Sorption of Polar and Ionogenic Organic Chemicals

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Contents

Abstract The sorption process of polar chemicals to soil is in general similar to that of nonpolar chemicals and is in most cases still dominated by interactions with soil organic matter. In contrast, the sorption process for ionogenic organic chemicals (IOCs) is very different from that of nonpolar chemicals, particularly for IOCs where >90% is ionized as a cation, anion, or zwitterion. Organic ions in soil sorb to different parts of organic matter, by different processes, and often also to different soil components, such as minerals. This chapter provides a summary of several relatively recent studies that aimed to systematically uncover how the interactions between polar chemicals and ionic chemicals and soil components are influenced by (a) sorbate descriptors, (b) sorbent composition, and (c) aqueous phase conditions. The sorption data in several of these studies were collected on a single type of soil organic matter, micronized Pahokee peat, by a single method, dynamic high-pressure flow-through column studies using controlled aqueous medium. This

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chapter collected these consistent K_{OC} values obtained for a structurally diverse range of (non)polar, cationic, (perfluorinated) anionic, and zwitterionic chemicals, which could serve as a (growing) reference database for environmental scientists, modelers, regulators, and registrants.

Keywords Linear free energy relationships, Minerals, Organic matter, Polyparameter relationships, Sorption mechanisms

1 Sorption of Polar (Nonionic) Chemicals

The sorption process of polar chemicals to soil is not too different from that of nonpolar chemicals. In most cases it is still dominated by the chemical's hydrophobicity, the disruption of the cohesive energy of water, making it more favorable to be absorbed in the far less cohesive matrix of soil organic matter (SOM). Polar interactions such as hydrogen bonding typically weaken the sorption process, because they result in more favorable chemical interactions with water molecules relatively to SOM [1]. Whereas the octanol-water partitioning coefficient does include hydrogen bond interactions, it has been shown that when multiple polar functional groups are present in a chemical, the overall set of interactions with SOM is significantly from those with octanol [2, 3]. Only for a few neutral chemical classes such as anilines and alcohol ethoxylates do other sorption processes and soil components become more dominant in controlling their sorptive properties, thereby controlling their environmental fate [4–6].

1.1 Classical Linear Free Energy Relationships

The classic hydrophobic sorption model dating back to the 1981 paper of Karickhoff [7] is a simple single-parameter relationship between the OC-normalized soil partition coefficient (K_{OC}) and the octanol-water partition coefficient (K_{OW}). It was carefully evaluated with a relatively large dataset, but it should be kept in mind that it was basically based on a K_{OC}-K_{OW} relationship for a series of only five polycyclic aromatic hydrocarbon (PAH) components: benzene, naphthalene, phenanthrene, anthracene, and pyrene.

The first starting point of Karickhoff's approach was to define that the OC content was the dominant soil binding component. For each of the five PAHs, a strong correlation was found between the sorption coefficient and the OC content of a set of 17 sediments and soils. Convincingly, a constant K_{OC} could be derived for each evaluated compound that explained sorption to all these environmental substrates.

From this set of five PAH structures, the now famous equation was derived using K_{OW}:

$$\mathrm{Log}\,K_{\mathrm{OC}} = 0.989 \cdot \log\ K_{\mathrm{OW}} - 0.346 \tag{1}$$

As Karickhoff noted, the near-unity coefficient for log K_{OW} "substantiates the constancy of the ratio of fugacity coefficients in the organic phases" (i.e., octanol and organic matter) for this series of chemicals, which allows for the linear form of:

