flowrates. Concerning BT, R_f increases from 4.74 to 5.12 for the flowrates 100 and 20 µL/min, respectively. The difference is about 7% (i.e., the effect of flowrate might be negligible). For the less retarded compounds (e.g., 1MPR), the results from these two methods are consistent.

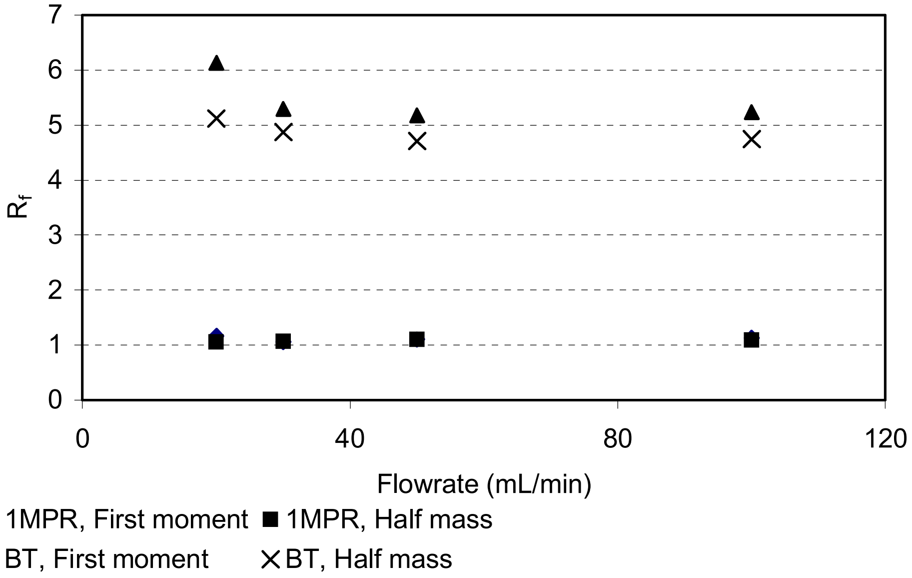


Figure 3-4 Retardation factor evaluated by different methods (column E4b, 25°C, injection volume 5 µL, sample concentrations: 1MPR 130 mg/L and BT 146 mg/L).

3.2.3 Local equilibrium? — flowrate effect

It is difficult to achieve equilibrium in the column experiment. The mechanisms in non-equilibrium sorption processes include diffusion through natural organic matter matrices and diffusion through intraparticle nanopores (Pignatello and Xing, 1996). The smaller particle size from grinding reduces the impact of diffusion through natural organic matter matrices. Previous studies showed that for neutral organic chemicals, the more hydrophobic the compound, the longer it takes to achieve equilibrium between the solid and aqueous phase (Brusseau and Rao, 1989).

The sorption distribution coefficient K_d is an equilibrium coefficient, and should be independent of mobile phase linear velocity. Therefore, to determine K_d from soil column chromatography, first of all, flow-rate effects should be evaluated. One option is to choose one certain velocity, below which there is no apparent change of K_d. Stopped-flow experiments also can be conducted to check the sorption nonequilibrium (Brusseau et al., 1989). However, depending on the compound and environmental solid of interest, true sorption equilibrium may require weeks to months to be achieved (Pignatello and Xing, 1996). Therefore, in some cases, these two options are impracticable due to the long time duration. Another option is to do the column test at two or three selected flowrates (q_i), and calculate the apparent distribution coefficient (K_{di}'). When plotting K_{di}' vs. q_i, the regressed K_{di}' line can be extrapolated to the point of zero velocity. The intercept is considered as the equilibrium K_d. In Figure 3-5, it is shown that flowrate has little effect on the retardation factor

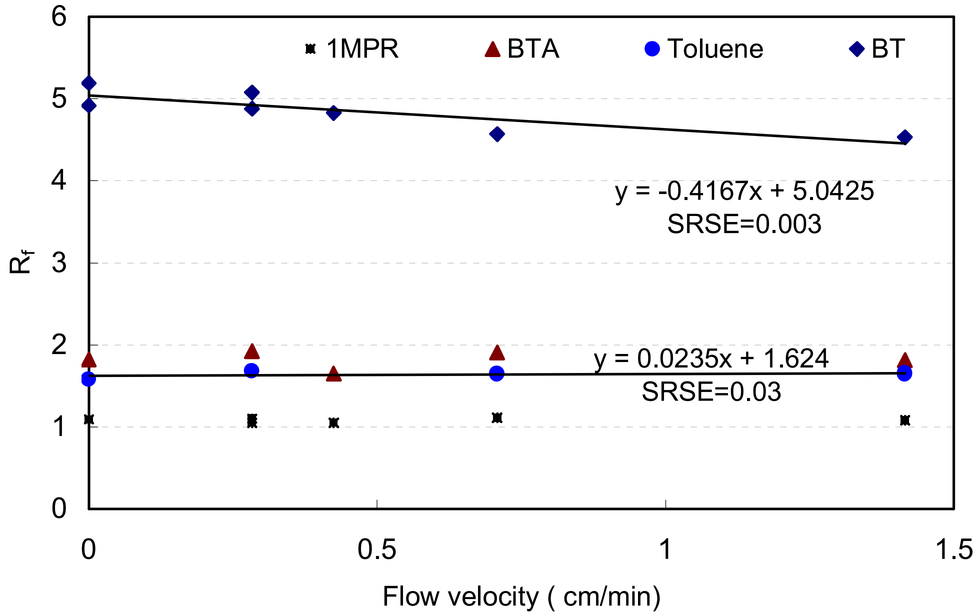


Figure 3-5 Retardation factor as a function of flow velocity in column E4b (25°C, sample injection volume 5 µL, sample concentration: 1MPR 130 mg/L, BTA 174 mg/L, toluene 203 mg/L, and BT 146 mg/L. R_f at zero velocity was obtained by interrupt flow experiment, q=100 µL/min (i.e., 1.415 cm/min), stop-flow period: toluene 15 min., 1MPR 15 min., BTA 30 min., BT 60 and 660 min.). Sum of residual squared error (SRSE) $=\sum_{i=1}^{n}$((predicted – measured)/measured)^2, n is the number of data points.)

of hardly retarded compounds. R_f varies slightly at different pore water velocities. In the eluent flowrate range from 0 to 1.42 cm/min, R_f values for 1MPR, BTA, and toluene are 1.11 ± 0.03, 1.82 ± 0.11, and 1.64 ± 0.03, respectively. Even for the relatively highly retarded compounds, for example BT, R_f varies just about 10% (4.86 ± 0.24). This may be a further indication that polar compounds may achieve equilibrium in a short time. For some polar pesticides, such as bromacil, napropamide, and prometryn, the equilibrium was achieved within 2 hours in batch experiments (Turin and Bowman, 1997).

In a natural dynamic groundwater system, sorption equilibrium is often not achieved. Therefore, according to the natural situation, to adjust the flowrate to mimic the real condition would give a more realistic result for the retardation factor (R_f). The assumption of equilibrium sorption in dynamic field systems may result in overestimating sorption. Models based upon local equilibrium assumption (LEA) do not always accurately simulate solute transport. If local equilibrium is not attained, LEA-based models will predict a breakthrough response that occurs too late and exhibits too little dispersion. For hazardous solutes, such a miscalculation could have serious consequences (Valocchi, 1985).

3.2.4 Comparison of soil column chromatography and batch experiment results

In SCC, at appropriate temperatures and flowrates, R_f can be calculated from the breakthrough curves at various injected concentrations (see section 2.2.3). Another option for dealing with the nonlinear case is to approximate a linear sorption over a finite concentration range (Spurlock et al., 1995) and determine K_d at different aqueous concentrations by using Equation 2-5. The concentration at the mean retention time (i.e., the half mass point) on the breakthrough curve is taken as the equilibrium aqueous concentration. Then, the relationship between K_d and aqueous concentration can be found. By using this approach, the isotherms of toluene, benzotriazole, quinoline, quinaldine were determined from the breakthrough curves in E4Q-3 column (Table 3-4). As mentioned in the previous part, the tested flow velocities exhibit only a minor influence on the retardation factor of the investigated organic compounds. The K_f and n values from different pore water velocities are in a very narrow range. This indicates the tailing of the chromatogram is mainly caused by nonlinear sorption, and the effect from nonequilibrium sorption is not significant. The results are consistent with those from modeling (see Chapter 6).

The results indicate that sorption of toluene is almost linear, which implies that partitioning into soil organic matter is the dominant sorption process. The K_{oc} of toluene determined here by SCC is about 37, which is comparable to the reported K_{oc} range of 37 ~ 160 (Nathwani and Phillips, 1977) to 250 (Schwarzenbach and Westall, 1981).

Table 3-4 Coefficients of the Freundlich isotherm from the R_f - K_d relationship (Equation 2-5) at various water velocities in column E4Q-1 at 25°C

Compounds	Aqueous concentration range (mg/L	1.05 mm/s		0.544 mm/s		0.279 mm/s		0.116mm/s	
		K_f	n	K_f	n	K_f	n	K_f	n
QUI	0.19-4.03	1.29	0.830	1.21	0.798	1.39	0.830	1.43	0.815
2MQUI	0.08-0.88	4.25	0.772	-	-	-	-	-	-
BTA	1.25-20.3	0.325	0.833	0.360	0.835	0.392	0.818	0.361	0.854
Toluene	1.44-8.50	0.366	0.926	0.374	0.940	0.393	0.927	0.388	0.957

Table 3-5 Results from the batch experiments

Compounds	Sorbent	pH	K_f	N	Aqueous concentration range (mg/L)
BTA	Eurosoil 4: quartz = 2:1	6.5	1.88	1	2.3~714
QUI			1.88	0.96	0.4~493
2MQUI			6.47	0.96	0.5~407

Comparing the results of the batch and column experiments, shown in Tables 3-4 and 3-5 respectively, the isotherms for QUI, 2MQUI, and BTA determined from the batch experiments show a higher linearity than those from column experiments. Due to differences in experimental conditions (aqueous equilibrium concentration range, solid to solution ratio, pH, etc), the results of these two approaches are not consistent, and thus they should not be compared directly. This has also been reported by other researchers (Bayard et al., 1998; Benker et al., 1998; Schwarzenbach and Westall, 1981).

3.3 Summary

Soil column chromatography (SCC) is an appropriate method to investigate the transport of NSOs in the subsurface and to determine the sorption distribution coefficient (K_d) of NSOs at low aqueous concentration ranges in groundwater-soil systems. It can also be applied to quickly determine parameters influencing the sorption processes for given compounds and soils. Using the SCC method one must consider the importance of certain parameters such as flow velocity, effective porosity, sorption equilibrium, column dimensions, and injection volume. In the data evaluation, the half mass method is shown to be reliable to determine the mean retention time from breakthrough curves. Though it is not appropriate to directly compare the results of the batch and column experiments; nevertheless, differences between these experiments are likely due to difference in soil/water ratio and/or the contribution of specific interaction to overall sorption.

4. Sorption Process Identification

For the large set of NSOs investigated in this study, their sorption to various soils may be controlled by different processes. For example, sorption of benzothiophene (BT) is probably related to non-specific interactions (namely van der Waal's forces) (Broholm et al., 1999), and sorption of ionizable NSOs (e.g., quinoline) may be controlled by specific interactions (e.g., cation exchange or complexation with soil constituents other than OC) (Ainsworth et al., 1987; Burgos et al., 2002; O'Loughlin et al., 2000; Zachara et al., 1987; Zhu et al., 2003). All previous work on NSOs sorption has been carried out with a limited set of compounds and solids, and thus allows only limited generalization. Therefore, the objective of the work described in this chapter was to generate a comprehensive data set for sorption of NSOs in order to identify the compound specific and environmental factors influencing sorption processes of NSOs. The soil column chromatography (SCC) method was applied to characterize the sorption behavior of a wide variety of NSOs to a set of soils exhibiting very different properties (Eurosoils 1-5).

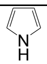
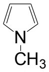
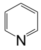
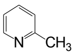
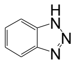
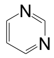
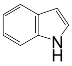
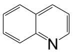
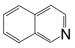
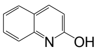
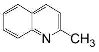
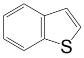
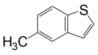
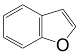
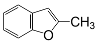
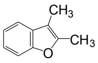
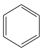
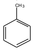
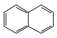
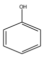
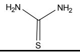
4.1 Sorption of non-ionizable organic compounds

In Figure 4-1, the straight lines that indicate non-specific interactions (van der Waal's forces) as dominant sorption mechanism were fitted from the compounds shown as solid circles. For compounds appearing above these non-specific-interaction (NSI) lines, additional interactions (i.e., specific sorption mechanisms) are significant. The slopes of NSI lines are very close to 1.0, except a somewhat higher value for Eurosoil 3. A very similar picture is obtained when $\log K_d$ is plotted vs. logS (aqueous solubility in mg/L, Figure not shown).

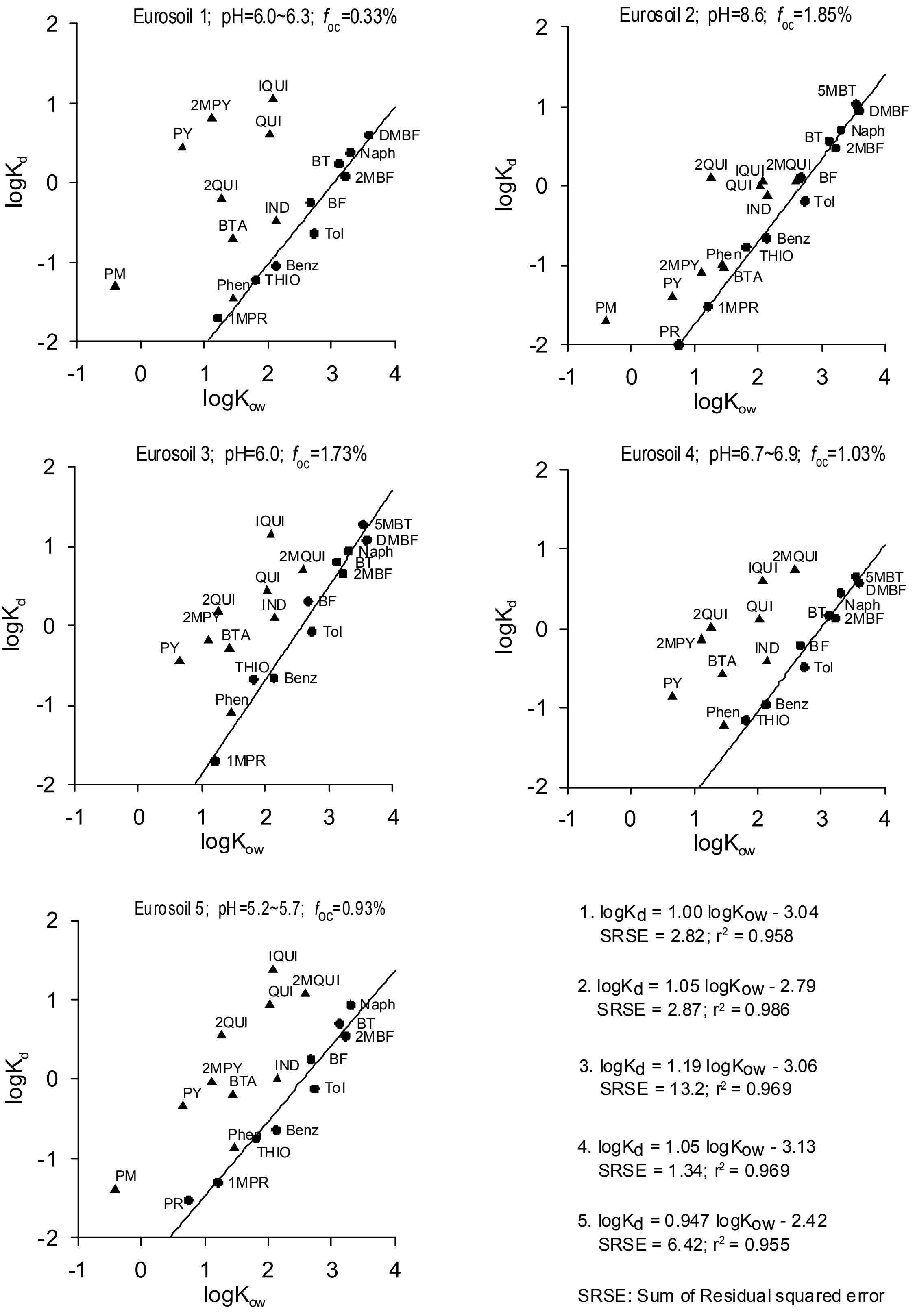
The sorption of *S*- and *O*-heterocyclic compounds was highly correlated to their K_{oc} values and soil OC content. The deviation of their K_{oc} (K_d normalized by f_{oc}) varies for the 5 investigated soils only by a factor of 3, and their K_{oc} values decrease with increasing f_{oc} (Figure 4-2). The K_d data in Table 4-1 clearly indicate that the presence of a methyl group or benzene ring increases the sorption of *S*- and *O*-heterocyclic compounds of the same class. The sorption affinity orders of *S*- and *O*-heterocyclic compounds in each soil are 5MBT>BT>THIO and DMBF>2MBF>BF. This can also be seen in Figure 4-2.

