

Part V—sorption of pharmaceuticals and personal care products

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Abstract

Background, aim, and scope Pharmaceuticals and personal care products (PPCPs) including antibiotics, endocrine-disrupting chemicals, and veterinary pharmaceuticals are emerging pollutants, and their environmental risk was not emphasized until a decade ago. These compounds have been reported to cause adverse impacts on wildlife and human. However, compared to the studies on hydrophobic organic contaminants (HOCs) whose sorption characteristics is reviewed in Part IV of this review series, information on PPCPs is very limited. Thus, a summary of recent research progress on PPCP sorption in soils or sediments is necessary to clarify research requirements and directions.

Main features We reviewed the research progress on PPCP sorption in soils or sediments highlighting PPCP sorption different from that of HOCs. Special function of humic substances (HSs) on PPCP behavior is summarized according to several features of PPCP–soil or sediment interaction. In addition, we discussed the behavior of xenobiotic chemicals in a three-phase system (dissolved organic matter (DOM)–mineral–water). The complexity of three-phase systems was also discussed.

Results Nonideal sorption of PPCPs in soils or sediments is generally reported, and PPCP sorption behavior is relatively a more complicated process compared to HOC sorption, such as the contribution of inorganic fractions, fast degradation and metabolite sorption, and species-specific sorption mechanism. Thus, mechanistic studies are urgently needed for a better understanding of their environmental risk and for pollution control.

Discussion Recent research progress on nonideal sorption has not been incorporated into fate modeling of xenobiotic chemicals. A major reason is the complexity of the three-phase system. First of all, lack of knowledge in describing DOM fractionation after adsorption by mineral particles is one of the major restrictions for an accurate prediction of xenobiotic chemical behavior in the presence of DOM. Secondly, no explicit mathematical relationship between HS chemical–physical properties, and their sorption characteristics has been proposed. Last but not least, nonlinear interactions could exponentially increase the complexity and uncertainties of environmental fate models for xenobiotics. Discussion on proper simplification of fate modeling in the framework of nonlinear interactions is still unavailable.

Conclusions Although the methodologies and concepts for studying HOC environmental fate could be adopted for PPCP study, their differences should be highly understood. Prediction of PPCP environmental behavior needs to combine contributions from various fractions of soils or sediments and the sorption of their metabolites and different species.

Recommendations and perspectives More detailed studies on PPCP sorption in separated soil or sediment fractions are needed in order to propose a model predicting PPCP sorption in soils or sediments based on soil or sediment properties. The information on sorption of PPCP metabolites and species and the competition between them is still not enough to be incorporated into any predictive models.

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1 Background, aim, and scope

Pharmaceuticals and personal care products (PPCPs) include a wide range of chemicals, such as human and veterinary drugs, “nutraceuticals,” and sunscreen agents. These compounds have been reported to cause adverse impacts on wildlife and human; thus, they are emerging organic contaminants (Daughton and Ternes 1999). More background information on PPCPs is available from EPA website (<http://www.epa.gov/esd/chemistry/pharma/overview.htm>), and the readers could refer to several reviews on occurrence, detection, and degradation of PPCPs (Daughton and Ternes 1999; Sarmah et al. 2006). The presence of hormonal pharmaceuticals or their metabolites in the environment, which are synthesized to adjust endocrine system for human body, could unexpectedly interfere with natural hormones of human and wildlife (Snyder et al. 2003), and they are noted as endocrine disrupting chemicals (EDCs). Researchers sometimes classify EDCs as an individual group of chemicals independent of PPCPs (Daughton and Ternes 1999). Because this review will mainly focus on synthetic EDCs, which are also pharmaceuticals, we consider EDCs as one type of PPCPs. Antibiotics or anti-microorganisms are another major class of pharmaceuticals of concern. The demand of environmental risk assessment of PPCPs has been highly stressed a decade ago (Desbrow et al. 1998; Daughton and Ternes 1999). Reviews are available on the occurrence, detection, and toxicology of EDCs (Hollert et al. 2005; Ying et al. 2002), veterinary pharmaceuticals (Boxall et al. 2004; Sarmah et al. 2006; Tolls 2001), and antibiotics (Thiele-Bruhn 2003). Knowledge on the fate of PPCPs in soils or sediments is critical for their environmental exposure and risk assessment (Kuster et al. 2004; Peck et al. 2004), but the study on PPCP–soil or sediment interactions is very limited compared to the occurrence and toxicology investigations (Ying et al. 2002). This review summarizes the studies on PPCPs sorption in soils or sediments with an emphasis on their differences from HOCs. The special functions of humic substances (HSs) on PPCP adsorption will be summarized in the features of nonideal sorption, contribution of both organic and inorganic soil fractions, fast degradation, and influences of environmental conditions. The complexity of modeling xenobiotic behavior in three-phase system will also be presented.