$$K_{\mathrm{OC}} = 0.411 \cdot K_{\mathrm{OW}} \tag{2}$$

Of course, these five PAH compounds are structurally not very diverse, so it was questionable from the start how this relationship applies to polar and ionogenic compounds. Karickhoff [7] already evaluated this equation against an extensive set of K_{OC} values derived for pesticides, which included a wide variety of polar features. Compounds for which solute speciation was expected (such as organic bases with p$K_a > 3$) were, wisely, already excluded by Karickhoff. From this dataset evaluation, Karickhoff found that the calculated K_{OC} deviated in most cases not more than a factor of 3 (or 0.48 log units), which could be considered adequate for risk assessment modeling. Phenyl ureas (e.g., diuron) presented an interesting exception, however, with K_{OW} calculations consistently more than an order of magnitude lower than measured K_{OC} values. Since octanol is also closely related to physicochemical parameters such as water solubility, early "linear free energy relationships" to predict K_{OC} were also derived with water solubility as a parameter. Water solubility, however, relates to the interactions between the solute with itself in a crystalline form, and for many chemicals these are often less accurate than the interactions with octanol in describing the interactions with organic matter. Karickhoff already presented the example of the chloro-S-triazines, where the least soluble (simazine) is also the least sorbed. Another well-known example for PAHs is the three-ringed isomer pair of anthracene and phenanthrene, for which both the log K_{OW} and log K_{OC} are nearly equal (4.53/4.48 and 4.3/4.2, resp.) while the maximum aqueous solubility of anthracene is a factor of 20 lower than that of phenanthrene [8].

A major source of uncertainty in deriving, modeling, and predicting the K_{OC} for more complex polar chemicals is that for collecting a sufficiently large database, data is extracted from multiple sources that performed experiments with different soil types and different experimental setups and in different labs. Bronner and Goss (2011) derived their own independent and highly consistent set of K_{OC} values for a systematic series of organic chemicals with high structural variability, including a broad series of pesticides, as listed in Table 1 [2, 3]. They used dynamic column binding studies with a single batch of micronized Pahokee peat as a purified form of soil organic matter [2, 3]. This systematic evaluation of how nonpolar and polar functionalities influence the sorption to soil confirmed the strong relationship between K_{OW} and K_{OC} for nonpolar organic chemicals, following the same trend line as defined by Karickhoff, within a window of 1 log unit with the Karickhoff line as a maximum level (Fig. 1 – Left). Nonpolar chemicals were defined as having a

Table 1 Sorption coefficients for neutral chemicals on micronized Pahokee peat [2, 3]

Chemical name	Log K_{oc}	Chemical name	Log K_{oc}	Chemical name	Log K_{oc}
C_8-based neutral		*Other neutral*		*Neutral pesticides*	
2,2,4-Trimethylpentane	3.60	1-Heptene	2.84	Alachlor	1.84
1-Octene (unsaturated)	3.33	1-Nonene	3.84	Atrazine	1.82
1-Chlorooctane (halogen)	3.83	1-Decene	4.39	Azoxystrobin	2.44
2-Octanone (ketone)	1.24	1-Chloropentane	2.47	Bensulide	3.47
2-Ethyl-1-hexanol (hydroxy)	1.51	1-Chloroheptane	3.36	Bromacil	1.4
Di-*n*-butyl ether (ether)	1.65	Di-*n*-pentyl ether	2.78	Carbamazepine	2.29
1-Nitrooctane (nitro)	2.47	Di-*n*-hexyl ether	3.60	Carbaryl	2.31
Ethylbenzene (aromatic)	2.08	Ethyl tert-butyl ether	0.64	Carbendazim	2.96
		Ethyl tert-pentyl ether	0.99	Chlorobenzilate	3.26
Simple cyclic neutral structures		3-Ethyl-3-hexanol	1.05	Chlorothalonil	2.96
Cyclohexene	1.84	4-Ethyl-3-hexanol	1.28	Clothianidin	2.05
1-Methylcyclohexene	2.08	2-Nonanone	1.87	Cyanazine	1.76
Benzene	1.32	2-Decanone	2.37	Cymoxanil	1.22
Toluene	1.77	2-Undecanone	2.82	Cyproconazole	2.3
Chlorobenzene	2.08	1-Nitropentane	1.4	Desethylatrazine	1.56
4-Chlorophenol	1.94	1-Nitrohexane	1.95	Diazinon	2.46
1,4-Dichlorobenzene	2.88	Isoflurane	1.26	Dichlofluanid	1.75
2-Chloroaniline	1.59	Enflurane	1.19	Dimethenamid	1.75
Propiophenone (ketone)	1.99	Halothane	1.46	Diuron	2.56
Anisole (ether)	1.46	Methoxyflurane	1.44	Endosulfan	2.89
Methyl benzoate (ester)	1.55	2-Nitroanisole	1.89	Ethofumesate	1.84
2,6-Dimethylaniline	1.38	3-Nitroanisole	2.11	Fenthion	3.44
Indole	2.04	4-Nitroanisole	2.28	Fluazinam	1.95
Benzofuran	2.04	2-Nitrotoluene	1.82	Flumioxazin	2.29
Thiophene	1.33	2-Chloronitrobenzene	2.08	Flusilazole	3.02
1,2-Dicyanobenzene	1.69	2,4-Dinitrotoluene	2.23	Fosthiazate	1.27
Nitrobenzene	1.90	2,4,6-Trinitrotoluene	1.92	Imiprothrin	2.18
Naphthalene	2.48			Irgarol	2.73
1,2-Dimethylnaphthalene	3.64	*Neutral personal care products/drugs*		Isoproturon	1.65
Acenaphthene	3.22	Estradiol	2.76	Metamitron	1.99
Fluorene	3.63	Testosterone	2.24	Metazachlor	1.69