As shown in Figure 4-2 all compounds, for which non-specific interaction is a dominant sorption mechanism, have a higher K_{oc} in Eurosoil 1 and 5, even though the OC in these two columns is lower than in the other columns. Both soils are of high humification degree (Senesi et al., 2003), and there is a rather high amount of micropores in these soils. Therefore,

Table 4-1 K_d (L/kg) of the NSOs determined from each column

Compound	Structure	Log K_{ow} 1)	pK_a 1)	Eurosoil 1 (E1Q-2) pH 6.0-6.3; CEC 7.48; OC 0.33%	Eurosoil 2 (E2Q-3) pH 8.6; CEC 14.2; OC 1.85%	Eurosoil 3 (E3Q-1) pH 6.0; CEC 9.2; OC 1.73%	Eurosoil 4 (E4Q-1) pH 6.7-6.9; CEC 11.7; OC 1.03%	Eurosoil 5 (E5Q-4) pH 5.2-5.7; CEC 3.3; OC 0.93%
Pyrrole (PR)		0.75	17.5	0.00	0.01	0.00	0.00	0.03
1-Methylpyrrole (1MPR)		1.21	-3.15*	0.02	0.03	0.02	0.00	0.05
Pyridine (PY)		0.65	5.23 *	2.75	0.04	0.35	0.14	0.45
2-Methylpyridine (2-Picoline) (2MPY)		1.11	6.00 *	6.52	0.08	0.65	0.72	0.93
Benzotriazole (BTA)		1.44	1.6 * 8.6 2)	0.20	0.10	0.53	0.27	0.64
Pyrimidine (PM)		-0.40	1.23 * (20°C)	0.05	0.02	0.00	0.00	0.04
Indole (IND)		2.14	-2.40*	0.33	0.75	1.25	0.39	1.02
Quinoline (QUI)		2.03	4.90 * (20°C)	4.01	1.01	2.80	1.31	8.52
Isoquinoline (IQUI)		2.08	5.42 * (20°C)	11.6	1.17	11.5	4.01	23.9
2-Hydroxyquinoline (2QUI)		1.26	11.76(NH) -0.31(OH)3)	0.63	1.25	1.48	1.01	3.49
Quinaldine (2MQUI)		2.59	5.71 *	NP	1.17	5.59	2.2	11.8
Thiophene (THIO)		1.81	-	0.06	0.17	0.21	0.07	0.18
1-Benzothiophene (BT)		3.12	-	1.74	3.66	6.35	1.45	4.98
5-Methyl benzo[b]thiophene (5MBT)		3.54	-	**	10.7	18.8	4.48	**
Benzofuran (BF)		2.67	-	0.57	1.27	2.03	0.61	1.77
2-Methylbenzofuran (2MBF)		3.22	-	1.20	3.01	4.56	1.35	3.46
2,3-Dimethylbenzofuran (DMBF)		3.63	-	4.02	8.81	12.0	3.71	**
Benzene (Benz)		2.13	-	0.09	0.22	0.22	0.11	0.23
Toluene (Tol)		2.73	-	0.23	0.64	0.84	0.33	0.76
Naphthalene) (Naph)		3.30	-	2.41	5.07	8.76	2.79	8.55
Phenol (Phen)		1.46	9.99	0.035	0.094	0.08	0.059	0.14
Thiourea (THS)		-1.08	2.03 *	0.00	0.00	0.00	0.00	0.00

1): Data from database SRC (http://www.syrres.com/esc) except logK_{ow} values of DMBF and 5MBT were calculated with the SRC-KowWin (http://www.syrres.com/esc/kowdemo.htm); 2): data from Ref. (Albert et al., 1948); 3): data from Ref. (Vasudevan et al., 2001); *: pK_a is valid for corresponding cation; **: Note that due to very high sorption to OC, the retardation of 5MBT in Eurosoil 5 and Eurosoil 1 and of DMBF in Eurosoil 5 could not be quantified precisely enough to determine reliable K_d values.



1. $\log K_d = 1.00 \log K_{ow} - 3.04$
SRSE = 2.82; $r^2 = 0.958$

2. $\log K_d = 1.05 \log K_{ow} - 2.79$
SRSE = 2.87; $r^2 = 0.986$

3. $\log K_d = 1.19 \log K_{ow} - 3.06$
SRSE = 13.2; $r^2 = 0.969$

4. $\log K_d = 1.05 \log K_{ow} - 3.13$
SRSE = 1.34; $r^2 = 0.969$

5. $\log K_d = 0.947 \log K_{ow} - 2.42$
SRSE = 6.42; $r^2 = 0.955$

SRSE: Sum of Residual squared error

Figure 4-1 Relationship between logK_d (L/kg) and logK_{ow} (Octanol-water distribution coefficient) (The non-specific-interaction (NSI) line was fitted from the data of Naph, BT, 2MBF, BF, Tol, Benz, THIO, PR and 1MPR for which specific interaction with soil components can be neglected)

micropore filling might contribute to the overall sorption in these two soils as suggested by Celis et al. (Celis et al., 2005). Due to similar properties of humic acids in Eurosoil 1 and 5 (Senesi et al., 2003), the sorption of compounds dominated by non-specific interaction shows the same pattern as other soils.

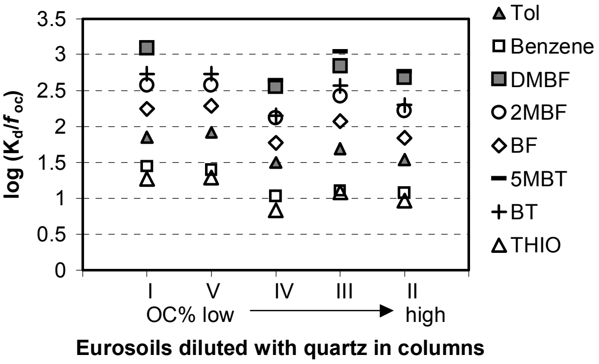
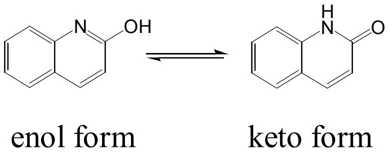


Figure 4-2 K_{oc} (K_d normalized by OC) in soils for Tol, Benz, and S-/O- heterocyclic compounds

Non-ionizable *N*-heterocyclic compounds (PR, 1MPR, IND, and PM) in the ambient pH range, exhibit less consistent sorption patterns. PR, 1MPR, and PM show very low sorption and are hardly retarded in all soils tested (Table 4-1). Weak non-specific interaction appears to dominate the sorption of PR and 1MPR. However, the deviation of PM from the NSI-line in Figure 4-1 and data in Table 4-2 imply that specific interactions (possibly by surface complexation) dominate (≥96%) the sorption of PM. The specific interactions may occur through the lone pair electrons on the two N atoms, and this contribution to the K_d is in a range from -1.30 to -1.71 log units (Table 4-2). However, due to the low sorption of PM, a quantitative interpretation of the data seems inappropriate. With regard to IND, the deviation from the NSI line and the data in Table 4-3 show that specific interactions contribute 60-75% (-0.03 to -0.69 log units, Table 4-2) to the K_d. The reason for the relatively strong sorption of IND could be the enhanced interaction between cations and the π-electron system of *N*-heterocyclic compounds compared with aromatic hydrocarbons (e.g., benzene), which has recently been reported (Chatterjee et al., 2001; Zhu et al., 1999).

2QUI is far from the NSI line (Figure 4-1) in all soils, which indicates strong specific interaction between compound and solid matrix. As shown in Table 4-3, sorption of 2QUI is controlled by specific interaction with a contribution of 97-98% in all soils. This indicates that the sorption is independent of f_{oc}. 2QUI is expected to exist mainly as the keto form (oxo tautomer, see equation 4-1) in aqueous solution, and no sorption to aluminium and iron oxide was found in batch experiments with an oxide loading of 20 g/L and 2QUI concentration of 5×10^{-5}M (Vasudevan et al., 2001).



(4-1)

The absolute value of specific interaction for 2QUI varies among the 5 investigated soils by 0.75 log units (Table 4-2). The specific sorption of 2QUI may be due to surface complexation. We found a loose correlation (r^2=0.6) between the K_d of 2QUI and the content of clay and silt, which reflects the total surface area.

Table 4-2 Sorption resulting from specific interactions

Compounds (pK_a)	$\log(K_d - K_{d,part}(1-f_{ion}))$*				
	E5Q-4 pH 5.2-5.7	E3Q-1 pH 6.0	E1Q-2 pH 6.0-6.3	E4Q-1 pH 6.9	E2Q-3 pH 8.6
IND (-2.4)	-0.21	-0.03	-0.69	-0.59	-0.33
2QUI (-0.31/11.76)	0.54	0.16	-0.21	0.00	0.08
PM (1.23)	-1.42		-1.30		-1.71
BTA (1.6/8.6)	-0.26	-0.32	-0.76	-0.61	-1.13
QUI (4.9)	0.92	0.42	0.59	0.08	-0.10
PY (5.23)	-0.36	-0.47	0.44	-0.86	-1.49
IQUI (5.42)	1.37	1.14	1.05	0.59	-0.04
2MQUI (5.71)	1.05	0.65		0.71	-0.49
2MPY (6.00)	-0.04	-0.20	0.81	-0.15	-1.25

*: K_d data are from Table 4-1, $K_{d,\,part}$ (sorption due to partitioning) values are calculated by inserting the compound K_{ow} (Table 4-1) into the equations fitted in Figure 4-1; f_{ion} (fraction of ionic species) data is shown in Table 4-4.

Table 4-3 Contribution from specific interaction to the overall sorption*

Compounds (pK_a)	$(K_d-K_{d,part}(1-f_{ion}))/K_d\bullet100$				
	E5Q-4 pH 5.2-5.7	E3Q-1 pH 6.0	E1Q-2 pH 6.0-6.3	E4Q-1 pH 6.9	E2Q-3 pH 8.6
IND (-2.4)	60	75	61	67	63
2QUI (-0.31/11.76)	98	98	97	98	97
PM (1.23)	96		99		97
BTA (1.6/8.6)	86	91	87	91	74
QUI (4.9)	97	93	98	93	79
PY (5.23)	97	99	100	98	81
IQUI (5.42)	99	99	99	97	79
2MQUI (5.71)	95	87		94	29
2MPY (6.00)	99	99	100	99	71

*: Calculation for K_d and $K_{d,\,part}$ is the same as in 4-2.

From Figure 4-1, one can conclude that specific interactions dominate the sorption of BTA, which is consistent with findings of a previous study (Hart et al., 2004). The contribution of specific interactions to the overall sorption of BTA is shown in Table 4-3. Except for Eurosoil

2, BTA (pK_a=8.6) is present mainly in its neutral form in the solution. In Eurosoil 2, 50% of BTA is present as an anion (Table 4-4). Repulsion between the anion and the negatively charged sites of the soil reduces the sorption of BTA significantly. The interaction between neutral BTA and the solid matrix is possibly via surface complexation, as is described for the sorption of veterinary pharmaceuticals in soils (Tolls, 2001).

4.2 Sorption of ionizable N-heterocyclic organic compounds

The group of ionizable basic *N*-heterocyclic compounds (PY, 2MPY, QUI, IQUI, and 2MQUI) significantly deviates from the NSI lines (Figure 4-1). Their overall sorption is dominated by specific interactions, except for 2MQUI in Eurosoil 2 (Table 4-3). These compounds are only slightly retarded in Eurosoil 2 (Table 4-1), which has the highest OC content and a pH of 8.6, which causes these compounds to be present in their neutral forms only. The methyl group of 2MQUI increases its hydrophobicity, and thus the sorption of 2MQUI is dominated by non-specific interaction to soil f_{oc} when there is no cationic form of this molecule present. For the other compounds within this group, the contribution of specific interaction is still more than 70% of the overall sorption. In the other soils studied, a significant albeit small fraction of the compound is present in the cationic form. Previous studies on PY (Baker and Luh, 1971; Zachara et al., 1987; Zachara et al., 1990; Zhu et al., 2003), 2MPY (O'Loughlin et al., 2000) and quinoline (Thomsen et al., 1999; Zachara et al., 1987; Zachara et al., 1986) showed that cation exchange is a dominant sorption mechanism for the protonated forms of these compounds. *N*-heterocyclic compounds (e.g., PY, 2MPY, QUI) have been found to sorb prefererntially as cations even when the pH of the solution was greater than the pK_a –values (Ainsworth et al., 1987; O'Loughlin et al., 2000; Zachara et al., 1986; Zachara et al., 1990). In this study, a great impact of the cation fraction on sorption was also observed.

Table 4-4 Speciation of compounds under different conditions

Compounds	E5Q-4		E3Q-1		E1Q2		E4Q-1		E2Q-3	
	pH	Ion (%)	pH	Ion (%)	pH	Ion (%)	pH	Ion (%)	pH	Ion (%)
PY	5.7	28	6	15	6	14	6.8	3	8.6	0
2MPY	5.6	71	6	52	6.3	35	6.9	11	8.6	0
QUI	5.5	20	6	8	6.1	6	6.7	2	8.6	0
IQUI	5.7	34	6	22	6.2	14	6.7	5	8.6	0
2MQUI	5.7	51	6	35	6	33	6.7	9	8.6	0
BTA*	5.2	0	6	0	6.3	1	6.7	2	8.6	50

*: Species of BTA refers to the anion form, for others to the cation form.

4.3 Conceptual model

We propose the following model (Equation 4-2) to assess the contribution of each sorption process to the overall sorption.

$$K_d = K_{d,part} + K_{d,BH^+} + K_{d,B} \tag{4-2}$$

$$K_d = K_{part}(1 - f_{ion}) + K_{BH^+} f_{ion} + K_B(1 - f_{ion}) \tag{4-3}$$

where $K_{d,part}$ is contribution due to partitioning to soil OC; f_{ion} is the cation fraction of protonated *N*-heterocyclic compounds; K_{d,BH^+} is the contribution due to cation exchange of the protonated NSOs, $K_{d,B}$ is the contribution of specific interactions (likely via surface complexation) of the neutral forms of *N*-heterocyclic compounds [L/kg]; K_{part}, K_{BH^+} *and* K_B are the partitioning constants for each mechanism, respectively.

$K_{d,part}$ values were calculated using the compound K_{ow} (Table 4-1) and the equations fitted in Figure 4-1. The fraction present in cationic form (f_{ion}) was taken from Table 4-3. Knowing these parameters, K_B and K_{BH^+} were fitted in Grapher 4.0 (Golden Software, Inc.) and the results are shown in Figure 4-3.

QUI and IQUI sorption resulting from specific interactions is well correlated to the cation fraction in all soils. Compared with the other soils, 2MPY and PY show extraordinarily high sorption resulting from specific interaction in Eurosoil 1. Therefore, sorption data points from Eurosoil 1 for these two compounds were excluded in the fitting. The sorption of QUI and IQUI in Eurosoil 1 exhibits the same phenomenon, but not so pronounced. The fitting results of K_{BH^+} indicate that the cation exchange partitioning constant decreases for the compounds tested in the following order IQUI>QUI>2MQUI>>PY>2MPY. This order is consistent with the expected impact of hydration (or surface charge density) on cation exchange. The molecular size of two-ring compounds is larger than those of one-ring compounds. Therefore, they have a lower surface charge density and a smaller hydration shell. This reduces the distance between the compounds and the solid surfaces and causes a higher electrostatic attraction, which consequently leads to a higher sorption affinity.