2 Nonideal sorption of PPCPs in soils or sediments

Nonlinear sorption of PPCPs in soils or sediments has been generally reported (Li and Lee 1999; Thiele-Bruhn et al. 2004; Yu et al. 2004; Loffredo and Senesi 2006; Yu et al. 2006; Zeng et al. 2006; Gu et al. 2007). After HOC sorption concept, dual reactive domain model was also employed to describe the sorption of bisphenol A on sediments (Zeng et al. 2006). Consistent with nonlinear sorption, desorption hysteresis was also reported (Li and Lee 1999; During et al. 2002; Zeng et al. 2006; Williams et al. 2006; Gu et al. 2007). Nonlinear sorption and desorption hysteresis have been attributed to black carbon (Yu et al. 2006; Zeng et al. 2006). However, it could be easily predicted that heterogeneous nature of soils or sediments can contribute to nonideal PPCP sorption. Nonideal sorption is also supported by concentration-dependent sorption kinetics (Yu et al. 2004), two-stage (Loffredo and Senesi 2006; Zhou 2006), and three-site sorption (Wehrhan et al. 2007). Fan et al. (2006) observed that soil samples with higher organic carbon content showed longer equilibrium time. Thus, the diffusion and entrapment of PPCPs in organic matter could be a rate-limiting step as for HOCs. By analyzing pyrolysis-mass spectra and adsorption coefficients, phenolic and carboxylic groups, N-heterocyclic compounds, and lignin decomposition products in HSs were believed to be preferred binding sites and responsible to site-specific sorption (Thiele-Bruhn et al. 2004). However, the dominated contribution by a given organic fraction could not be easily concluded as discussed in the next section.

Chemical extraction was applied to distinguish sorbed PPCPs according to their sorption strength, and non-extractable fraction was observed (Colucci et al. 2001; Colucci and Topp 2002). This non-extractable fraction showed very low availability to chemical and biological process (Colucci et al. 2001; Heise et al. 2006) and was attributed to strong binding with HSs (Fan et al. 2007). A detailed investigation of PPCP bound residue distribution in soil or sediment fractions is not available yet. Introduction of the concepts developed in pesticide-bound residue studies (Gevao et al. 2000) will greatly improve our understanding of the mechanisms of PPCP bound residue.

3 Both organic and inorganic fractions controlling PPCP sorption

Both Freundlich sorption parameter K_F and distribution coefficient K_d of PPCPs were found to be positively related to organic carbon content (During et al. 2002; Bowman et al. 2002; Holthaus et al. 2002; Loffredo and Senesi 2006; Maskaoui et al. 2007; Uslu et al. 2008). This is not

surprising because most of PPCPs are moderately hydrophobic compounds. The interactions between PPCPs and soil or sediment organic matter (SOM) control their environmental fate greatly, such as enhancing sorption, reducing bioavailability (Jacobsen et al. 2005) and, thus, reducing their environmental risk (Fan et al. 2007). PPCP-SOM interactions also caused antigenotoxic action of humic substances to both human cells (Ferrara et al. 2006) and plant species (Ferrara et al. 2001).

The importance of SOM on PPCP sorption promotes the application of carbon normalized sorption coefficient, K_{OC} . However, large variation of K_{OC} was observed (Tolls 2001; Zhou et al. 2007) and was attributed to SOM property difference (Thiele 2000; Fan et al. 2006; Stumpe and Marschner 2007). Very limited studies examined the relationship of SOM chemical properties with their sorption characteristics (such as aromaticity in Sun et al. 2007). Because of PPCP amphiphilic characteristic, they can interact with both polar and nonpolar surfaces (Suntisukaseam et al. 2007). Thus, it is not surprising that the application of linear free energy concept to predict K_{OC} of PPCPs from K_{OW} generally failed (Holbrook et al. 2004; Liu et al. 2005; Patrolecco et al. 2006), and none of the separate soil property could explain the variation of sorption coefficient (ter Laak et al. 2006b). PPCP sorption in soil or sediment could not be adequately explained by hydrophobic interaction because a combination of mechanisms of cation exchange, cation bridging, surface complexation, and hydrogen binding in addition to hydrophobic interaction are operating (Tolls 2001; Kwon and Armbrust 2008).