(continued)

Table 1 (continued)

Chemical name	Log K_{oc}	Chemical name	Log K_{oc}	Chemical name	Log K_{oc}
Phenanthrene	4.26	Deoxycorticosterone	2.53	Methidathion	2.16
Propylbenzene	2.53	Hydrocortisone	1.79	Metolachlor	1.87
Butylbenzene	2.99	Progesterone	3.02	Metoxuron	2.04
Pentylbenzene	3.51	Phenylbutazone	2.08	Metribuzin	1.48
Hexylbenzene	3.93	Ibuprofen (neutral form)	2.63	Monuron	2.06
1,2,4-Trichlorobenzene	2.95	Bisphenol A	2.49	Napropamide	2.70
1,2,3,4-Tetrachlorobenzene	3.51	Triclosan (neutral form)	4.02	Nitrofen	3.98
1-Naphthol	2.36			Octhilinone	2.75
2-Chlorophenol	1.85	*Neutral mycotoxins* (Schenzel et al.) [9]		Orbencarb	3.19
3,4-Dichlorophenol	2.40	Aflatoxin M1, B1, B2, G1, G2	2.6–3.2	Parathion	3.23
2,4,5-Trichlorophenol	2.90	Alternariol	2.1	Phenmedipham	2.16
2-Methylbenzofuran	2.37	Altenuene	2.6	Procymidone	2.23
Dibenzofuran	3.51	Tentoxin	1.4	Propachlor	1.35
Pentanophenone	2.32	Zearalenone	3.3	Propiconazole	2.77
Heptanophenone	3.16	α-Zearalenol and β-zearalenol	2.8	Propoxur	1.53
Ethyl benzoate	1.92	Verrucarin A	2.2	Sulfentrazone	1.52
Diethyl phthalate	1.53	Verrucarol, DON	<0.7	Tebutam	1.91
Di-*n*-propyl phthalate	2.01	T-2 toxin/HT-2 toxin	1.0	Terbutryn	2.55
Di-*n*-butyl phthalate	3.20	Patulin	1.2	Thiazopyr	2.33
Di-*n*-pentyl phthalate	3.73	Diacetoxyscirpenol	<0.7		
		Daidzein	3.0		
		Equol	2.6		

mass fraction of oxygen + nitrogen atoms in the molecule $\leq$ 12%, so this also includes simple monofunctional organic chemicals that are relatively hydrophobic. However, for the polar chemicals, mostly multifunctional compounds, the K_{OC}-K_{OW} relationship is actually very weak (Fig. 1 – Right), with much wider deviations observed both higher and lower than the Karickhoff trend line. This uncertainty margin may not be considered desirable from a risk assessment point of view, and improved modeling of the sorption interactions with OM is required to more accurately assess the sorptive affinity of polar (nonionic) chemicals.