The magnitude of K_B decreases in the compounds tested in the following order 2MQUI > IQUI > QUI >> 2MPY > PY. The contribution of $K_{d,B}$ to the sorption of 2MPY and PY is relatively small, and consequently results in small K_B values. According to the order of K_B and K_{BH^+} for these compounds, it seems that the presence of a methyl group on the ring influences

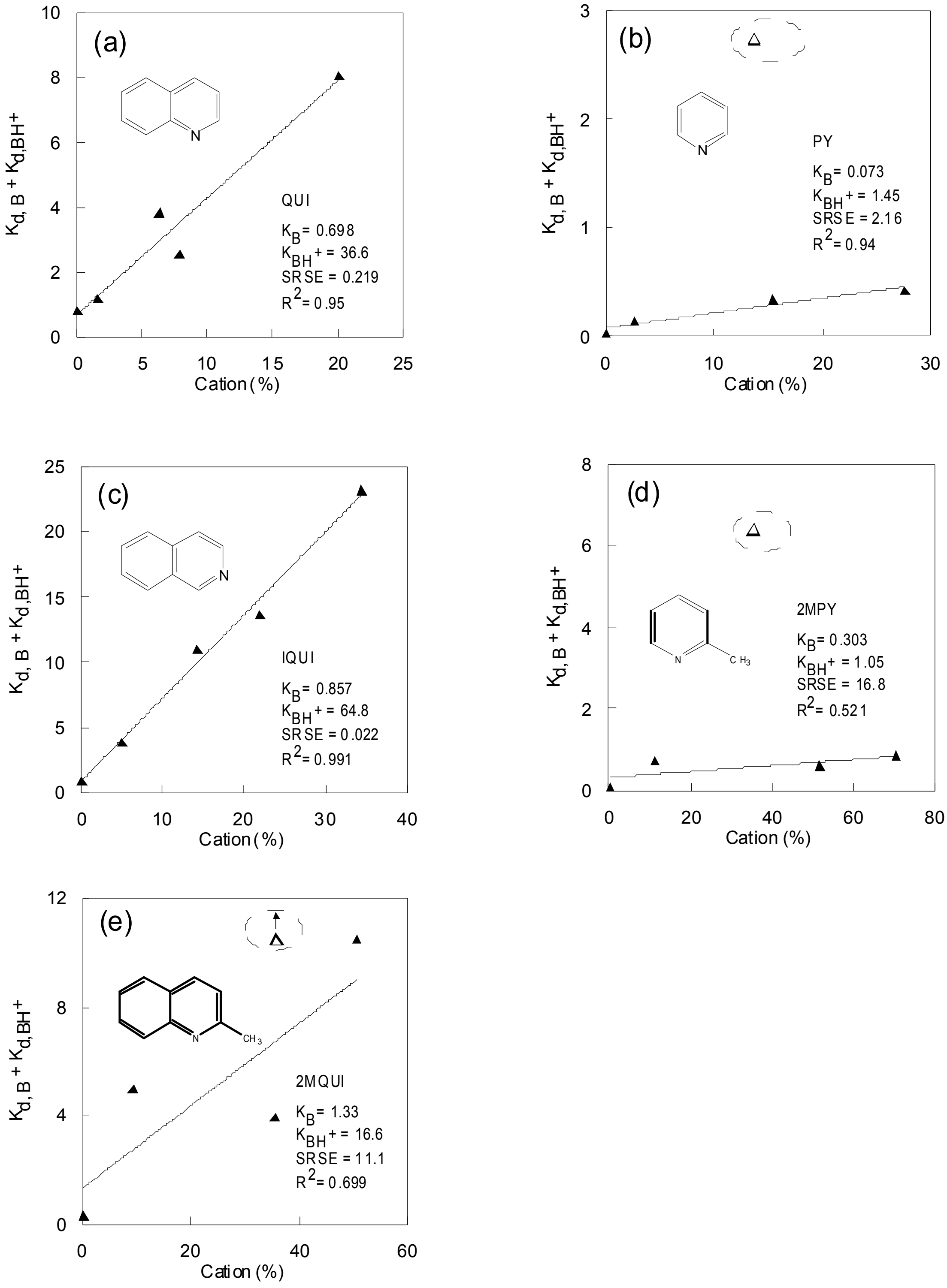


Figure 4-3 Relationship between cation fraction and K_d resulting from specific interactions. The fitting equation is Y = K_B*(1-x/100)+K_{BH^+}*x/100. Empty triangle points (from Eurosoil 1 Column) in plots (b) and (d) were excluded. In plot (e) the data in the dashed circle means a higher value is expected but could not be quantified.

both cation exchange and the relevant complexation interaction. However, further work is needed to clarify this issue.

Now having the fitted K_B and K_{BH^+} values the sorption of each compound, and the contribution of each sorption mechanism., can be calculated by using Equation 4-3 for the different soils. The predicted values were normalized by the measured data and the results are shown in Figure 4-4. The dominant contribution of cation exchange to the overall sorption even at small cation fractions is clearly visible in the plots, which corroborates previous findings (Ainsworth et al., 1987). In all soils, sorption of QUI and IQUI was well predicted. For PY and 2MQUI, the estimated values are within a factor of two of experimental data. The relatively high deviation of 2MPY in Eurosoil 2 is caused by higher uncertainty of the data due to very low retardation (see Figure 4-3).

For PY, 2MPY, and 2MQUI, their sorption to Eurosoil 1 was not calculated. The reason is that these compounds showed higher sorption in Eurosoil 1 column than in the other soil columns, which indicates that there must be additional interaction besides that included in Equation 4-4, especially for PY and 2MPY sorption. Based on previous studies, in addition to pH, other factors such as the total accessible surface area (Broholm et al., 1999), and other soil properties (Gawlik et al., 1998) might also be important for the sorption of these compounds in a certain system. Due to high clay content, Eurosoil 1 has a high BET specific surface area even after dilution with quartz (12.5 m^2/g in column E1Q-2, Table 3-1). The accessible surface might be a reason for higher sorption observed in Eurosoil 1. However, this additional interaction cannot be characterized based on the available data in this study.

4.4 Summary

Overall, the results show that SCC is a suitable approach to investigate sorption of polar organic compounds to natural sorbents. The environmental pH is a critical index to assess the sorption of ionizable *N*-heterocyclic compounds in the suggested conceptual model. However, the effect of the environmental factors such as aqueous phase composition and ionic strength should be further studied.

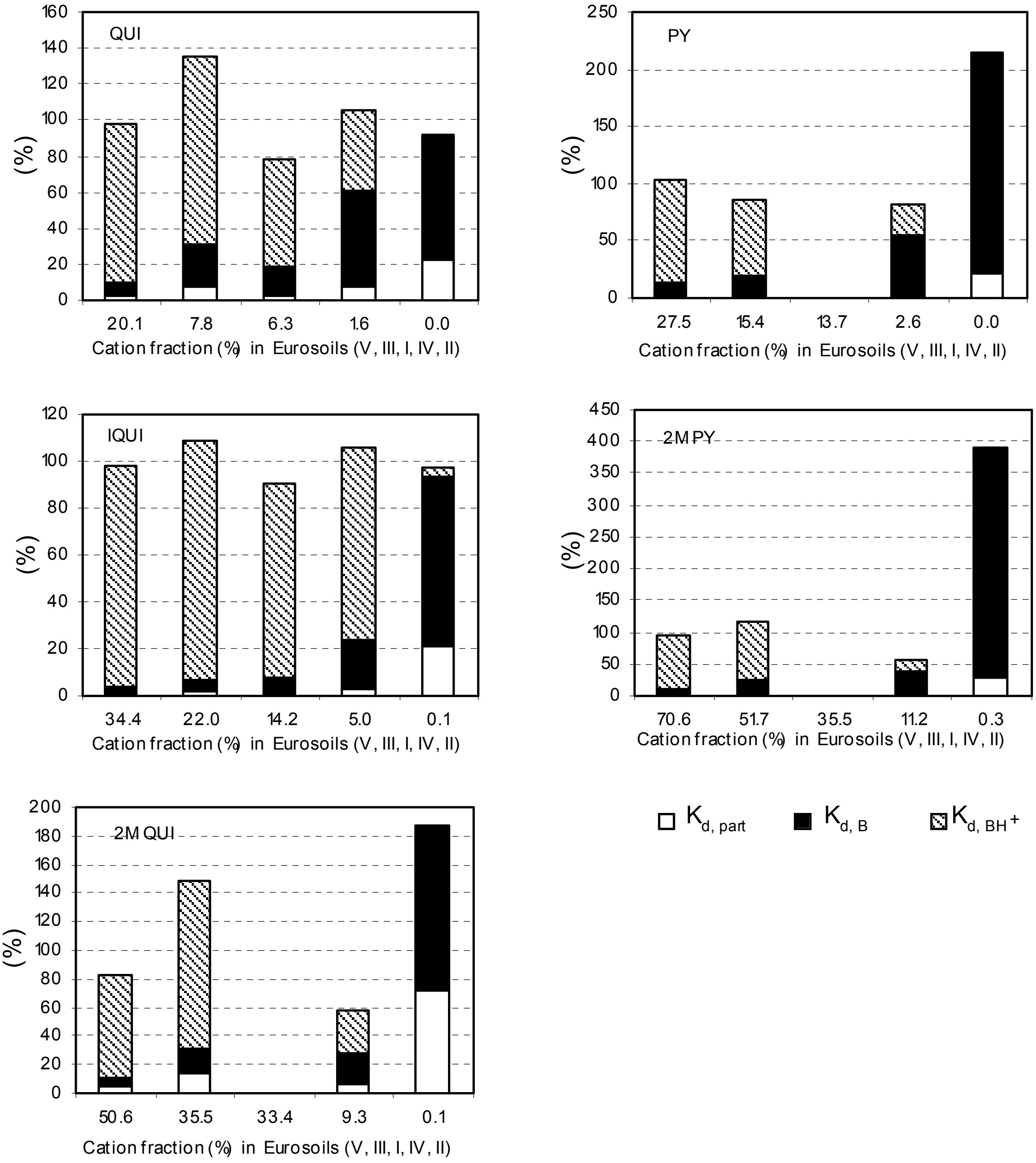


Figure 4-4 Comparisons of the predicted K_d values based on Equation 4-3 with measured data. Values are show as (predicted value/experimental value) in percentage.

5. Effect of Environmental Factors on Sorption Processes

In soil-water systems, the sorption of investigated NSOs, especially for the compounds that undergo specific interactions such as cation exchange and surface complexation, might be significantly affected by environmental variables (temperature, ionic strength, exchangeable cations, etc.). The study on the effects of environmental factors on the sorption processes of NSOs would provide a better understanding of the transport of these compounds in the subsurface.

In the previous chapter, sorption mechanisms of NSOs at various soils were elucidated and a general model to quantify these different processes was suggested. However, the effect of temperature, ionic strength, and ion composition on the sorption of NSOs has not been systematically studied. In this chapter, the effect of these factors on the sorption of selected NSOs in Eurosoil 4 was investigated by soil column chromatography. The experimental results are discussed in terms of the suggested sorption mechanisms.

5.1 Influence of Temperature

The influence of temperature on the sorption of NSOs is shown in Figure 5-1. Sorption coefficients decrease with increasing temperature for all NSOs studied. This indicates that the sorption is an exothermic process. However, there is very little effect of temperature on the sorption coefficients of PY and 2MPY. According to van't Hoff equation, the enthalpy change ΔH was calculated and shown in Figure 5-2.

$$\ln K_d = \Delta S/R - \Delta H/R \cdot 1/T \qquad (5\text{-}1)$$

where ΔS is entropy change [kJ/(mol·K)]; ΔH is enthalpy change [kJ/mol]; R is gas constant [8.3145 J/(mol·K)]; T is temperature [K].

K_{ow} was used as a descriptor for non-specific interactions to categorize the ΔH values of NSOs (Figure 5-2). The enthalpy change (ΔH) of all compounds is higher than -25 kJ/mol (the absolute values are less than 25 kJ/mol). This is consistent with the absence of covalent bonding (i.e., chemisorption which generally gives ΔH in the range from -60 to -80 kJ/mol (Delle Site, 2001)) and with our observation that sorption is fully reversible. Three clusters of compounds can be observed in Figure 5-2. The ΔH of compounds in group A is in the range from -6.0 to -11.0 kJ/mol. This indicates that van der Waal's forces (normally corresponding to a ΔH from -4 to -8 kJ/mol (Delle Site, 2001)) dominate the sorption of these *S*- and *O*-

heterocyclic compounds, which implies that partitioning is the dominant sorption mechanism (see chapter 4).

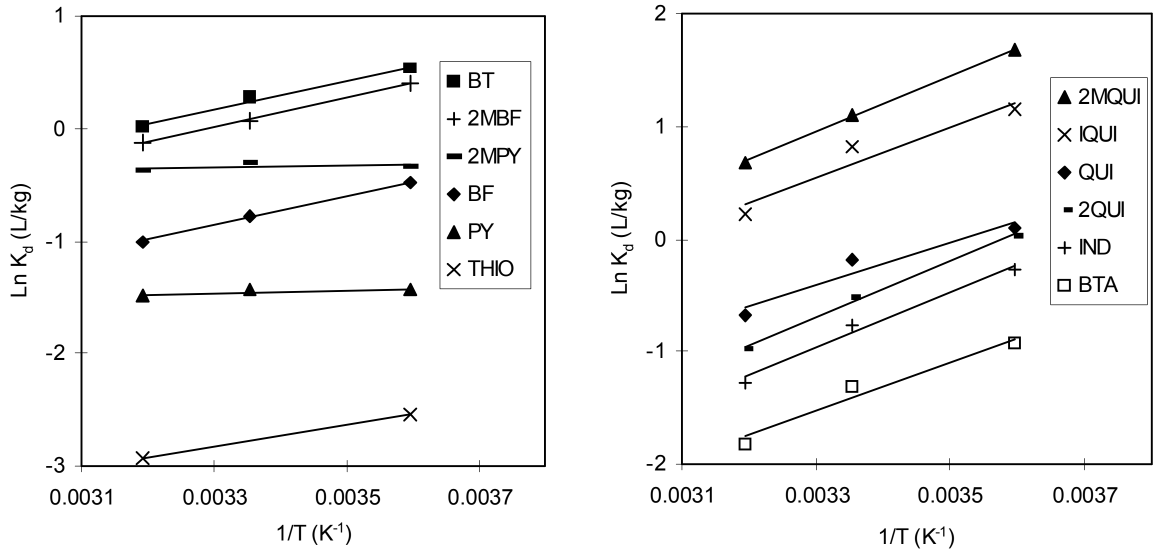


Figure 5-1 van't Hoff plots for the sorption of target compounds to Eurosoil 4 (Column E4b; at 5, 25 and 40°C; $CaCl_2$ 0.005 M in mobile phase; flowrate 100 μL/min; injection volume 5 μL; injected concentration (mg/L): BT 146, 2MBF 151, 2MPY 30.5, BF 153, PY 31.7, THIO 151, 2MQUI 34.2, IQUI 16.3, QUI 35.3, 2QUI 45.8, IND 9.77, BTA 39.4)

Two data points for each compound in Figure 5-2 show that ΔH changes with aqueous concentration of *N*-heterocyclic compounds. Due to the sorbent surface being energetically heterogeneous, the enthalpy of *ad*sorption varies with the amount adsorbed. A lower aqueous concentration (corresponding to a lower loading of adsorbate) leads to a more negative ΔH. The difference in ΔH at low and high concentrations, however, is not large.

For the compounds of group B, the ΔH is in the range from -15 to -22 kJ/mol. This implies that besides van der Waal's forces, other interactions also play a role in sorption. For the ionizable compounds 2MQUI, QUI and IQUI, cation exchange (corresponding to an average ΔH of -8 kJ/ mol (Delle Site, 2001)) dominates the overall sorption. With respect to 2QUI (existing mainly as the keto form (oxo tautomer) (Vasudevan et al., 2001)), IND, and BTA, additional interactions other than cation exchange predominate the overall sorption. For BTA, surface complexation might be one of the important processes (see below).