Different from HOC sorption by soils or sediments in which sorption by inorganic fractions could be neglected in the presence of water, the sorption capacity of PPCPs by inorganic particles is 10–40% of that by a whole soil or sediment sample (Lai et al. 2000; Schafer et al. 2002). Jones et al. (2005) observed that organic carbon dominated PPCP sorption only in soil with organic carbon content higher than 9%. Therefore, in assessing EDC sorption capacity by soils or sediments, the contribution by inorganic fractions can be of great importance. Table 1 showed that the sorption coefficient K_d for PPCP sorption on soils or sediments is comparable to those on mineral particles. Therefore, in most cases, organic and inorganic fractions are equally important for PPCP sorption (Lai et al. 2000; Schafer et al. 2002; Strock et al. 2005). Pils and Laird (2007) further concluded that SOM could mask sorption sites or inhibit interlayer diffusion in clays, and reduce tetracycline sorption. Normalization of sorption coefficient by organic carbon content neglects contribution by inorganic components in soils or sediments, thus, generally overestimating the contribution of SOM. Thereby, it is safe not using organic carbon normalized sorption coefficient to describe PPCP sorption in soils or sediments, and character-

ization of soil or sediment properties regarding both organic and inorganic fractions is required for understanding PPCP-soil or sediment interactions. In addition, because different PPCPs vary greatly in their behavior (Ra et al. 2008), proper classification according to their chemical properties is required in order to establish predictive models to describe PPCP behavior.

PPCP sorption on pure mineral particles provides important information to understand PPCP sorption mechanism. Compared to goethite, illite, and kaolinite, montmorillonite showed slower sorption kinetics, higher sorption capacity, and stronger desorption hysteresis (Van Emmerik et al. 2003; Shareef et al. 2006). Montmorillonite interlayer spaces contribute greatly to PPCP sorption. Other particle properties, such as pore distribution (Tsai et al. 2006a, b), surface charge density (Strock et al. 2005), and particle size (Casey et al. 2003) are also reported to be important for PPCP sorption. In addition, chemical reaction is involved between PPCPs and metal oxides (Rubert and Pedersen 2006). Therefore, dual mode model or dual reactive domain model of SOM would be too simple to describe PPCP sorption in soils or sediments. Unfortunately, data from previous studies are not enough to propose a realistic and accurate model to predict the interactions between PPCPs and soils or sediments.

After attenuated total reflection Fourier transformed infrared analysis of ciprofloxacin (antibiotics) sorption to hydrous oxides of Al (HAO) and Fe (HFO), Gu and Karthikeyan (2005b) proposed a weak hydrogen-bonding association between the keto group of ciprofloxacin and the protonated surface hydroxyl group of HAO and a mononuclear bidentate complex (i.e., a six-membered ring) with an Fe atom on the HFO surface through the keto O and one of the oxygen in the carboxyl group. Their proposed mechanism explained well the different sorption properties of HAO and HFO with ciprofloxacin. Gao and Pedersen (2005) excluded formation of π complexes of basal plane oxygen on smectite surface with either the aniline or 4,6-dimethyl-pyrimidine rings of sulfamethazine. They concluded that water and cation bridging is a possible interaction mechanism. On montmorillonite surface, because sulfamethazine could complex with exchangeable cations through a pyrimidine N and/or the $-SO_2-$ group, pyrimidine forms inner and outer sphere complexes with exchangeable metal cations (Akyuz and Akyuz 2003). Therefore, the sorption mechanism varies for different chemicals on various mineral particles, which needs future investigations.

4 Fast degradation and sorption of metabolites

PPCPs can quickly degrade in the environment, with half-lives generally within 1 month (Cousins et al. 2002; Lucas