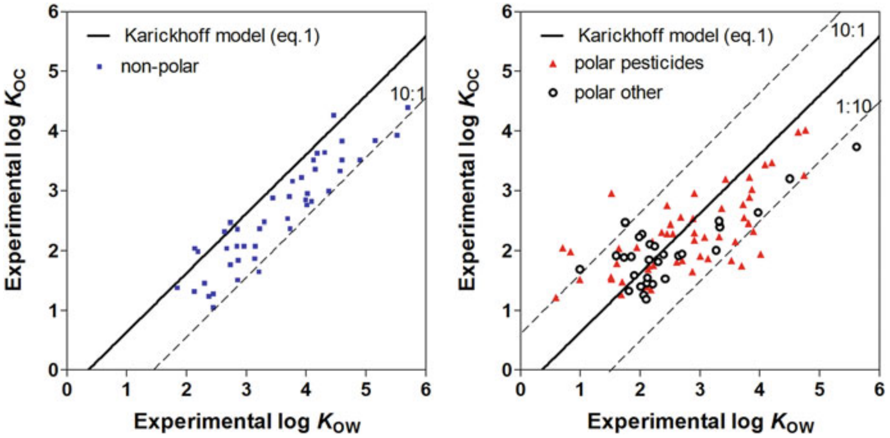


Fig. 1 Left: K_{OC}-K_{OW} plot for nonpolar sorbates. Right: Plot of log K_{OC} values for polar sorbates from this work (including pesticides, pharmaceuticals, and hormones) versus the respective log K_{OW} values. Definition of nonpolar: mass fraction of oxygen + nitrogen atoms in the molecule $\leq 12\%$. Redrawn from data from Bronner and Goss [2]

1.2 Using a Systematic Polyparameter Approach to Account for all Nonionic Sorptive Interactions

The key assumption in the K_{OW} approach as a single descriptor for K_{OC} for neutral molecules, as indicated by Karickhoff already, is that a solute's chemical interaction with octanol molecules represents that with soil organic matter (SOM). This may indeed be true for nonpolar chemicals and many chemicals with a relatively simple polar moiety, with clear exceptions such as phenyl ureas. Many pesticides, however, are often multifunctional and highly polar. The solvation interactions between molecules in octanol may substantially differ with those in SOM, and it becomes more unlikely that the single parameter K_{OW} approach to derive K_{OC} results in an accurate prediction [1]. From a mechanistically sound approach of the K_{OC} of the compound, it is thus more important to derive the average properties of SOM itself, rather than relying on octanol, that are involved with sorption interactions with the full spectrum of polar chemicals. The polyparameter linear free energy relationship (pp-LFER) approach is based on a concept that considers all interactions involved in partitioning by separate parameters, calibrated with a sorption dataset for the partitioning phases. The minimal set of five parameters should cover the prevalent nonpolar and polar chemical interactions between the whole solute molecules and average SOM structures and are also ideally derived experimentally, to avoid accumulated predictive uncertainties. One of the most comprehensive sets of the five pp-LFER includes molecular volume (V_x) and hexadecane-air partitioning (L), to cover nonpolar interactions, two hydrogen bond descriptors that relate to the capacity to act as an H donor (A) or H acceptor (B) in a hydrogen bond, and a residual polar interaction term (S), all scaled to standardized ranges [10]. Based on these five

Table 2 Examples of pp-LFER parameters for some C_8-based chemicals and two polar chemicals