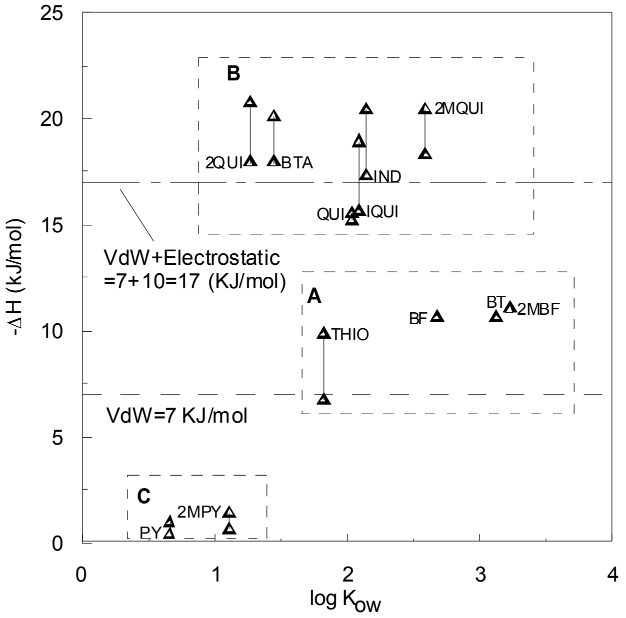


Figure 5-2 Enthalpy changes of compounds in the sorption to Eurosoil 4 (Column E4b, determined at a temperature range of 5 to 40°C, flowrate 100 µL/min; $CaCl_2$ 0.005 M in mobile phase). There were two ΔH values at two different injected concentrations for each compound. The lower -ΔH value was obtained from the higher injected concentration. The lower concentration range is from 10 to 45 mg/L, and higher concentration range is from 150 to 350 mg/L.

Previous results suggested that specific interactions dominate the overall sorption of PY and 2MPY (see chapter 4). However, the ΔH of PY and 2MPY are relatively low (-0 to -2 kJ/mol, group C in Figure 5-2). This might be due to the specific properties of PY and 2MPY. Both of them are totally water miscible, and the molecular sizes (only one ring) are smaller than that of the other compounds.

5.2 Effect of solution properties on cation exchange

5.2.1 Cation type

As shown in Figure 5-3, when changing the Ca^{2+}/K^{+} ratio in the aqueous phase at constant ionic strength, there is little effect on the sorption of THIO, Tol, BF, 2MBF, DMBF, IND, 2QUI, and BTA (with a variation of K_d less than 20 %). For the other compounds (PY, 2MPY, QUI, IQUI, and 2MQUI), their K_d values increased by a factor from 1.5 to 10.

Exchangeable cations influence the sorption of cationic organic compounds mainly by competing for negatively charged sorption sites on the solid surfaces. The significantly higher sorption of protonated N-heterocyclic compounds with K^+ in the mobile phase confirms the cation exchange sorption mechanism. This is because hydrated K^+ is much less effective than hydrated Ca^{2+} in competing with cationic organic compounds for sorption sites of negative charge (Ikhsan et al., 2005).

It was found that among the common exchangeable base cations in soils (Ca^{2+}, Mg^{2+}, K^+, and Na^+), minerals saturated with weakly hydrated cations (e.g., K^+) manifest a higher affinity for many polar, nonionic pesticides compared with clays saturated with more strongly hydrated cations (Li et al., 2004). Changing Ca^{2+} to K^+ in solution, however, did not cause substantial increase of BTA sorption. One reason for this might be the diminishing of a surface complexation mechanism undergone by BTA, which involves Ca^{2+} (see below).

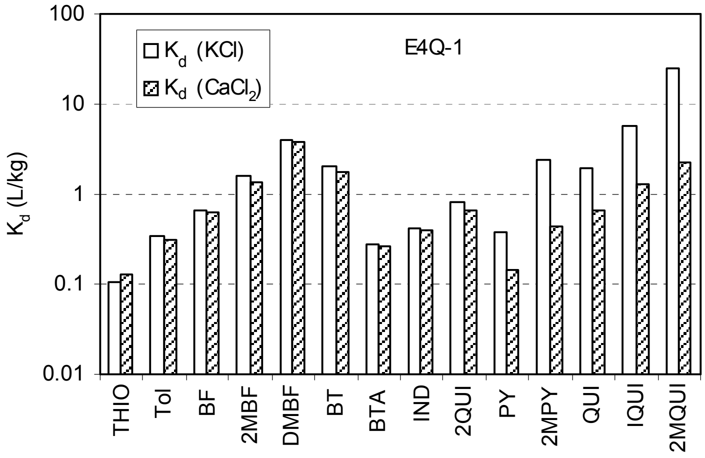


Figure 5-3 Effect of ion type (K^+ vs. Ca^{2+}) in mobile phase at ionic strength of 0.015 M (column) E4Q-1, flowrate 100 µL/min; 25 °C; pH 6.7 to 6.9 for both cases)

5.2.2 $CaCl_2$ concentration

As shown in Figure 5-4, for certain compounds (THIO, Tol, BF, 2MBF, DMBF, BT, BTA, IND, and 2QUI), the concentration of $CaCl_2$ has a negligible effect on sorption. However, for compounds in which cation exchange is supposed to be the main sorption mechanism, changing the $CaCl_2$ concentration resulted in a substantial influence on the sorption/transport of these compounds through column E4Q-1. Therefore, only the effect of $CaCl_2$ concentration change on the cation exchange process is discussed here.

Both pH and ionic strength concentration have an effect on the sorption of ionizable organic compounds. The pH governs the presence of charges on solid surface and the fraction of sorbate in ionized form. In column E4Q-1, there was no significant pH variation (6.7-6.9) resulting from changes in the $CaCl_2$ concentration; thus, the fractions of the organic cationic species at different $CaCl_2$ concentrations are roughly the same. The reduction in sorption at high $CaCl_2$ concentrations results from increased competition between Ca^{2+} and protonated organic compounds for binding sites on the solid matrix (Schwarzenbach et al., 2002). This is further evidence that cation exchange is the main sorption process of ionizable *N*-heterocyclic compounds. The results indicate that pK_a is not the only indicator necessary to describe the sorption of these compounds (Zachara et al., 1986), as the ionic strength of the system should also be considered.

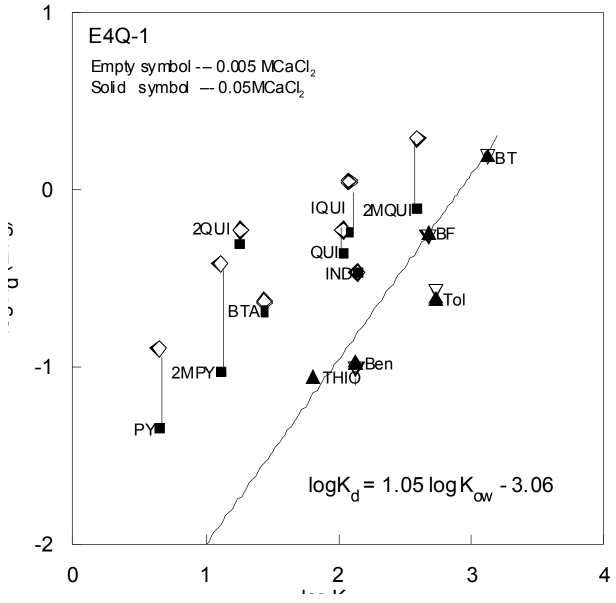


Figure 5-4 Effect of $CaCl_2$ concentrations in the mobile phase on the sorption of NSOs (in E4Q-1 column, pH values at 0.005 M and 0.05 M $CaCl_2$ are 6.7 to 6.9)

One alternative effect of increasing the $CaCl_2$ concentration is the potential formation of neutral ion pair complex $[BH\text{-}Cl]^0$ (where B is an organic base) as suggested by other researchers regarding the sorption of TBT^+ (Arnold et al., 1997; Bueno et al., 1998; Weidenhaupt et al., 1997). This hypothesis is, however, not consistent with the effects of pH on the sorption of NSOs (see chapter 4).

5.3 Ternary surface complexation

Our previous work suggests that surface complexation of the neutral species of BTA and 2MPY contributes to the overall sorption of these compounds. Although stability constants of metal-BTA complexes are not available (e.g., Ca-BTA) in the NIST Standard Reference Database 46 (Martell et al., 2004), the formation of BTA complexes, especially with copper, is well known (Botenschuetz et al., 1978). Complex formation of BTA with metals is the basis for its usage as a corrosion inhibitor. According to our experimental data, we suggest that ternary surface complexation (Fein, 2002) of the neutral BTA species contributes to the overall sorption of the compound.

$$\equiv SO^- + Me^{m+} + L \rightleftharpoons \equiv SOMeL^{(m-1)+} \qquad (5\text{-}2)$$

where $[\equiv SO^-]$ refers to interface of minerals to the water phase; [Me] is metal ion; [m] is the valence of the metal ion; [L] is the neutral organic ligand.

For BTA, the complex formation with Ca^{2+} is postulated to occur both in aqueous solution and at the mineral surface and can be described as:

In solution:

$$Ca^{2+} + BTA \rightleftharpoons [Ca\text{-}BTA]^{2+} \qquad (5\text{-}3)$$

On solid surface:

$$[\equiv SO^- \cdots Ca^{2+}] + BTA \rightleftharpoons [\equiv SO \cdots Ca\text{-}BTA]^+ \qquad (5\text{-}4)$$

According to this model, the contribution of surface complexation to overall sorption depends both on the Ca^{2+} density on the solid surface and is affected by the complexation occurring in solution. In our experiments (see Figure 5-5), when increasing the $CaCl_2$ concentration from 0 to 0.05 M (t_1 to t_2), there is a substantial increase of Ca^{2+} density on the solid surface, due to ion exchange between Ca^{2+} and H^+ on the surface, as is shown by the drop in the mobile phase's pH. This leads to an increased sorption of BTA due to surface complexation (Figure 5-5 (A) and Figure 5-6). Removal of Ca^{2+} from the mobile phase at the time step t_3, leads to excess Ca^{2+} on the solid surface. Because of less $[Ca\text{-}BTA]^{2+}$ complexation in the mobile phase, higher sorption and stronger tailing occurred in the BTA breakthrough curve (Figure 5-5(A, t_3)). When BTA complexation in solution and on the solid surface was at equilibrium, the concentration of Ca^{2+} (0.005 to 0.05M) had little effect on the sorption of BTA (Figure 5-6). Apparently, in this Ca^{2+} concentration range the formation of BTA complexes with Ca^{2+} both in solution and on the solid surface occurred to an extent that led to no net change in BTA retardation.

Another possible mechanism for BTA/Ca^{2+} interactions is a complex formation of the anionic species of BTA with a Ca^{2+} ($[BTA\text{-}Ca]^-$; $[BTA_2\text{-}Ca]^0$) (Lee et al., 1990). This would prevent electrostatic repulsion between BTA^- and the negatively charged solid surface. However, in our system the pH was much lower than pK_a of BTA, thus the fraction of anionic BTA species was negligible.

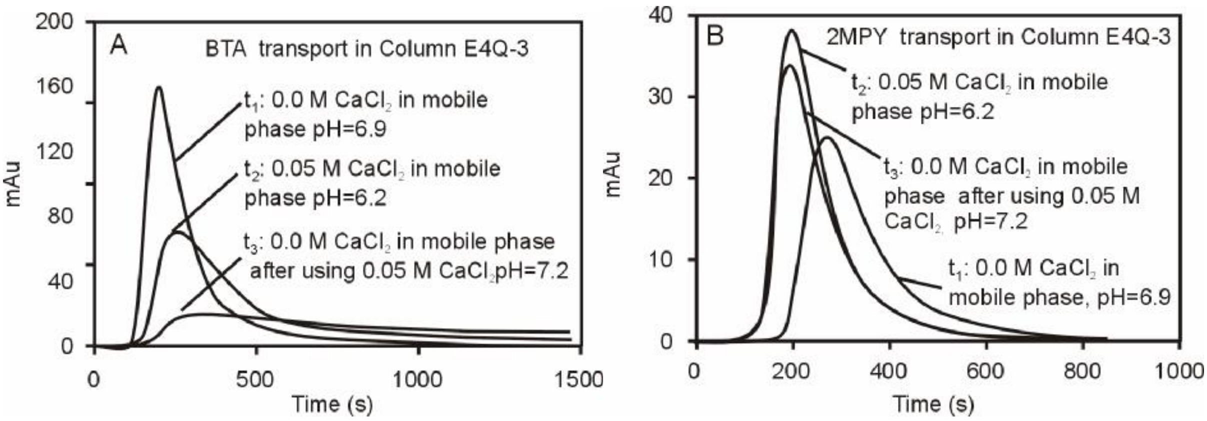


Figure 5-5 Effect of preload of high $CaCl_2$ on the sorption of (A) BTA and (B) 2MPY (25°C, flowrate 100 μL/min) in column E4Q-3

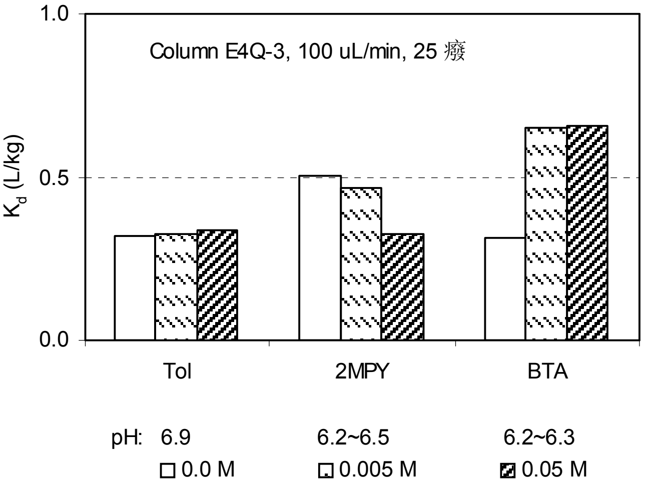


Figure 5-6 Effect of Ca^{2+} concentration on the sorption of toluene, 2-methylpyridine, and benzotriazole

In comparison, sorption of 2MPY decreases with increasing Ca^{2+} concentration due to the superposition of the effects of pH dependent speciation of 2MPY and increased competition between $2MPY^+$ and Ca^{2+} at high ionic strength (Figure 5-4 and Figure 5-6). As shown in Figure 5-5 (B), changing $CaCl_2$ concentration back to 0.0 M resulted in a similar pH as before, which means that the same fraction of cationic species is present. However, the sorption of 2MPY was lower than before, because the sorption sites on the solid surface were still occupied by Ca^{2+} ions. Unfortunately, there are no stability constants published for complexes of 2MPY with Ca^{2+} or Mg^{2+}. The complex stability constants of PY-Ca^{2+} and PY-Mg^{2+} are $10^{-0.4}$ to $10^{-0.48}$ and $10^{-0.29}$ to $10^{-0.37}$, respectively (Martell et al., 2004). If the constants of 2MPY are of a similar magnitude, surface complexation involving Ca^{2+} and Mg^{2+} would play a minor role in the overall sorption of 2MPY in our system.

5.4 Summary

The effects of various factors influencing the sorption of NSOs to reference soils have been successfully studied by soil column chromatography. The lack of significant effects of ionic strength, ion type and temperature on the sorption of *O*- and *S*-heterocyclic compounds show that partitioning to soil organic matter is the dominant sorption mechanism for these compounds. In contrast, specific interactions are involved in the sorption of N-heterocyclic compounds. The concentration of $CaCl_2$ in the mobile phase significantly affects the cation exchange of organic cationic species with negatively charged surfaces. Thus, at given ionic strength, substituting Ca^{2+} with K^+ in the mobile phase enhances the sorption of organic cationic species. Furthermore, our data suggest that ternary surface complexation with Ca^{2+} is involved in the sorption of benzotriazole.

6. Numerical Modeling of Column Experimental Data

Column experiments are often applied to determine the sorption parameters in laboratory-scale (Altfelder et al., 2001; Bayard et al., 1998; Buergisser et al., 1993; Young and Ball, 1999). In column experiments, the breakthrough curves (BTCs) may be influenced by nonequilbrium sorption and/or nonlinear sorption. Common measures to overcome sorption nonequilibrium are the use of low pore water velocities. Stop flow experiments and experiments at different flow velocities can be used to study nonequilibrium effects (Brusseau et al., 1989). Taking into account such experimental conditions, to simulate the BTCs from column experiments considering sorption kinetics can provide information not only on sorption nonequilibrium but on sorption nonlinearity as well. This is of great importance for the sorption of polar compounds, which normally show higher nonlinearity than apolar compounds (Chiou et al., 2000).