Table 1 A summary table of PPCP sorption on soils or sediments

Solute chemical names	pK_a	S_w (mg/L)	$\log K_{ow}$	MW	Sorbent description	pH	TOC (%)	K_d (mL/g)	Reference
Bisphenol A (BPA)	9.59–10.2	120– 300	3.4	228.3	Sediment	7.15–7.71	2.06–6.29	3.7–11.5 ^a	Zeng et al. 2006
					Soil	8.9	1.9	2.75 ^a	Ying et al. 2003
					Soil	6.9–8.13	0.92–2.11	4.94–8.62 ^a	Fent et al. 2003
					Minerals	4–10		12.3–212.8 ^a	Shareef et al. 2006
					Zeolite			11.2 ^a	Tsai et al. 2006a
17 β -Estradiol (E2)	N/A	3.6	3.1 to 4.0	272.3	Soil	7.2–7.6	0.8–1.4	16.0–29.6 ^a	Stumpe and Marschner 2007
					Soil		3.3–9.2	80.2–455.5 ^a	Casey et al. 2003
					Soil	7.9	9.2	84.41	Casey et al. 2005
					Soil			3.6–83.2	Lee et al. 2003
					Minerals			4.9–177.2	Van Emmerik et al. 2003
					Minerals		0	11.3–40 ^a	Casey et al. 2003
					Minerals			41.4–744.9 ^a	Shareef et al. 2006
17 α -Ethinyl Estradiol (EE2)	10.4	11–44	4.15	296.4	Sludge	7.1	27.7	584	Andersen et al. 2005
					Soil		0.95–1.88	53.7–97.7 ^a	Yu and Huang 2005
					Soil	8.9	1.9	6.98 ^a	Ying et al. 2003
					Soil	6.4–7.3	0.22–2.91	2.33–23.4	Lee et al. 2003
					Minerals	4–10		41.4–744.9 ^a	Shareef et al. 2006
Carbadox (CBX)	N/A	N/A	–1.40 to 0.15	262	Soil	4.4–7.3	0.22–2.39	1.4–154	Strock et al. 2005
					Kaolinite	4.63		19.8	Strock et al. 2005
Desoxycarbadox (DCBX)	N/A	N/A	1.9 to 2.1	230	Soil	4.3–6.9	0.36–2.39	7.07–62.4 ^a	Strock et al. 2005
					Clay	4.67	0	7.6	Strock et al. 2005
Tetracycline (TC)	3.3; 7.7; 9.7	231– 52000	–1.97 to – 0.47	444.4	Soil	3.8–7.5	0.48–2.91	3102– 312447	Sassman and Lee 2005
					HS	7		1.0–5.7E4	Pils and Laird 2007
					Al or Fe oxide	5.3		41.8–133 ^a	Gu and Karthikeyan 2005a
					MMLT	5.5		865 ^a	Figuerola et al. 2004
					Clay	7		2.2–6.5E4	Pils and Laird 2007
Oxytetracycline (OTC)	3.27; 7.32; 9.11	300	–1.97 to – 0.45	460	Soil	3.8–7.5	0.48–2.91	1229– 269097	Sassman and Lee 2005
								950–7200	ter Laak et al. 2006a
					MMLT	1.5–11		2691– 33884 ^a	Kulshrestha et al. 2004
Sulfathiazole (STZ)	2.4; 7.1	590	1	255.3	MMLT	4–7.5		0.5–1.5	Kahle and Stamm 2007
					Ferrihydrite	5.3–7.2		3–20	Kahle and Stamm 2007
Sulfapyridine (SPY)	8.4	270	0.35	249.3	Soil			0.4–3.5	ter Laak et al. 2006a
					Whole soil	7	1.61	1.75 ^a	Thiele-Bruhn et al. 2004
Sulfamethazine (SMZ)	2.3; 7.4	1500	0.8	278.33	Mineral			4	Gu and Karthikeyan 2005b
					Soil	7.2–7.5	0.94–1.8	2.4–4.2 ^a	Accinelli et al. 2007
p-Aminobenzoic acid (pABA)	4.9	6100	0.83	137.1	Mineral			7.8–14.2 ^a	Gao and Pedersen 2005
					Soil	7	1.61	0.47 ^a	Thiele-Bruhn et al. 2004
					Coarse silt	6.4	0.1	1.82 ^a	Thiele-Bruhn et al. 2004

S_w solubility in water, MW molecular weight, N/A not available, $MMLT$ montmorillonite

^a K_d was calculated at 10 $\mu\text{g/L}$ if the data was provided as fitting results using the Freundlich or Langmuir model.

and Jones 2006; Accinelli et al. 2007), especially in aerobic environments (Ying et al. 2004; Ying and Kookana 2005). Therefore, they have been reported to be nonpersistent in the environment (Klecka et al. 2001; Lucas and Jones 2006). This information is encouraging because PPCPs can

be easily dissipated. However, new problems emerged. Fan et al. (2007) reported that although significant degradation was observed for EDCs in soils, mineralization, as detected by CO_2 production, was not observed. Thus, EDCs may be transformed to other compounds, such as estradiol to

estrone (Hildebrand et al. 2006). The presence of metabolites may compete with parent compounds for sorption sites (Strock et al. 2005; Casey et al. 2004) and, hence, increase the mobility of parent compounds. More importantly, the metabolites of PPCPs have potential environmental risk. Although some metabolites are inactive, such as glucuronide and sulfated conjugates, these chemicals can be deconjugated by the bacteria producing β -glucuronidase (Dray et al. 1972) or sulfate enzymes (Ternes et al. 1999) and, thus, be activated. Because the conjugates have stronger polarity, higher solubility, and low sorption affinity with soils or sediments (Ternes et al. 1999), the mobility of these compounds is higher than their parent compounds. Therefore, the potential environmental risk of those metabolites should be taken into consideration for PPCP fate modeling and risk assessment. The competition between PPCPs and their metabolites and the behavior of the inactive metabolites should also be incorporated in future environmental fate studies.