	Vx	*L*	*S*	*A*	*B*
2,2,4-Trimethylpentane	1.24	3.11	0	0	0
1-Chlorooctane	1.36	4.77	0.40	0	0.10
Ethylbenzene	1.00	3.78	0.51	0	0.15
2-Octanone	1.25	4.26	0.68	0	0.51
Di-*n*-butyl ether	1.29	3.92	0.25	0	0.45
2-Ethyl-1-hexanol	1.29	4.38	0.39	0.37	0.48
Bisphenol A	1.86	8.95	1.56	0.99	0.91
Estradiol	2.20	11.11	1.77	0.86	1.10

descriptors, the coefficients (italics small font) for each descriptor (capital font) the pp-LFER can be derived based on multiple linear regression of high-quality sorption coefficients and the five descriptors:

$$\text{Log}\ K_{\text{sorbent-water}} = v \cdot V_x + l \cdot L + s \cdot S + a \cdot A + b \cdot B + c \tag{3}$$

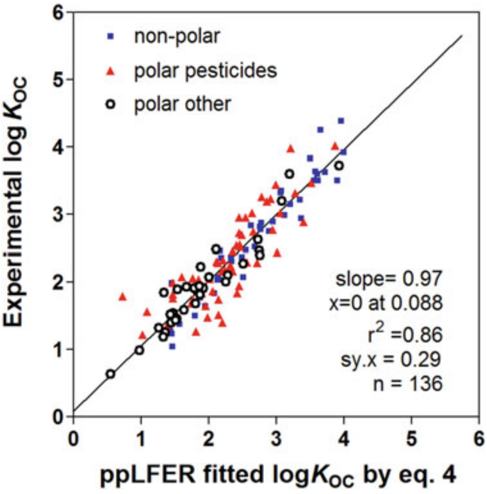
whereas *V* is readily calculated via standardized methods and the other four parameters *L*, *A*, *B*, and *S* are best derived experimentally for each chemical using four of five substantially different sorbent phases, for which chromatographic columns provide sufficient discriminative power and consistent results [11]. These descriptors are becoming available for large sets of pesticides too [12, 13]. An online database of these descriptors is available [14]. Fitting the pp-LFER equation to the K_{OC} obtained for 79 chemicals resulted in the equation:

$$\begin{aligned}\text{Log}\ K_{\text{OC}} = {} & 1.2 \cdot V_x + 0.54 \cdot L - 0.98 \cdot S - 0.42 \cdot A - 3.34 \cdot B \\ & + 0.02\ \left(\text{SE} : 0.24, n = 79, R^2 = 0.929\right)\end{aligned} \tag{4}$$

The pp-LFER descriptors are shown in Table 2 for several chemicals tested by Bronner and Goss [2]. Nonpolar compounds have values of 0 for polar descriptors *S*, *A*, and *B*, but chlorine increases *S* to 0.4 and *B* to 0.1, and similarly an aromatic ring increases *S* and *B*. Ketones and ether are only hydrogen bond acceptors and only have increased *B* descriptors while *A* remains 0. A hydroxy moiety adds to both *A* and *B*. The more polar and bulky bisphenol A and estradiol accordingly have higher *V* and *L* values and higher *S*, *A*, and *B*.

As shown in Fig. 2 for the training set of 79 chemicals, which included as diverse a range of properties to cover the range of descriptors, this pp-LFER approach provides for a good description of the interactions involved in the SOM sorption process. Whereas the diverse set of pesticides showed a poor correlation with K_{OW} (Fig. 1), an evaluation set of 56 pesticides and pharmaceuticals showed a relative mean standard error (rmse) of 0.4 log units, within the factor 3 recommended by Karickhoff, which corresponds also to the variation observed between K_{OC} values reported. In addition to the large set of reference neutral molecules, pesticides, and drugs, determined by Bronner and Goss [2, 3], Schenzel et al. [9] used the same