In this chapter, the effects of nonequilibrium sorption and nonlinear sorption on the transport of N-heterocyclic compounds (Benzotriazole, Quinaldine and Quinoline) in soil columns were investigated by an one-site first order model. Such models (Cryer, 2005; Hornsby and Davidson, 1973; Spurlock et al., 1995; Van Genuchten et al., 1974) have been successfully used to simulate solute transport in column experiments. The BTCs were numerically simulated by fitting the sorption parameters (K_f and n in the Freundlich isotherm, and mass transfer coefficient α) using the code AQUASIM. Toluene was taken as a reference compound and Eurosoil 4 was used as a model sorbent.

6.1 Transport of the conservative tracer in the column

Hydrodynamic dispersion coefficients (D) at different flow velocities in the column E4Q-3 (see Table 3-2) were obtained by fitting BTCs of thiourea. The results are shown in Table 6-1. There was no observed effect of injected concentration of thiourea on D. Averaged D values at each velocity were then used for the reactive transport modeling.

As long as the dispersion is small (i.e. the Peclet number is large, where P_e=vL/D, v the column velocity and L is the length of the column), the effect of dispersion on the diffuse part (Tailing part) of the isotherm is small. In our experiments, the corresponding column Peclet numbers are greater than 50. A column Peclet number Pe > 50 can be considered sufficient for the determination of isotherms (Buergisser et al., 1993). Supposing the isotherm is convex, an increase in the injected concentration leads to a shortening of the tailing (self-sharpening).

Table 6-1 dispersion coefficients determined from the breakthrough curves of thiourea

Flow Rate		Average Flow Velocity	Dispersion Coefficient D (mm^2/s)	
µL/min [1)]	mm/s [2)]	(mm/s) [3)]	Average	Range
20	0.11	0.12	0.07	0.066-0.073
50	0.27	0.28	0.17	0.165-0.180
100	0.53	0.54	0.38	0.360-0.400
200	1.06	1.05	0.97	0.964-1.03

[1)]: set value in the HPLC pump; [2)]: calculated velocity (linear velocity divided by porosity); [3)]: measured value by gravimetric method (used for modeling).

The hydrodynamic dispersion includes molecular diffusion, which is related to both specific compound and mechanical dispersion, the later being a property of the transport media. The molecular diffusion coefficient (D_m) was roughly estimated by using molecular mass (Schwarzenbach et al., 1993) at 25°C. For thiourea, the estimated D_m is 0.0012mm^2/s, which is only 0.1%-1.7% of dispersion coefficient in Table 6-2. The D_m values of other compound are in the range of 0.00087 to 0.0011 mm^2/s, so the mechanical dispersion (longitudinal dispersion D_L for one dimensional transport model) in this case dominates the hydrodynamic dispersion. Klotz et al. suggested the following relationship between longitudinal dispersion coefficients and flow velocities (Klotz et al., 1980).

$$D_L = \alpha_L \overline{V}^m \qquad (6\text{-}1)$$

where α_L is longitudinal dispersivity [mm], $\overline{V}$ is the mean flow velocity [mm/s] and m is an empirical exponent [-].

The fitted α_L (0.842 mm) and m (1.14) (Figure 6-1) from this experiment are comparable to the values (0.3mm-70mm for α_L, and 1.0-1.2 for m) in literature (Fetter, 1999; Sun, 1996).

Table 6-2 Hydrodynamic properties of the column E4Q-3

pore water velocity (mm/s)	D (mm^2/s)	P_e=v*L/D
0.12	0.07	103
0.28	0.17	99
0.54	0.38	85
1.05	0.97	65

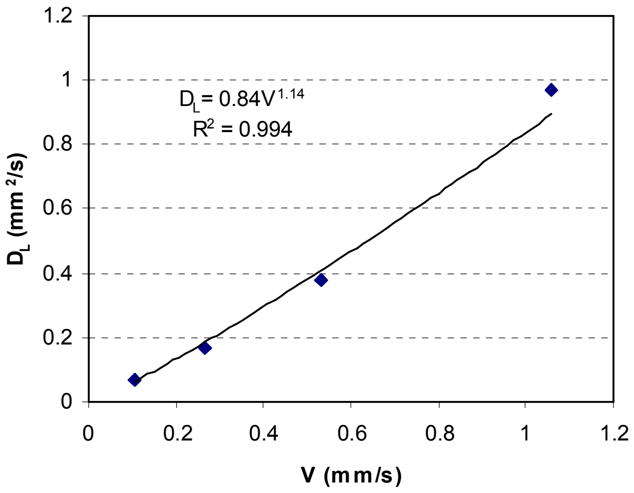


Figure 6-1 Relationship between flow velocity (v) and the dispersion coefficient (D_L)

6.2 Sorption and transport of reactive compounds

6.2.1 Toluene

In order to obtain reliable sorption parameter values (K_f, n, and α (mass transfer coefficient)), the BTCs of different injection concentrations at each pore water velocity were combined into one dataset. Then the parameters were fitted from the measured BTCs. The fitting quality was very good (same as that shown in Figure 6-2) and the fitted values of K_f (0.434~0.453) and n (0.834~0.865) at various velocities are quite similar, particularly when the pore water velocity is higher than 0.279 mm/s. However, the fitted mass transfer rate coefficient α (0.037~0.223) was found to be dependant on the flow velocity, in that higher pore water velocities caused higher α values (data not shown).

In column experiments, the reason for non-equilibrium is normally attributed to diffusion in immobile water, and these diffusion-limited mass transfer processes are approximated using first-order kinetics (Heyse et al., 2002; Hollenbeck et al., 1999). The α obtained from extensive literature data appears to be dependent on aqueous-phase diffusion and duration of contact (Heyse et al., 2002). The shorter contact time (higher flow velocity) normally corresponds to higher α. This seems to contradict the original assumption, i.e., the larger the magnitude of the rate constant, the less time is required until equilibrium is attained (Cryer, 2005). Possible explanation for pore water velocity dependency of α are: (i) α is a function not only of the intrinsic diffusion rate, but also of the column length, the step experiment's duration, the input pulse width, the fluid velocity, and the solute retardation factor. Effects which may be misinterpreted as being the result of differences in the intrinsic diffusion rate, even though rate differences of less than an order of magnitude may still not be mechanistically significant (Young and Ball, 1995); (ii) accuracy of the α representation requires the knowledge of pore geometry of the sorbed phase, which is not well-understood. (Das et al., 2004); (iii) the kinetics of contaminant sorption are still relatively poorly understood (Pignatello and Xing, 1996), and the approximation of mass transfer rate by using first-order kinetics may, in some cases, be inaccurate; and (iv) in modeling, when linear sorption (n=1) is often assumed (Brusseau et al., 1991; Culver et al., 1997; Maraqa, 2001), the change of α might just be a result from fitting BTCs.

For the reasons mentioned, direct comparison of the fitted first order mass transfer coefficients can only be made with great caution (Young and Ball, 1995). Variations in fitted α are not necessarily related to variations in underlying diffusion rates, but rather, may be simply dependent upon the column run conditions. One should be cautious in using first-order modeling for mechanistic diffusion rate interpretations, especially when additional fitting parameters have been applied, in order to improve the quality of the first-order model fit, as in the common “two-site” modeling approach (Young and Ball, 1997).

In AQUASIM, the equilibrium sorption was approximated by kinetic sorption with a very large rate constant of α of 3 s^{-1} (Reichert, 1998). In the following simulation, it was assumed that the sorption was close to equilibrium, and α was set to 3. Then, K_f and n at different pore water velocities were fitted (Table 6-3). The fitted results at each velocity are good; therefore, only the result at one velocity is shown in Figure 6-2. The results of fitting indicate that the effect of nonequilibrium on BTCs in these experiments is negligible.

Although the fitting for each velocity is good, and normally a higher K_f is accompanied by a lower n (Table 6-3), it is hard to select a set of K_f and n values for describing the isotherm. Therefore, fitting was also performed by combining all the data at different pore water velocities and concentrations together with an α of 3. The resulting n value is close to 1, and the K_f is lower than that obtained from the fittings at each individual flow velocity (see the last part of Table 6-3). The fitted curve is lower than the measured curve at the peak of the BTCs (Figure not shown). This is probably due to fewer data points at this area and the low resolution set in AQUASIM simulation. The latter uncertainty emerges because for large data sets which include all concentrations and velocities, there is a limit set up by what the computer can handle (in terms of processor speed and RAM) and a lower resolution has to be applied. In AQUASIM, the peak of a simulated BTC at a low resolution is lower than that of a high resolution (Reichert, 1998). Regardless of the differences in peak height, however, changing the resolution has no effect on the simulated retention time. Therefore, the fitting parameters from the whole data set can be used for the Freundlich isotherm.

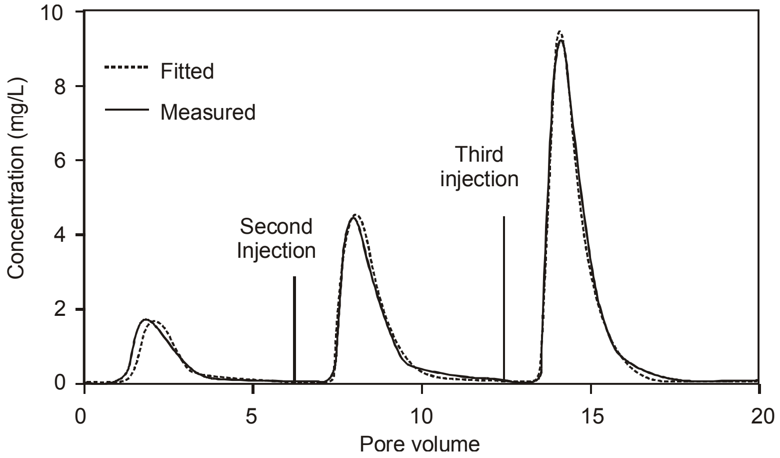


Figure 6-2 Fitting BTCs of toluene (α = 3; v=0.279 mm/s, K_f=0.435 ; *n*= 0.849)

With α as a fitting parameter, its value was changed from 3 to 4 ~ 6 (depending on the grid number and calculation step in the model), but there was no change in K_f and *n* (Table 6-3 and Table 6-4). The sensitivity analysis confirms that BTCs of toluene are not sensitive to α (Figure 6-3 (a)). The parameter α showed almost the same trend as the measured BTC. Further, it has little effect on the tailing part of BTC, though it can influence the peak height. Parameters K_f and *n* are more sensitive than α, and control the peak height and apex position of BTCs. Due to the similar effect on BTC, K_f and *n* can compensate each other. The modeling results indicate that the sorption of toluene in the column can be approximated as equilibrium sorption. The non-equilibrium resulting from diffusion in immobile water was negligible.

6.2.2 *N*-heterocyclic compounds

The sensitivity analysis showed that the mass transfer coefficient (α) has only a slight effect on the peak height of BTC for quinoline (Figure 6-3 (b)), which indicates that the effect of designed pore water velocity on the tailing of the BTC is negligible. This can also be confirmed by the plots of BTCs vs. pore volumes, in which BTCs at different pore water velocities were superimposed (data not shown). The exponent *n* shows high impacts on the asymmetry of BTCs (Figure 6-3 (b)), which means that the sorption is nonlinear. QUI and 2MQUI exhibited the same phenomena.

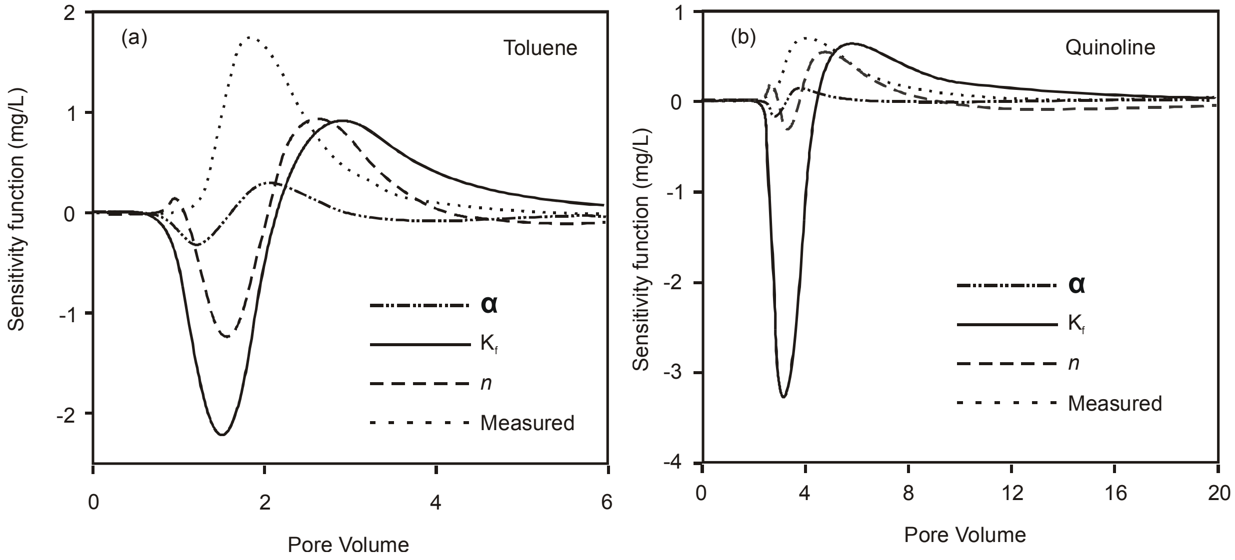


Figure 6-3 Sensitivity analysis (injection concentrations of toluene and quinoline are 84.9 mg/L and 108.2 mg/L, respectively; pore water velocity is 0.544 mm/s)

The tailing of the BTCs can be caused by nonequilibrium and/or nonlinear sorption processes. As discussed above, we may hypothesize that the tailing was mainly caused by nonlinear sorption processes. Therefore, α was set to 3 to approximate an equilibrium process for each modelled pore water velocity. The results are shown in Table 6-3. The fitting of QUI is also shown in Figure 6-4. BTA and 2MQUI show similar fitting qualities (Figures not shown). The success of the fit proved our original hypothesis that in our system the sorption is very close to the equilibrium.

As with toluene, a higher fitting K_f of N-heterocyclic compounds at each velocity is normally accompanied by a lower *n*, and it is hard to say which set of parameters better represent the real sorption isotherm.

With α also being treated as a fitting parameter, the simulation results for the whole data set of each compound at different concentration and pore water velocity were shown in Table 6-4. Changing α caused only slight variation in K_f and *n* of 2MQUI, but no change was observed for QUI and BTA. Due to the same reason discussed for Toluene, the fitted curves were lower at the peak part of BTCs. For BTA, QUI, and 2MQUI, the estimated results of the whole dataset show smaller K_f and larger *n* values than from those the datasets from each of the individual pore water velocities (Table 6-3).

Table 6-3 Modeling results of BTA, QUI and 2MQUI by using one-site model (α=3 for all)

Compound	pH	Pore water velocity (mm/s)	Fitting parameters***		χ^2/m
			K_f	n	
Toluene	5.8~6.0	1.05	0.448±0.002	0.820±0.002	0.032
			0.447±0.002	0.820±0.002	0.036
		0.544	0.448±0.002	0.748±0.01	0.037
			0.433±0.002	0.743±0.1	0.037
		0.265	0.435±0.001	0.849±0.001	0.031
			0.432±0.001	0.852±0.01	0.033
		0.116	0.412±0.001	0.876±0.001	0.053
BTA	5.8~6.0	1.05	0.441±0.002	0.7378±0.002	0.070
			0.456±0.006	0.726±0.003	0.066
		0.544	0.446±0.03	0.748±0.001	0.080
			0.450±0.002	0.743±0.1	0.076
		0.265	0.457±0.001	0.756±0.001	0.083
			0.458±0.001	0.759±0.001	0.094
		0.116	0.395±0.001	0.796±0.001	0.34
QUI	5.8~6.2	1.05 **	1.51±0.004	0.760±0.002	0.012
			1.52±0.004	0.751±0.002	0.012
		0.544	1.61±0.003**	0.692±0.001**	0.017
			1.58±0.003	0.707±0.001	0.015
		0.265	1.58±0.03	0.771±0.1	0.72
			1.58±0.03	0.744±0.001	0.010
		0.116	2.26±0.002	0.612±0.004	0.009
2MQUI	5.8	1.05	4.64±0.003	0.75±0.001	0.0024
		0.544	4.99±0.03	0.646±0.004	0.009
		0.265**	4.68±0.03	0.76±0.1	0.002
Tol	Tol	All data for each compound used for fitting	0.353±0.003	0.945±0.004	0.389
BTA	BTA		0.350±0.003	0.837±0.003	0.855
QUI	QUI		1.40±0.003	0.806±0.001	0.067
2MQUI	2MQUI		5.00±0.002	0.700±0.002	0.004

*: The values were fitted by using all BTCs of different concentrations and three different pore water velocities (0.279, 0.544, 1.05 mm/s); **: first α was used as a fitting parameter, after getting K_f and n, α was changed to 3 , but there was no effect from changing α on the BTCs; ***: two lines at each velocity are fitted from two sets of experimental data.