HSs play very important roles in PPCP deactivation by either Michael addition with PPCP active functional groups (Bialk et al. 2007; Bialk and Pedersen 2008) or acting like a photosensitizer and, thus, promoting PPCP photodegradation (Werner et al. 2005; Kwon and Armbrust 2005). On the other hand, PPCPs may be protected by HSs from photodegradation through nonchemical interaction, possibly be released later on, causing environmental risk (Belden et al. 2007). Therefore, for some PPCPs, HSs are inner filters which decrease photodegradation. But for other PPCPs, HSs are photosensitizers which promote photodegradation (Andreozzi et al. 2003; Lam and Mabury 2005). Again, because of the diverse PPCP properties, a proper classification scheme is needed.

5 Influence of environmental conditions on PPCP behavior

The importance of dissolved organic matter (DOM) for PPCP behavior is expected from its effect on HOC behavior. The effect of third-phase or solid concentration on apparent sorption coefficient was observed for EDCs (Bowman et al. 2002; Zhou 2006). As estimated by Zhou et al. (2007), colloid-associated EDC accounted for 10–29% in the environment, and more than 70% in aqueous phase. Nonlinear sorption and sorption–desorption hysteresis between tetracycline and DOM have been recently observed (Gu et al. 2007), which could be valuable evidence to attract research interest on nonideal PPCP–DOM interactions. Also, because of the presence of functional groups, various species, and metabolites, PPCPs could bind with DOM in a more complicated way compared to HOCs, such as amorphous inclusion complex

(Agarwal et al. 2008). Because the same methods as for HOC–DOM studies are employed for investigating PPCP–DOM interactions, such as fluorescence (Yamamoto et al. 2003), equilibrium dialysis (Gu et al. 2007; Yamamoto et al. 2004), solubility enhancement (Yamamoto et al. 2003), and cross-flow ultrafiltration (Zhou et al. 2007), the limitations of those methods are the same as presented in part IV of this review series.

For HOC–soil or sediment interactions, the change of water chemistry mainly alters the properties of soils or sediments, thus, affecting their sorptive characteristics. However, because pK_a values of PPCPs are in the range of pH values in soils or sediments, these compounds can be protonated or deprotonated in soil or sediment solution and, thus, can exist as different species, such as cation, zwitterion, and anion (Figuerola et al. 2004; MacKay and Canterbury 2005; Gu et al. 2007). Different mechanisms for PPCP–soil or sediment interactions are involved for different species (Kulshrestha et al. 2004). For example, cation exchange has been proven to be the most important mechanism for the sorption of PPCP cation species, while for the zwitterion species, surface complexation (Figuerola et al. 2004) and hydrophobic interactions (Kulshrestha et al. 2004; Sibley and Pedersen 2008) are important. Therefore, species-specific sorption coefficient is one of the most important differences between PPCPs and HOCs and should be coupled in PPCP–soil or sediment modeling (ter Laak et al. 2006a). In addition, the increase of pH increases PPCP solubility (Campbell et al. 2006; Zeng et al. 2006) and decreases their sorption. ter Laak et al. (2006a) also explained the decrease of sorption by the competition between cations and positively charged PPCP species or complexes.

Ternary complexation of PPCP–metal–SOM may enhance their sorption capacity and strength in soils or sediments (MacKay and Canterbury 2005; Gu et al. 2007), which is why K_d was generally reported to increase with increasing salinity (Zhou and Liu 2000; Bowman et al. 2002; Zhou 2006). On the other hand, metals could also compete with PPCPs for SOM sorption sites depending on PPCP charges (Sibley and Pedersen 2008; Bai et al. 2008). In addition, HS conformational changes (as discussed in Part IV of this review series) in the presence of metal ions further complicate PPCP–HS interaction system. Therefore, it is safe to say that limited information is available on PPCP–metal–SOM complexation and systematical research is warranted.

Existence of various contaminants is a common case in the environment. PPCPs could compete with each other (Lai et al. 2000; Sanders et al. 2008) or with their metabolites (Casey et al. 2004; Strock et al. 2005), HOCs (Yu and Huang 2005), and DOM (Graham et al. 2000) for sorption sites. The competition can modulate PPCP activity, or increase their mobility (Kannan et al. 2000). Unfortu-

nately, the competition study regarding PPCPs is still rare. Various models have been proposed to describe PPCP environmental fate (such as Rose and Pedersen 2005); however, co-solute competition, species-specific sorption, metabolites, and inorganic fraction sorption need to be examined and factored in future predictive models.