Table 6-4 Simulation results for whole data set with α as a fitting parameter

Parameter	Toluene	BTA	QUI	2MQUI
a	6.17	3.9	1.8	1366
K_f	0.354	0.350	1.39	4.63
n	0.941	0.830	0.810	0.756

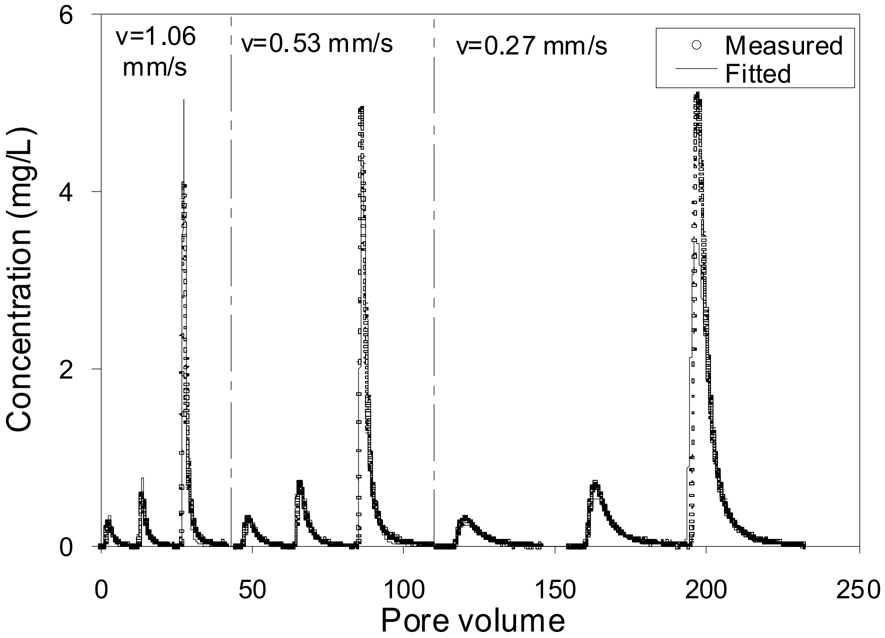


Figure 6-4 Fitting based on the combined data set of quinoline (α=3; K_f=1.40; n= 0.806; with three injected concentrations (54.4, 108.2, and 520.8 mg/l) at each velocity)

The results above are consistent with those isotherms determined from retardation factors at different concentrations, in which the retention time was determined by the half mass point of the BTCs and the linear sorption was approximated in each finite concentration range (see chapter 3).

Compared to the apolar compounds, polar compounds undergo more complex processes, such as ion exchange. This is shown by the higher sorption nonlinearity indicated by n. For example, n is 0.70~0.76 for 2MQUI. According to the modeling results, toluene has a very similar K_f value to BTA, although K_{ow} value of toluene is 20 times higher than that of BTA. The modelled K_f values of QUI and 2MQUI have even 4 and 10 times higher values, respectively, than that of toluene, although toluene has the highest K_{ow} among the four investigated compounds. This indicates further that specific interactions rather than partitioning into soil organic matter dominate the sorption of N-heterocyclic compounds.

6.3 Summary

A one-site first order model can successfully simulate the BTCs of N-heterocyclic compounds in column experiments. The fitting results presented here were not sensitive to mass transfer coefficients, which probably shows that either there is little effect from the investigated pore water velocities or the fitted rate parameters did not capture the intrinsic rate limitations of the system. Nevertheless, it is suggested that column experiments with different concentrations and flow velocities should be conducted in order to obtain reliable sorption parameters.

7. Conclusions and Outlook

Soil column chromatography proved to be a suitable approach to determine the small sorption coefficients for polar organic compounds or in soils with very low organic carbon content. The results from the modeling by AQUASIM show that kinetically limited sorption (i.e., nonequilibrium sorption) has a negligible influence on experimental data.

For ionizable *N*-heterocyclic compounds, it is often assumed that they show less sorption than their apolar analogues. However, much higher sorption than that of the apolar analogues was observed from our experimental data. All of the *N*-heterocyclic compounds exhibited K_d values higher than those estimated based on a linear free energy relationship correlation with K_{ow} (Figure 7-1). This is due to specific interactions in the sorption process that *N*-heterocyclic compounds exhibit with soils. Sorption of these compounds can be well predicted by a conceptual model that includes partitioning to the soil organic carbon, cation exchange, and an additional sorption process (e.g., surface complexation of the neutral species). The sorption of *S*- and *O*-heterocyclic compounds is generally dominated by partitioning into the soil organic matter.

For compounds in which cation exchange is the main sorption mechanism, the pH of the system is a critical parameter in predicting the sorption process, and the ionic strength and chemical composition in the solution must also be accounted for. Higher sorption was observed in solutions that contained K^+ than in those that contained Ca^{2+} with the same ionic strength. Increasing the ionic strength (e.g., by the addition of $CaCl_2$) leads to the decrease of sorption of these compounds. Surface complexation is suggested as the dominant mechanism for the compounds that cannot undergo cation exchange but nevertheless show a high contribution from specific interaction to the overall sorption. Ternary complexation involving Ca^{2+} is considered as a main sorption mechanism for benzotriazole.

Our findings have shown that besides partitioning and cation exchange, additional processes contribute to the overall sorption for *N*-heterocyclic compounds. Therefore, further work should be carried out to characterize the specific sorption processes, especially for benzotriazole. To this end, it would be worthwhile to carry out the work on the stability of the benzotriazole complex with various inorganic cations. The effect of compound properties (e.g., structure) on the complex formation might also be a topic of interest.

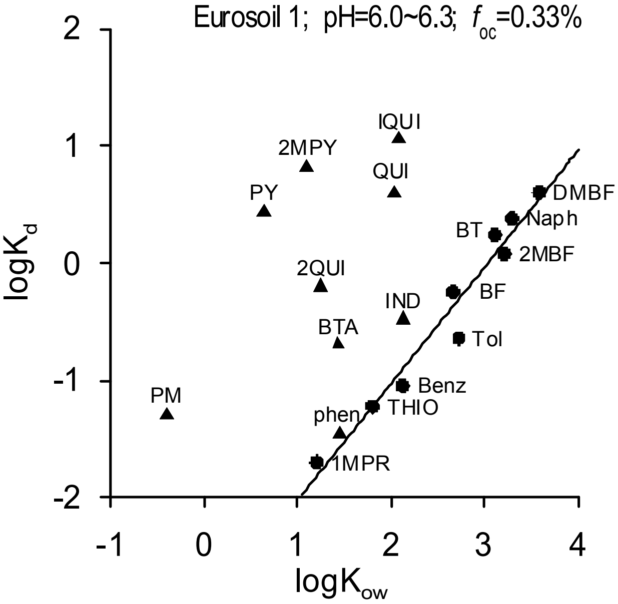


Figure 7-1 Relationship between logK_d (L/kg) and logK_{ow} (as shown before in Figure 4-1). K_d values were determined via soil column chromatography in which the column was packed with Eurosoil 1 and quartz with a weight ratio of 1 to 3. The non-specific-interaction line was fitted from the data of compounds for which specific interaction with soil components can be neglected. Abbreviations are listed in Table 2-1.

Although the specific sorption processes have been addressed for NSOs in this study, further work on the correlation between the specific properties of compounds, soil properties and aqueous chemical compositions is needed in order to better predict the sorption of these contaminants in groundwater systems.

Stable isotope fractionation of organic compounds is used as an indicator of biodegradation of organic contaminants in the subsurface (Schmidt et al., 2004). The effect of partitioning process on isotope fractionation is generally thought to be not important (Slater et al., 2000). However, the effect of cation exchange and surface complexation processes, which are the main sorption mechanisms for the N-heterocyclic compounds, on isotope fractionation is not clear yet. More studies on this aspect might be quite useful in determining the biodegradation processes of N-heterocyclic compounds in the subsurface.

Reference

Ainsworth, C.C., Zachara, J.M. and Schmidt, R.L., 1987. Quinoline sorption on Na-montmorillonite: Contributions of the protonated and neutral species. Clays & Clay Minerals, 35(2): 121-128.

Albert, A., Goldacre, R.J. and Phillips, J., 1948. Strength of heterocyclic bases. Journal of the Chemical Society: 2240-9.

Altfelder, S., Streck, T., Maraqa, M.A. and Voice, T.C., 2001. Nonequilibrium sorption of dimethylphthalate - Compatibility of batch and column techniques. Soil Science Society of America Journal, 65(1): 102-111.

Alva, A.K. and Singh, M., 1991. Sorption-desorption of herbicides in soil as influenced by electrolyte cations and ionic strength. Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes, 26(2): 147-163.

Arnold, C.G. et al., 1997. Aqueous speciation and 1-octanol-water partitioning of tributyl- and triphenyltin: Effect of pH and ion composition. Environmental Science & Technology, 31(9): 2596-2602.

Baker, R.A. and Luh, M.D., 1971. Pyridine sorption from aqueous solution by montmorillonite and kaolinite. Water Research, 5(10): 839-848.

Ball, W.P. and Roberts, P.V., 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. Environmental Science and Technology, 25(7): 1237-49.

Bayard, R.M., Barna, L., Mahjoub, B. and Gourdon, R., 1998. Investigation of naphthalene sorption in soils and soil fractions using batch and column assays. Environmental Toxicology and Chemistry, 17(12): 2383-2390.

Benker, E., Davis, G.B. and Barry, D.A., 1998. Estimating the retardation coefficient of trichloroethene for a sand aquifer low in sediment organic carbon - a comparison of methods. Journal of Contaminant Hydrology, 30(1-2): 157-178.

Botenschuetz, A.F., Buettner, U., Jostan, J.L., Marten, A. and Merk, H., 1978. Analysis of edge-Protecting deposits containing benzotriazole and etching media for printed circuit manufacture. Galvanotechnik, 69(12): 1076-1082.

Broholm, M.M., Broholm, K. and Arvin, E., 1999. Sorption of heterocyclic compounds on natural clayey till. Journal of Contaminant Hydrology, 39(3-4): 183-200.

Brusseau, M.L., 1994. Transport of reactive contaminants in heterogeneous porous media. Reviews of Geophysics, 32(3): 285-314.

Brusseau, M.L., 1995. The effect of nonlinear sorption on transformation of contaminants during transport in porous media. Journal of Contaminant Hydrology, 17(4): 277-291.

Brusseau, M.L., Jessup, R.E. and Rao, P.S.C., 1990. Sorption kinetics of organic chemicals: Evaluation of gas-purge and miscible-displacement techniques. Environmental Science & Technology, 24: 727-735.

Brusseau, M.L., Jessup, R.E. and Rao, P.S.C., 1991. Nonequilibrium sorption of organic chemicals: Elucidation of rate-limiting processes. Environmental Science & Technology, 25(1): 134-142.

Brusseau, M.L. and Rao, P.S.C., 1989. The influence of sorbate-organic matter interactions on sorption nonequilibrium. Chemosphere, 18(9-10): 1691-1706.

Brusseau, M.L., Rao, P.S.C., Jessup, R.E. and Davidson, J.M., 1989. Flow interruption: A method for investigating sorption nonequilibrium. Journal of Contaminant Hydrology, 4: 223-240.

Bucheli, T.D. and Gustafsson, O., 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. Environmental Science & Technology, 34(24): 5144-5151.

Bueno, M., Astruc, A., Astruc, M. and Behra, P., 1998. Dynamic sorptive behavior of tributyltin on quartz sand at low concentration levels: Effect of pH, flow rate, and monovalent cations. Environmental Science & Technology, 32(24): 3919-3925.

Buergisser, C.S., Cernik, M., Borkovec, M. and Sticher, H., 1993. Determination of nonlinear adsorption isotherms from column experiments: An alternative to batch studies. Environmental Science & Technology, 27: 943-948.

Burgos, W.D., Pisutpaisal, N., Mazzarese, M.C. and Chorover, J., 2002. Adsorption of quinoline to kaolinite and montmorillonite. Environmental Engineering Science, 19(2): 59-68.

Cancilla, D.A., Martinez, J. and Van Aggelen, G.C., 1998. Detection of aircraft deicing/antiicing fluid additives in a perched water monitoring well at an international airport. Environmental Science & Technology, 32(23): 3834-3835.

Celis, R., Real, M., Hermosin, M.C. and Cornejo, J., 2005. Sorption and leaching behaviour of polar aromatic acids in agricultural soils by batch and column leaching tests. European Journal of Soil Science, 56(3): 287-297.

Chatterjee, A., Ebina, T. and Iwasaki, T., 2001. Best dioctahedral smectite for nitrogen heterocyclics adsorption - A reactivity index study. Journal of Physical Chemistry A, 105(47): 10694-10701.

Chiou, C.T., 2002. Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons, 257 pp.

Chiou, C.T., Kile, D.E., Rutherford, D.W., Sheng, G. and Boyd, S.A., 2000. Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: Potential sources of the sorption nonlinearity. Environmental Science and Technology, 34(7): 1254-1258.

Cox, L., Hermosin, M.C., Celis, R. and Cornejo, J., 1997. Sorption of two polar herbicides in soils and soil clays suspensions. Water Research, 31(6): 1309-1316.

Cryer, S.A., 2005. Determining kinetic and nonequilibrium sorption behavior for chlopyrifos using a hybrid batch/column experiment. Journal of Agricultural and Food Chemistry, 53(10): 4103-4109.

Culver, T.B., Brown, R.A. and Smith, J.A., 2000. Rate-limited sorption and desorption of 1,2-dichlorobenzene to a natural sand soil column. Environmental Science & Technology, 34(12): 2446-2452.

Culver, T.B., Hallisey, S.P., Sahoo, D., Deitsch, J.J. and Smith, J.A., 1997. Modeling the desorption of organic contaminants from long-term contaminated soil using distributed mass transfer rates. Environmental Science & Technology, 31(6): 1581-1588.

Das, B.S., Lee, L.S., Rao, P.S.C. and Hultgren, R.P., 2004. Sorption and degradation of steroid hormones in soils during transport: Column studies and model evaluation. Environmental Science & Technology, 38(5): 1460-1470.

Delle Site, A., 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. Journal of Physical and Chemical Reference Data, 30(1): 187-439.

Dontsova, K.M. and Bigham, J.M., 2005. Anionic polysaccharide sorption by clay minerals. Soil Science Society of America Journal, 69(4): 1026-1035.

Doucette, W.J., 2003. Quantitative structure-activity relationships for predicting soil-sediment sorption coefficients for organic chemicals. Environmental Toxicology and Chemistry, 22(8): 1771-1788.

Dyson, N., 1998. Chromatographic Integration Methods. Royal Society of Chemistry, Cambridge, 201 pp.

Farrell, J., Grassian, D. and Jones, M., 1999. Investigation of mechanisms contributing to slow desorption of hydrophobic organic compounds from mineral solids. Environmental Science & Technology, 33(8): 1237-1243.

Fein, J.B., 2002. The effects of ternary surface complexes on the adsorption of metal cations and organic acids onto mineral surfaces. In: R. Hellmann and S.A. Wood (Editors), Water-Rock Interactions, Ore Deposits and Environmental Geochemistry: A Tribute to David A. Crerar. The Geochemical Society, Special Publication No. 7, pp. 365-378.

Fesch, C., Simon, W., Haderlein, S.B., Reichert, P. and Schwarzenbach, R.P., 1998. Nonlinear sorption and nonequilibrium solute transport in aggregated porous media: Experiments, process identification and modeling. Journal of Contaminant Hydrology, 31(3-4): 373-407.

Fetter, C.W., 1999. Contaminant hydrogeology (second edition). Prentice-Hall, Upper Saddle River, New Jesey, 500 pp.

Gawlik, B.M., Bo, F., Kettrup, A. and Muntau, H., 1999. Characterisation of a second generation of European reference soils for sorption studies in the framework of chemical testing - Part I: chemical composition and pedological properties. The Science of the Total Environment, 229(1-2): 99-107.

Gawlik, B.M., Feicht, E.A., Karcher, W., Kettrup, A. and Muntau, H., 1998. Application of the European reference soil set (EUROSOILS) to a HPLC-screening method for the estimation of soil adsorption coefficients of organic compounds. Chemosphere, 36(14): 2903-2919.

Goerlitz, D.F., Troutman, D.E., Godsy, E.M. and Franks, B.J., 1985. Migration of wood-preserving chemicals in contaminated groundwater in a sand aquifer at pensacola, Florida. Environmental Science & Technology, 19: 955-961.

Grathwohl, P., 1990. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on Koc correlations. Environmental Science & Technology, 24(11): 1687-1693.

Grathwohl, P., 1998. Diffusion in natural porous media: contaminant transport, sorption/desorption and dissolution kinetics. Topics in environmental fluid mechanics. Kluwer, Boston, 207 pp.

Guo, R.B. et al., 2004. Prediction of soil organic carbon partition coefficients by soil column liquid chromatography. Journal of Chromatography A, 1035(1): 31-36.

Haderlein, S.B. and Schwarzenbach, R.P., 1993. Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. Environmental Science & Technology, 27: 316-326.

Haderlein, S.B., Weissmahr, K.W. and Schwarzenbach, R.P., 1996. Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. Environmental Science & Technology, 30(2): 612-622.

Hart, D.S., Davis, L.C., Erickson, L.E. and Callender, T.M., 2004. Sorption and partitioning parameters of benzotriazole compounds. Microchemical Journal, 77(1): 9-17.

Helmy, A.K., De Bussetti, S.G. and Ferreiro, E.A., 1983. Adsorption of quinoline from aqueous solutions by some clays and oxides. Clays & Clay Minerals, 31(1): 29-36.

Hem, L.J., Hartnik, T., Roseth, R. and Breedyleld, G.D., 2003. Photochemical degradation of benzotriazole. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering, 38(3): 471-481.

Heyse, E., Augustijn, D., Rao, P.S.C. and Defino, J.J., 2002. Nonaqueous phase liquid dissolution and soil organic matter sorption in porous media: Review of system similarities. Critical Reviews in Environmental Science and Technology, 32(4): 337-397.

Hollenbeck, K.J., Harvey, C.F., Haggerty, R. and Werth, C.J., 1999. A method for estimating distributions of mass transfer rate coefficients with application to purging and batch experiments. Journal of Contaminant Hydrology, 37(3-4): 367-388.

Hornsby, A.G. and Davidson, J.M., 1973. Solution and adsorbed flometuron concentration distribution in a water-saturated soil: Experimental and predicted evaluation. Proc Soil Sci Soc Am, 37(6): 823-828.

Ikhsan, J., Angove, M.J., Wells, J.D. and Johnson, B.B., 2005. Surface complexation modeling of the sorption of 2-, 3-, and 4-aminopyridine by montmorillonite. Journal of Colloid and Interface Science, 284(2): 383-392.

Johansen, S.S., Arvin, E., Mosbæk, H. and Hansen, A.B., 1998. Heteroaromatic compounds and their biodegradation products in creosote-contaminated groundwater. Toxicological and Environmental Chemistry, 66(1-4): 195-228.

Klotz, D., Seiler, K.P., Moser, H. and Neumaier, F., 1980. Dispersivity and velocitiy relationship from laboratory and field experiments. Journal of Hydrology, 45(3-4): 169-184.

Kromidas, S., 2000. Practical problem solving in HPLC. Wiley-VCH, Weinheim, 178 pp.

Kuhnt, G. et al., 1994. Pedological characterization and major element composition analysis. In: G. Kuhnt and H. Muntau (Editors), EURO-SOILS Identification, collection, treatment, characterization. Joint Research Centre European Commission.

Lee, L.S., Rao, P.S.C. and Brusseau, M.L., 1991. Nonequilibrium sorption and transport of neutral and ionized chlorophenols. Environmental Science & Technology, 25: 722-729.

Lee, L.S., Rao, P.S.C., Nkedi-Kizza, P. and Delfino, J.J., 1990. Influence of solvent and sorbent characteristics on distribution of pentachlorophenol in octanol-water and soil-water systems. Environmental Science & Technology, 24: 654-661.

Li, H., Teppen, B.J., Laird, D.A., Johnston, C.T. and Boyd, S.A., 2004. Geochemical modulation of pesticide sorption on smectite clay. Environmental Science & Technology, 38(20): 5393-5399.

Mader, B.T., Goss, K.U. and Eisenreich, S.J., 1997. Sorption of nonionic, hydrophobic organic chemicals to mineral surfaces. Environmental Science & Technology, 31(4): 1079-1086.

Maraqa, M.A., 2001. Prediction of mass-transfer coefficient for solute transport in porous media. Journal of Contaminant Hydrology, 53(1-2): 153-171.

Maraqa, M.A., Zhao, X., Wallace, R.B. and Voice, T.C., 1998. Retardation coefficients of nonionic organic compounds determined by batch and column techniques. Soil Science Society of America Journal, 62(1): 142-152.

Martell, A.E., Smith, R.M. and Motekaitis, R.J., 2004. NIST Standard reference database 46: NIST critically selected stability constants of metal complexes database, Version 8.0. Texas A & M University, College Station, TX.

Miyabe, K. and Guiochon, G., 1999. Estimation of the column radial heterogeneity from an analysis of the characteristics of tailing peaks in linear chromatography. Journal of Chromatography A, 830(1): 29-39.

Nathwani, J.S. and Phillips, C.R., 1977. Adsorption-desorption of selected hydrocarbons in crude oil on soils. Chemosphere, 6(4): 157-162.

OECD, 2000. OECD guideline 106 for the testing of chemicals - adsorption-desorption using a batch equilibrium method, Pairs, 52 pp.

O'Loughlin, E.J., Traina, S.J. and Sims, G.K., 2000. Effects of sorption on the biodegradation of 2-methylpyridine in aqueous suspensions of reference clay minerals. Environmental Toxicology and Chemistry, 19(9): 2168-2174.

Pignatello, J.J. and Xing, B., 1996. Mechanisms of Slow Sorption of Organic Chemicals to Natural Particles. Environmental Science & Technology, 30(1): 1-10.

Ptak, T., Piepenbrink, M. and Martac, E., 2004. Tracer tests for the investigation of heterogeneous porous media and stochastic modelling of flow and transport - a review of some recent developments. Journal of Hydrology, 294(1-3): 122-163.

Rao, B.H. and Asolekar, S.R., 2001. QSAR models to predict effect of ionic strength on sorption of chlorinated benzenes and phenols at sediment-water interface. Water Research, 35(14): 3391-3401.

Reichert, P., 1994. Aquasim - A tool for simulation and data analysis of aquatic systems. Water Science and Technology, 30(2 pt 2): 21-30.

Reichert, P., 1995. Design techniques of a computer program for the identification of processes and the stimulation of water quality in aquatic systems. Environmental Software, 10(3): 199-210.

Reichert, P., 1998. AQUASIM 2.0-Tutoria, Computer program for the identification and simulation of aquatic systems, EAWAG, Dübendorf, Switzerland.

Relyea, J.F., 1982. Theoretical and experimental considerations for the use of the column method for determining retardation factors. Radioactive Waste Management and the Nuclear Fuel Cycle, 3(2): 151-166.

Schmidt, T.C. et al., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: A critical review of the state of the art, prospects, and future challenges. Analytical and Bioanalytical Chemistry, 378(2): 283-300.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 1993. Environmental Organic Chemistry. Wiley, New York, 681 pp.

Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 2002. Environmental organic chemistry. Wiley, New York, 1313 pp.

Schwarzenbach, R.P. and Westall, J.C., 1981. Transport of nonpolar organic compounds from surface water to groundwater: Laboratory sorption studies. Environmental Science & Technology, 15: 1360-1367.

Senesi, N., D'Orazio, V. and Ricca, G., 2003. Humic acids in the first generation of EUROSOILS. Geoderma, 116(3-4): 325-344.

Slater, G.F., Ahad, J.M.E., Sherwood Lollar, B., Allen-King, R. and Sleep, B., 2000. Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs. Analytical Chemistry, 72(22): 5669-5672.

Spadotto, C.A. and Hornsby, A.G., 2003. Soil sorption of acidic pesticides: Modeling pH effects. Journal of Environmental Quality, 32(3): 949-956.

Spurlock, F.C., 1995. Estimation of humic-based sorption enthalpies from nonlinear isotherm temperature dependence: Theoretical development and application to substituted phenylureas. Journal of Environmental Quality, 24(1): 42-49.

Spurlock, F.C., Huang, K. and Van Genuchten, M.T., 1995. Isotherm nonlinearity and nonequilibrium sorption effects on transport of fenuron and monuron in soil columns. Environmental Science & Technology, 29(4): 1000-1007.

Stoob, K., 2000. Verhalten ausgewählter polarer Verbindungen aus Treibstoffen im Untergrund. Diploma Thesis, ETH, Zürich, 65 pp.

Sun, N.Z., 1996. Mathematical modeling of groundwater pollution. Springer-Verlag, New York, 377 pp.

Thomsen, A.B., Henriksen, K., Møldrup, P. and Grøn, C., 1999. Sorption, transport, and degradation of quinoline in unsaturated soil. Environmental Science & Technology, 33(17): 2891-2898.

Thomson, B.M., Finfrock, D.J. and McHaley, C.P., 1999. Development of permeable barriers for groundwater remediation: Air stripping of methyl tertiary-butyl ether (MTBE). Journal of Environmental Science and Health, A, 34(2): 263-287.

Tolls, J., 2001. Sorption of veterinary pharmaceuticals in soils: A review. Environmental Science & Technology, 35(17): 3397-3406.

TorresLapasio, J.R., BaezaBaeza, J.J. and GarciaAlvarezCoque, M.C., 1997. A model for the description, simulation, and deconvolution of skewed chromatographic peaks. Analytical Chemistry, 69(18): 3822-3831.

Turin, H.J. and Bowman, R.S., 1997. Sorption behavior and competition of bromacil, napropamide, and prometryn. Journal of Environmental Quality, 26(5): 1282-1287.

Valocchi, A.J., 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. Water Resources Research, 21(6): 808-820.

Van Genuchten, M.T., Davidson, J.M. and Wierenga, P.J., 1974. Evaluation of kinetic and equilibrium equations for the prediction of pesticide movement throgh porous media. Proc Soil Sci Soc Am, V 38(N 1): 29-35.

van Genuchten, M.T., Wierenga, P.J. and O'Connor, G.A., 1977. Mass transfer studies in sorbing porous media: 3. Experimental evaluation with 2,4,5-T. Soil Science Society of America Journal, 41(2): 278-285.

Vasudevan, D., Dorley, P.J. and Zhuang, X., 2001. Adsorption of hydroxy pyridines and quinolines at the metal oxide-water interface: Role of tautomeric equilibrium. Environmental Science & Technology, 35(10): 2006-2013.

Weber, J.B., McKinnon, E.J. and Swain, L.R., 2003. Sorption and mobility of C-14-labeled imazaquin and metolachlor in four soils as influenced by soil properties. Journal of Agricultural and Food Chemistry, 51(19): 5752-5759.

Weidenhaupt, A., Arnold, C., Muller, S.R., Haderlein, S.B. and Schwarzenbach, R.P., 1997. Sorption of organotin biocides to mineral surfaces. Environmental Science & Technology, 31(9): 2603-2609.

Worch, E., 2004. Modelling the solute transport under nonequilibrium conditions on the basis of mass transfer equations. Journal of Contaminant Hydrology, 68(1-2): 97-120.

Xu, F., Liang, X.M., Lin, B.C., Schramm, K.W. and Kettrup, A., 2002. Estimation of soil organic partition coefficients: from retention factors measured by soil column chromatography with water as eluent. Journal of Chromatography A, 968(1-2): 7-16.

Xu, F. et al., 2001. Prediction of soil organic partition coefficients by a soil leaching column chromatographic method. Journal of Environmental Quality, 30(5): 1618-1623.

Yaron, B., Bresler, E. and Shalhevet, J., 1966. A method for uniform packing of soil column. Soil Science, 101(3): 205-209.

Young, D.F. and Ball, W.P., 1995. Effects of column conditions on the first-order rate modeling of nonequilibrium solute breakthrough. Water Resources Research, 31(9): 2181-92.

Young, D.F. and Ball, W.P., 1997. Effects of column conditions on the first-order rate modeling of nonequilibrium solute breakthrough: Cylindrical macropores versus spherical media. Water Resources Research, 33(5): 1149-1156.

Young, D.F. and Ball, W.P., 1998. Estimating diffusion coefficients in low-permeability porous media using a macropore column. Environmental Science & Technology, 32(17): 2578-2584.

Young, D.F. and Ball, W.P., 1999. Two-region linear/nonlinear sorption modeling: Batch and column experiments. Environmental Toxicology and Chemistry, 18(8): 1686-1693.

Young, D.F. and Ball, W.P., 2000. Column experimental design requirements for estimating model parameters from temporal moments under nonequilibrium conditions. Advances in Water Resources, 23(5): 449-460.

Zachara, J.M., Ainsworth, C.C., Cowan, C. and Thomas, B.L., 1987. Sorption of binary mixtures of aromatic nitrogen heterocyclic compounds on subsurface materials. Environmental Science & Technology, 21(4): 397-402.

Zachara, J.M., Ainsworth, C.C., Felice, L.J. and Resch, C.T., 1986. Quinoline sorption to subsurface materials: Role of pH and retention of the organic cation. Environmental Science & Technology, 20(6): 620-627.

Zachara, J.M., Ainsworth, C.C., Schmidt, R.L. and Resch, C.T., 1988. Influence of cosolvents on quinoline sorption by subsurface materials and clays. Journal of Contaminant Hydrology, 2(4).

Zachara, J.M., Ainsworth, C.C. and Smith, S.C., 1990. The sorption of N-heterocyclic compounds on reference and subsurface smectite clay isolates. Journal of Contaminant Hydrology, 6(3): 281-305.

Zamfirescu, D. and Grathwohl, P., 2001. Occurrence and attenuation of specific organic compounds in the groundwater plume at a former gasworks site. Journal of Contaminant Hydrology, 53(3-4): 407-427.

Zheng, C. and Bennett, G.D., 1997. Applied Contaminant Transport Modeling: Theory and Practice. Van Nostrand Reinhold, New York.

Zhu, D., Pignatello, J.J., Hyun, S. and Lee, L.L., 2003a. pH effects on sorption of nonionic compounds to soils: Possible involvement of pi-pi charge-transfer interactions for PAHs and other strong electron donor aromatic compounds, ACS Division of Environmental Chemistry, Preprints.

Zhu, D.Q., Herbert, B.E. and Schlautman, M.A., 2003b. Sorption of pyridine to suspended soil particles studied by deuterium nuclear magnetic resonance. Soil Science Society of America Journal, 67(5): 1370-1377.

Zhu, W.-L. et al., 1999. Density functional theory (DFT) study on the interaction of ammonium (NH4+) and aromatic nitrogen heterocyclics. Journal of the Chemical Society. Perkin Transactions 2(11): 2615-2622.

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Appendix 1: Validation of soil column chromatography method

(25°C injected volume 5 μL, $CaCl_2$ 0.005 M in mobile phase).

Retardation of compounds in quartz column and alumina column*

Column	BTA	BT	5MBT	2MBF	DMBF	Nitrite
Q-5	1.02±0.05	1.24±0.09	1.78±0.08	1.22±0.03	1.83±0.13	0.99±0.00
A-1	2.75±0.18	1.30±0.00	1.67±0.02	1.27±0.01	1.65±0.00	5.93±0.03
$C_{injected}$ (mg/L)	174.0	127.0	57.0	151.0	148.4	20.0

*: Flow velocities in Q-5 and A-1 were 1.42 and 7.1 cm/min, respectively.