6 Behavior of Xenobiotics in DOM–mineral–water three-phase system

Soils and sediments are a mixture of various components. Inevitably, SOM could interact with other non-humic components in soils or sediments, such as lipid, biopolymer, and minerals. This topic has generated great research interest on interaction between SOM and mineral particles (as reviewed by Schulten and Leinweber 2000) and the subsequent effect on HOC-SOM interactions. Unfortunately, studies on PPCP behavior in a three-phase system are very rare up to now (such as Gu and Karthikeyan 2008). The following discussion will be mainly based on the research of HOC behavior. However, the issues addressed below also apply to investigations of PPCP sorptive behaviors.

6.1 DOM–mineral complexation and its interaction with Xenobiotics

The DOM sorption on minerals as influenced by mineral types (Kaiser and Guggenberger 2000; Laor et al. 1998) and water chemistry (ion type, ionic strength, and pH) was investigated to study the sorption mechanism. Generally, decreasing pH (Laor et al. 1998; Weng et al. 2006 and references therein; Yoon et al. 2004) and increasing ionic strength (Tombacz et al. 2000) enhance DOM sorption by minerals. The importance of multivalence ions could not be emphasized enough in the formation of DOM–mineral complex. Yang et al. (2001) reported that the introduction of metal chelate could disrupt SOM–(metal ion)–mineral linkage, mobilize SOM, or reduce the cross-linking and, thus, accelerate HOC release.

As frequently mentioned in this review, SOM is a highly heterogeneous mixture. Different components have different affinities to mineral particles. Therefore, mineral adsorption process practically fractionates SOM. For example, large hydrophobic molecules showed higher affinity with kaolinite and montmorillonite (Specht et al. 2000). Wang and Xing (2005) observed that aliphatic fraction was preferentially adsorbed by kaolinite and montmorillonite, while aromatic fraction left in the solution. However, some other studies reported a priority sorption of aromatic carbons on kaolinite and goethite (Namjesnik-Dejanovic et al. 2000). Using HR-MAS NMR, Feng et al. (2006) observed that polymethylene groups were prevalent

at the surface of kaolinite, while aromatic groups were prevalent on montmorillonite. Thus, the properties of mineral particles, such as surface area and surface charges lead to different sorption affinity and selectivity of HS components (Baham and Sposito 1994).

SOM complexed on minerals had higher (Jones and Tiller 1999; Terashima et al. 2003) or lower (Laor et al. 1998) sorption affinity with HOCs compared with the original SOM depending on the differences of fractionated components. Hur and Schlautman (2004) observed both decrease and increase of K_{OC} after the formation of HS–mineral complex. For both sorbed and unsorbed HS, a strong positive correlation between $\log K_{OC}$ and $\log$ (weight-average molecular weight) was observed. Therefore, the change of sorption affinity after SOM adsorption on mineral particles depends on the fractionation process. More interestingly, physical reformation is also involved during the formation of HS–mineral complex. Wershaw (1993) stated that the interactions of SOM with mineral could result in a membrane-like structure and the interface between SOM and mineral is hydrophobic. Gunasekara and Xing (2003) proposed a more condensed structure when organo-mineral complex was formed at lower HA loading, contributing to the enhanced nonlinearity.

Imaginably, conformation of SOM in solution could also affect the formation of HS–mineral complex. Murphy et al. (1994) reported that low ionic strength resulted in an extended conformation, higher coverage on mineral surface, and greater HOC sorption than at high ionic strength. Feng et al. (2006) also observed that the conformation at acidic condition promoted the formation of HS–mineral complex with higher sorption affinity. Therefore, as for HOC sorption, SOM adsorption on minerals was also affected by both sorbate (HS) and sorbent (mineral) properties. Ionic type and strength, pH, and DOM type and concentration are all reported to alter the formation of DOM–mineral complex. However, how to consider all these factors in predictive models is still unclear. Furthermore, quantitative description of DOM fractionation and the subsequent change of K_{DOC} after adsorption on mineral particles are still lacking.

6.2 The complexity of the three-phase sorption

All the above-mentioned studies intend to provide more accurate information for HOC fate modeling and risk assessment. However, recent progress on HOC–SOM interactions has not been incorporated in any of HOC-fate modeling yet. For example, HOC multimedia fate models, such as the fugacity model (Cao et al. 2004), still use the linear free energy relationships proposed decades ago. The reason could be the lack of explicit mathematical relationships between SOM chemical–physical properties and its sorption characteristics.

The inland water body often contains 20 mg L^{-1} of DOM on average (Shi et al. 2005). Therefore, the behavior of HOC in a three-phase (water–particle–DOM) system is of more environmental relevance (Fig. 1). Various models have been proposed to consider HOC sorption on particles, DOM sorption on particles, and HOC sorption by DOM based on linear interaction, and overall sorption coefficient is:

$$K_p = \frac{S_b + S}{C_b + C_f} \quad (1)$$

or

$$K_p = \frac{K_b \cdot K_{\text{DOC}} \cdot [\text{DOM}] + K_d}{K_{\text{DOC}} \cdot [\text{DOM}] + 1} \quad (2)$$

where C_b and C_f are concentrations of HOCs bound with DOM left in aqueous phase and of free dissolved HOCs, respectively. S_b and S are concentrations of HOCs bound with DOM coated on solid particles and sorbed directly by solid particles, respectively. K_p is the overall sorption coefficient for HOCs sorption in the three-phase system, K_b is DOM sorption coefficient on particles, K_d is HOC sorption coefficient by particles, and K_{DOC} is HOC sorption coefficient by DOM.

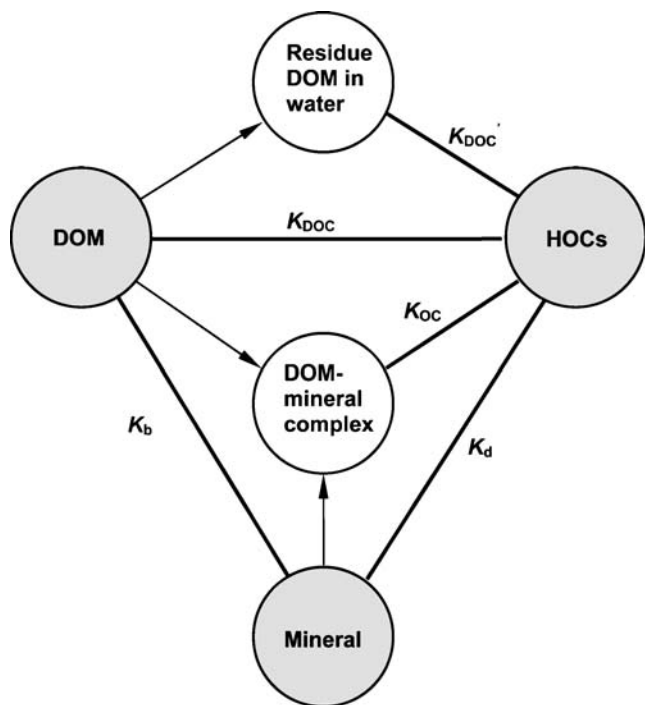


Fig. 1 HOC sorption in a three-phase-system. HOCs can be sorbed by both DOM and mineral particles. DOM sorption on mineral particles results in its fractionation. K_b sorption coefficient for DOM sorption on mineral particles; K_d sorption coefficient for HOCs on mineral particles; K_{DOC} sorption coefficient for HOCs by bulk DOM; K_{OC} sorption coefficient of HOCs on DOM–mineral complex; K_{DOC}' sorption coefficient of HOCs on residue DOM