Retardation factor evaluated by different methods (Column E4b)

Flow velocity (cm/min)	1MPR ($C_{injected}$ =130 mg/L)			BT ($C_{injected}$ =146 mg/L)		
	First moment	Apex	Half mass	First moment	Apex	Half mass
0.28	1.17	1.04	1.06	6.13	4.48	5.12
0.42	1.06	1.04	1.06	5.29	4.22	4.87
0.71	1.10	1.06	1.10	5.18	3.92	4.71
1.42	1.13	1.04	1.09	5.23	4.00	4.74

Retardation factor as a function of flow velocity in column E4b*

Flow velocity (cm/min)	PR	1MPR	BTA	Tol	BT
0	1.14	1.09	1.82	1.58	5.19
0.28	-	1.1, 1.05	1.92	1.68	4.92; 5.08
0.42	1.08	1.05	1.65	-	4.88
0.71	-	1.11	1.91	1.65, 1.64	4.83
1.42	1.1	1.08	1.81	1.64	4.57, 4.53

*: Injected concentrations: 1MPR 130 mg/L, BTA 174 mg/L, Tol 203 mg/L, and BT 146 mg/L. *R* at zero velocity was obtained by interrupt flow experiment, stop-flow period: toluene 15 min., 1MPR 15 min., BTA 30 min., BT 60 and 660 min.

Packed columns with reference materials (copy of Table 3-2)

Column	L * ID (mm*mm)	Packing material	OC (%)	Porosity	Density (g/cm^3)
Q-6	250 * 3	Quartz	-	0.409	2.65
Q-5	53 * 3	Quartz	-	0.393	2.65
Al-1	250 * 3	Alumina	-	0.565	3.5
E4-3	60 * 3	Eurosoil4	1.55	0.880	2.72
E4-9	53 * 3	Eurosoil4	1.55	0.539	2.72
E4Q-1	60 * 3	Eurosoil4 : Quartz = 1:0.5	1.03	0.444	2.69
E1Q-2	60 * 3	Eurosoil1 : Quartz = 1:3	0.325	0.388	2.68
E2Q-3	60 * 3	Eurosoil2 : Quartz = 1:1	1.85	0.413	2.69
E3Q-1	60 * 3	Eurosoil3 : Quartz = 1:1	1.725	0.545	2.68
E4b	53 * 3	Eurosoil4	1.55	0.476	2.72
E5Q-4	60 * 3	Eurosoil5 : Quartz = 1:9	0.925	0.437	2.65

Compounds / Abbreviations

Benzene / Benz
Benzofuran / BF
1-Benzothiophene / BT
Benzotriazole / BTA
2,3-Dimethylbenzofuran / DMBF
2-Hydroxyquinoline / 2QUI
Indole / IND
Isoquinoline / IQUI
2-Methylbenzofuran / 2MBF
2-Methylpyridine /2MPY
1-Methylpyrrole /1MPR
Naphthalene / Naph
Quinoline / QUI
Phenol / Phen
Pyridine / PY
Quinaldine / 2MQUI
Pyrimidine / PM
Pyrrole / PR
Thiophene / THIO
5-Methylbenzo[b]thiophene / 5MBT
Toluene / Tol

Appendix 2: Effect of environmental factors on sorption

(Injected volume 5 µL, flow velocity 1.42 cm/min, column data and abbreviations see Appendix 1)

Temperature effect on sorption*

Compounds	$C_{injected}$ (mg/L)	K_d			LnK_d		
		40°C	25°C	5°C	40°C	25°C	5°C
THIO	151	0.05	0.10	0.08	-2.93	-2.28	-2.55
PY	31.7	0.23	0.24	0.24	-1.49	-1.44	-1.44
BTA	39.4	0.16	0.27	0.39	-1.81	-1.31	-0.93
BF	153	0.37	0.46	0.61	-1.00	-0.77	-0.49
IND	9.77	0.28	0.47	0.76	-1.27	-0.76	-0.27
2QUI	45.8	0.38	0.60	1.03	-0.98	-0.52	0.03
2MPY	30.5	0.69	0.74	0.72	-0.37	-0.31	-0.33
QUI	35.3	0.51	0.83	1.10	-0.68	-0.19	0.09
2MBF	151	0.89	1.08	1.50	-0.12	0.07	0.41
BT	146	1.01	1.33	1.70	0.01	0.28	0.53
IQUI	16.3	1.24	2.25	3.18	0.22	0.81	1.16
2MQUI	34.2	1.98	2.99	5.36	0.68	1.09	1.68

*: Column E4b, $CaCl_2$ 0.005 M in mobile phase.

Enthalpy change of compounds in the sorption to Eurosoil 4*

Compounds	$C_{injected}$ (mg/L)	ΔH (KJ/mol)	Compounds	$C_{injected}$ (mg/L)	ΔH (KJ/mol)
2MBF	150.9	-11.0	BT	32.9	-10.6
2MPY	30.5	-0.6	2MQUI	34.2	20.4
	134.9	-1.4		151.3	18.3
BF	34.6	-10.6	IQUI	16.3	-18.9
	153.1	-10.6		351.4	-15.6
PY	31.7	-0.9	QUI	35.3	-15.5
	140.3	-0.4		156.1	-15.2
THIO	34.1	-9.8	2QUI	45.8	-20.7
	151.0	-6.7		202.9	-17.9
BTA	39.4	-17.9	IND	9.8	-20.4
	174.3	-20.1		210.7	-17.3

*: Column E4b, temperature between 5 and 40°C, $CaCl_2$ 0.005 M in mobile phase.

Effect of $CaCl_2$ concentration in mobile phase on the sorption*

Compounds	$C_{injected}$ (mg/L)	R_f			K_d		
		0.00 M	0.005 M	0.05 M	0.00	0.005 M	0.05 M
PR	138.4	1.00	0.99	1.01	0.00	0.00	0.00
1MPR	130.0	0.98	0.99	0.99	-0.01	0.00	0.00
Tol	203.0	2.09	2.12	2.17	0.32	0.33	0.34
2MPY	134.9	2.73	2.60	2.11	0.50	0.47	0.32
BTA	174.3	2.08	3.23	3.25	0.31	0.65	0.66
PY	140.3	1.51	1.56	1.38	0.15	0.16	0.11

*: Column E4Q-3 (same as E4Q-1); temperature 25 °C; eluent: MilliQ water with $CaCl_2$; measuring date: data for 0.0 M CaCl2: 04 Nov 2004; data for 0.005 M $CaCl_2$: 04-05 Nov 2004; data for 0.05 M CaCl2: 19-24 Nov 2004.

Effect of chemical composition in mobile phase on the sorption*

Compounds	$C_{injected}$ (mg/L)	R_f		K_d	
		0.005 M $CaCl_2$	0.015 M KCl	0.005 M $CaCl_2$	0.015 M KCl
THIO	173.3	1.43	1.36	0.13	0.11
Tol	299	2.03	2.16	0.31	0.35
BF	175.7	3.08	3.28	0.62	0.68
2MBF	173.2	5.57	6.50	1.36	1.56
DMBF	170.3	13.49	14.15	3.71	3.90
BT	127.1	6.87	7.92	1.74	2.06
BTA	337.7	1.91	1.94	0.27	0.28
IND	291.8	2.31	2.42	0.39	0.42
2QUI	130.2	3.24	3.80	0.67	0.81
PY	163.9	1.49	2.25	0.15	0.37
2MPY	154.8	2.46	9.05	0.43	2.39
QUI	179.2	3.28	7.68	0.68	1.98
IQUI	75.4	5.27	20.56	1.27	5.81
2MQUI	173.6	8.47	86.29	2.22	25.32

+: Column E4Q-1, pH range 6.7 –6.9 for both cases, temperature: 25 °C; eluent: MilliQ water with $CaCl_2$; Flow rate: 0.1 ml/min. Measuring date: KCl: 3-10 may 2005; $CaCl_2$: Oct 2004 (except data of THIO measured in June 2005.

Effect of $CaCl_2$ concentration in mobile phase on the sorption in column E4Q-1*

Compounds	$C_{injected}$ (mg/L)	0.05 M $CaCl_2$ (19-20 Oct 2004)			0.005 M $CaCl_2$ (22-23 Oct 2004)		
		R_f	pH	$\log K_d$	R_f	pH	$\log K_d$
Tol	203.0	1.7	7.2	-0.63	2	6.85	-0.57
		1.7	6.7	-0.62	2	-	-0.57
PCE	162.0	4	6.8	0	4.7	-	-0.01
		3.9	6.9	-0.02	-	-	-
THIO	151.0	1.3	-	-1.07	-	6.8	-
Phen	46.2	1.2	-	-1.22	-	6.7	-
1MPR	130.0	1.0	6.8	-	1.0	6.9	-
BT	145.7	5.5	6.8	0.18	6.8	6.7	0.18
		5.5	6.7	0.18	-	6.7	-
BF	153.1	2.7	6.4	-0.25	3.1	6.7	-0.27
		2.7	6.4	-0.25	3.1	6.7	-0.27
Benz	583.0	1.3	6.9	-0.99	1.4	6.7	-1.01
		1.3	6.9	-0.98	1.4	6.7	-1.01
PY	140.3	1.1	6.8	-1.36	1.5	6.9	-0.9
		1.1	6.8	-1.36	1.5	6.9	-0.9
IQUI	351.4	2.7	6.8	-0.24	5.3	7.0	0.05
		2.7	6.7	-0.25	5.2	6.9	0.04
IND	210.7	2.0	6.7	-0.47	2.3	6.9	-0.47
		2.0	6.7	-0.47	2.3	6.8	-0.47
QUI	156.1	2.3	6.7	-0.36	3.2	6.8	-0.23
		2.3	6.7	-0.36	3.3	6.8	-0.23
2MPY	134.9	1.3	6.9	-1.04	2.5	6.9	-0.42
		1.3	7.0	-1.03	2.5	6.9	-0.42
BTA	174.3	1.6	6.8-6.7	-0.7	1.9	6.9	-0.63
		1.6	6.7	-0.68	1.9	-	-0.64
2QUI	202.9	2.5	6.7	-0.3	3.2	6.9-6.7	-0.23
		2.5	6.7	-0.31	3.3	6.8	-0.23
2MQUI	151.3	3.3	6.7	-0.11	8.4	6.8	0.29
		3.3	6.7	-0.11	8.5	6.8	0.29

*: Temperature: 25 °C; eluent: MilliQ water with $CaCl_2$.

Effect of $CaCl_2$ concentration in mobile phase on the sorption in column E3Q-1 *

Compounds	C_{Inject} (mg/L)	pH	pH	R_f	R_f	$logK_d$	$logK_d$
		000M	0.005M	000M	0.005M	000M	0.005M
Tol	299.0	6.2	5.5	3.2	3.0	-0.01	-0.05
		6.3		3.1	3.0	-0.02	-0.05
Naph	52.2	6.2	5.5	23.1	23.8	0.99	1.01
		6.2	5.5	23.4	24.1	1.00	1.01
5MBT	52.6	6.5	5.2	43.8	43.0	1.28	1.27
		6.4	5.5	42.7	43.0	1.27	1.27
THIO	173.3	6.4	5.5	1.5	1.5	-0.65	-0.63
		6.3	5.5	1.5	1.5	-0.65	-0.64
DMBF	170.3	6.4	5.5	34.1	33.0	1.17	1.16
		6.4	5.6				
Benz	880	6.3	5.5	1.6	1.5	-0.59	-0.62
		6.2		1.5	1.5	-0.63	-0.63
2MBF	173.2	6.4	5.5	12.5	12.0	0.71	0.69
		6.4	5.5	-0.1	11.7		0.68
BT	127.1	6.5	5.2	17.3	16.2	0.86	0.83
		6.5	5.2	16.9		0.85	
1MPR	149.2	6.5	5.4	1.1	1.0	-1.47	-1.71
		6.5	5.5	1.1	1.0	-1.47	-1.71
BTA	337.7	6.5	5.2	2.5	2.8	-0.17	-0.09
		6.5		2.5	2.9	-0.18	-0.07
IQUI	351.4		5.2		54.4		1.38
	75.4	6.5	5.3	35.0	28.5	1.18	1.09
		6.4	5.2	65.7	25.0	1.46	1.03
PY	163.9	6.4	5.4	3.1	3.2	-0.03	0.00
		6.5	5.4	3.1	3.2	-0.02	0.00
2MPY	154.8	6.5	5.2	7.7	3.4	0.48	0.04
		6.5	5.2	7.7	3.4	0.48	0.04
IND	291.8	6.4	5.2	4.1	4.0	0.14	0.12
		6.5	5.2	4.1	4.0	0.14	0.13
QUI	179.2	6.5	5.2	10.4	7.8	0.62	0.48
		6.5	5.2		7.7		0.48
2QUI	130.2	6.4	5.2	5.40	5.07	0.29	0.26
		6.4	5.2	5.4	5.1	0.30	0.27
2MQUI5	173.6	6.4	5.2-5.5	30.7	14.3	1.12	0.77
		6.4	5.2	39.4		1.23	

*: Temperature: 25 °C; eluent MilliQ water with $CaCl_2$; flow rate: 0.1 ml/min. Measuring date: data for 0.0 M $CaCl_2$: 27 Jan – 8 Feb 2005; data for 0.005 M $CaCl_2$: 9 – 15 Feb 2005.

Appendix 3: Effect of pH on the UV signal of heterocyclic aromatic compounds

The solutions were prepared in 0.005M $CaCl_2 \cdot 2H_2O$. pH adjustment was made with 0.1M HCl and NaOH solutions and measured with pH-meter (PORTATEST 556).The UV signals were determined using a UV-vis spectrophotometer (Varian, Cary 50 Bio, Germany). Dependency of UV signals on pH is shown in the following tables. The pH value in brackets is measured before pH adjustment. Compounds abbreviations see Appendix 1.

BTA solution (6.64 mg/L, pH ≈ 6.59) at λ = 260 nm, pK_a = 8.37

pH	2.93	5.53	8.39	10.34	12.12
Signal	0.3607	0.3511	0.3479	0.3099	0.3020
Stdev	0.0002	0.0001	0.0002	0.0008	0.0006

Aniline solution (5.11 mg/L, pH ≈ 6.9) at λ = 221 nm, pK_a = 4.6

pH	2.57	4.46	6.62	8.56	10.11
Signal	0,0264	0,2364	0,4602	0,4735	0,4818
Stdev	0,0001	0,0004	0,0001	0,0002	0,0001

PY solution (4.91 mg/L, pH ≈ 6.36) at λ = 257 nm, pK_a = 5.23

pH	1.6	3.1	5.36	7.09	9.36
Signal	0,2526	0,3354	0,2419	0,1800	0,1871
Stdev	0,0010	0,0029	0,0051	0,0008	0,0000

2MPY solution (4.72 mg/L, pH ≈ 6.52) at λ = 260 nm, pK_a = 6.0

pH	2.17	3.76	6.01	7.9	10.2
Signal	0,3342	0,3520	0,2539	0,1811	0,1842
Std	0,0007	0,0002	0,0011	0,0005	0,0003

QUI solution (5.465 mg/L, pH ≈ 6.48) at λ = 225 nm, pK_a = 4.9

pH	2.35	3.13	4.83	7.09	9.08
Signal	0,4266	0,7302	1,1445	1,3420	1,4077
Stdev	0,0016	0,0027	0,0008	0,0001	0,0002

2MQUI solution (5.295 mg/L, pH ≈ 6.73?) at λ = 230 nm, pK_a = 5.71

pH	2.29	4.18	6.98	7.95	9.95
Signal	0,4182	0,9364	1,1081	1,1686	1,1831
Stdev	0,0006	0,0030	0,0008	0,0016	0,0014

IQUI solution (4.98 mg/L, pH ≈ 6.44) at λ = 216 nm, pK_a = 5.42

PH	1.95	2.43	3.44	5.4	7.4	9.29
Signal	1,0295	1,1538	1,1558	1,9251	2,3068	2,3305
Stdev	0,0011	0,0044	0,0009	0,0329	0,0014	0,0020

2QUI solution (5.41 mg/L, pH ≈ 6.47) at λ = 228 nm, pK_a = -0.31 (OH) and 11.76 (NH)

pH	2.08	2.11	3.07	4.85	6.47	8.14	8.78	10.32
Signal	1,0174	1,0287	1,1219	1,1256	1,1292	1,0743	1,1057	1,1298
Stdev	0,0003	0,0001	0,0009	0,0026	0,0010	0,0003	0,0008	0,0008

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