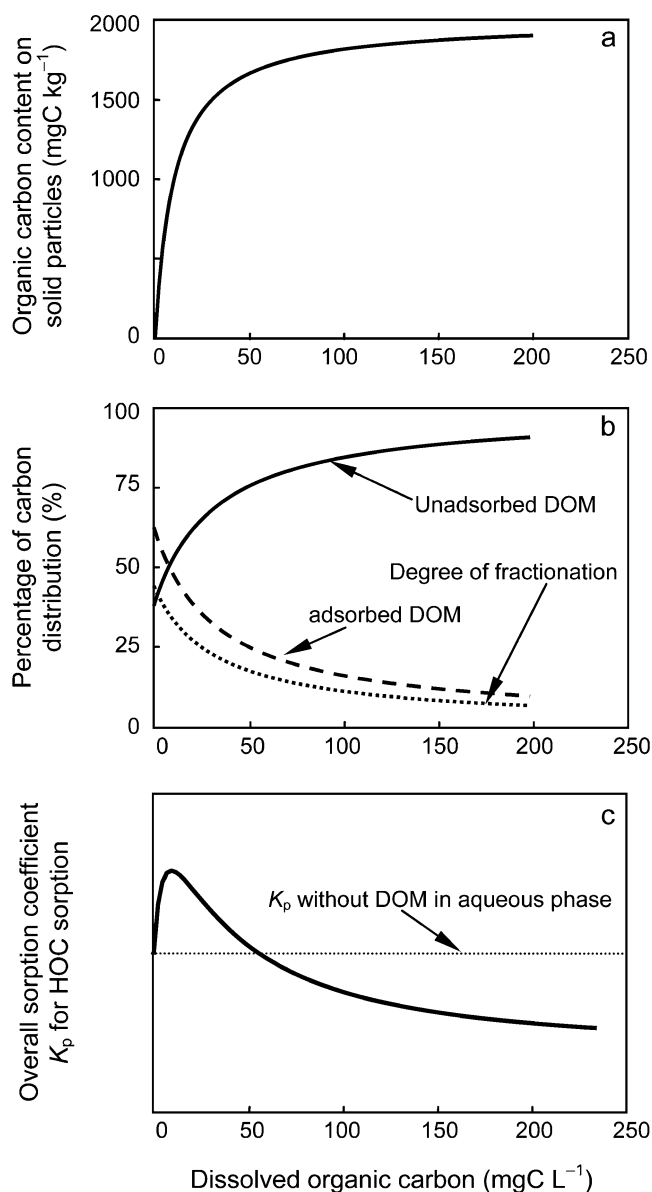


Fig. 2 The effect of DOM concentration on overall sorption coefficient K_p in a three-phase system. Typical DOM sorption isotherm on solid particles is a Langmuir curve (a). The sorption reaches saturation as DOM concentration increases. The percentage of adsorbed DOM of the overall DOM amount decreases, the percentage of unadsorbed DOM increases and the degree of fractionation decreases as free DOM concentration increases (b). The variation of K_p is due to combination of HOC binding with adsorbed, unadsorbed and fractionated DOM (c). At low DOM concentration, K_d increases because of the overwhelming contribution of adsorbed DOM (high percentage of carbon adsorbed) and DOM fractionation. As DOM concentration increases, both DOM fractionation and adsorption reach saturation, and HOC sorption by unadsorbed DOM dominates the overall sorption leading to the decrease of K_d

According to recent results, however, only limited studies considered nonlinear interaction of one of the bi-phase among the three bi-phase interactions (such as Lafrance et al. 1989). As has been widely reported, the

presence of DOM could enhance the solubility of HOCs and, thus, promote their transport (Chiou et al. 1986). However, adsorption of DOM by mineral particles decreased HOC mobility. The effect of DOM on HOC fate could be viewed by the following two aspects: the overall sorption can be enhanced because of the HOC sorption on bound DOM and the mobility of HOC was, therefore, decreased; on the other hand, the HOC sorption on unbound DOM led to increased mobility and decreased overall sorption. Considering the nonlinear sorption of DOM by mineral particles, the percentage and fractionation of bound DOM is higher at low DOM concentration than that at high DOM concentration (Fig. 2). Therefore, the apparent increasing or decreasing sorption depend on DOM concentration range and its sorption characteristics on the particles. However, as one can easily notice about the modeling, nonlinear interactions could exponentially increase the complexity and uncertainties of HOC environmental fate model. Furthermore, no method has been proposed to quantitatively describe DOM fractionation. Therefore, no study has even tried to establish a model combining all these nonlinear interactions.

The environmental risk of HOCs is dependent greatly on their bioavailability. The effect of DOM on bioavailability is even more complicated. Both increase (Bengtsson and Zerhouni 2003; Bogan and Sullivan 2003; Holman et al. 2002) and decrease (Bejarano et al. 2005; Gourlay et al. 2003) of HOC bioavailability in the presence of DOM have been reported. Classic results indicate that DOM-bound HOCs could not pass through the cell membrane and, thus, are impossible to be bioavailable. This statement supports the decrease of HOC bioaccumulation after the addition of DOM. Steinberg and his colleagues have systematically investigated the toxicology of DOM to aqueous organisms and reported that humic substances could be taken up by organisms and act as xenobiotic chemicals (Steinberg et al. 2003). Their results showed that SOM molecules could pass through the cell membrane carrying HOCs. Haitzer et al. (1998) reviewed that although most of the papers reported decreased bio-concentration factor (BCF) in the presence of DOM, one fourth of the reviewed studies presented increased BCF in the presence of low DOM concentration. The reason is not clear yet. If we simplify the living skin in contact with water as a sorbent, the apparent K_p for HOC sorption on the skin in the presence of DOM could also be described in Fig. 2. However, no laboratory study has incorporated this aspect in BCF investigation. Regarding HOC bioavailability in a three-phase system, other conditions need to be considered, such as the coverage of SOM on solid particles (Bogan and Sullivan 2003), micro-organism species, and HOC properties (Bejarano et al. 2005).

7 Conclusions, recommendations, and perspectives

The differences between HOC and PPCP sorption in soils or sediments should be clearly understood when introducing the methods and concepts of HOC experiments to the PPCP ones. More detailed studies on PPCP sorption in separated soil or sediment fractions is required in order to propose a model predicting PPCP sorption in soils or sediments based on soil or sediment properties. In addition, more studies are needed on sorption of PPCP metabolites and species and the competition between them in order to develop accurate predictive models for environmental fate and transport of PPCPs.

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