Fig. 2 Left: experimental K_{OC} values for 79 chemicals plotted against fitted K_{OC} values using the pp-LFER approach in Eq. (4). Redrawn with data taken from Bronner and Goss 2011 [2]



micronized peat and dynamic column retention setup to study the sorption affinity for a series of (mostly neutral) mycotoxins (both sets of K_{OC} values are listed in Table 2). Many of these mycotoxins represent complex polar structures, and the authors noticed that the K_{OW} values calculated with various commonly used algorithms (KowWin, ACDLabs, Marvin, etc.) often ranged over two orders of magnitude. For verrucarin A, which includes a large ring structure composed of 15 carbon atoms and 3 ester bonds, the calculated K_{OW} varied by up to four orders of magnitude. In the absence of (accurately) measured K_{OW} values, this clearly makes a K_{OW}-based estimation of K_{OC} highly uncertain, and experimental approaches or refined modeling efforts would be strongly preferred.

The key to understanding the sorption of polar chemicals to soils is thus to adequately capture the chemical interactions driving the affinity for binding to SOM over staying in water, using chemical descriptors that encompass the complexity of a multifunctional structure. Other soil components, such as black carbon phases (soot), clay minerals, and metal oxides, may also be involved in the sorption process for specific types of polar organic compounds. For example, alcohol ethoxylates, the group of mostly used nonionic detergents, sorb mostly to clay minerals in sediment because of their extensive chains of ethylene oxide units that allow for strong hydrogen bonding with silica surfaces [6]. Aniline moieties may even form (irreversible) covalent bonds with quinone moieties of SOM [4, 5]. Whereas black carbon itself is a highly variable sorbent type, typically adsorbing planar chemical structures (containing aromatic rings with little functionalities attached) more effectively than more bulky chemicals, the influence of other soil solids on overall sorption is highly specific for certain chemical classes, or even few chemicals within a class, and only applies to certain soil types (e.g., with relatively low OC content). Only systematic screening may elucidate which relevant chemical descriptors and soil properties should be included in soil sorption models and how to quantify these. It is important to notice that such additional sorbent components in soil hamper the calculation of a K_{OC} based on soil sorption data, because the sorption is not only related to the fraction organic matter/carbon.

2 Sorption of Ionogenic Chemicals

The sorption process for ionogenic organic chemicals (IOCs) is very different from that of (non)polar chemicals, particularly for IOCs where >90% is ionized as a cation, anion, or zwitterion. Upon ionization of an IOC, the aqueous solubility is typically enhanced by orders of magnitude. However, whereas water molecules are still neutral molecules that may engage in dipole-charge interactions, many environmental substrates are also full of charged or ionizable moieties, which may strongly attract oppositely ionized molecules by various charge-charge-based electrostatic interactions. Organic ions in soil sorb to different parts of soil organic matter than neutral chemicals, by different processes, and often also to different soil components, such as minerals [15–17]. Therefore new molecular rules apply to adequately describe these sorption processes, requiring carefully calibrated new sets of models specific for each type of IOC. Most environmental substrates are predominantly negatively charged, causing organic cations to be attracted and organic anions to be somewhat repulsed from the diffusive aqueous layers surrounding these surfaces. This includes clay minerals and weathered organic matter, although commonly present metal oxides and clay mineral edges do provide for positive surface potentials. This indifferent electrostatic attraction/repulsion is strongly influenced by the aqueous chemistry. The actual interactions of these attracted or repulsed organic ions with a wide variety of charged and neutral surface functionalities are nearly always still in a hydrated phase and are influenced both by specific nonionic molecular features and by competitive inorganic and organic sorbates.

2.1 Relevance of Ionogenic Chemicals for Risk Assessment

An ionic, ionogenic, or ionizable organic chemical (IOC) is a substance that is or can become an ion in water under relevant conditions. The respective ionic species has a negative charge (anion), a positive charge (cation), or multiple charges. IOCs also include ions that have both negative and positive charges in the molecular structure but with the zero net charge (i.e., zwitterions). The terms that are most often associated with IOCs are of course "acids" and "bases." In the context of environmental risk assessment (ERA), the terms acids and bases principally follow the Brønsted-Lowry definition. In this instance, an acid is defined as a chemical that releases a proton (H^+), and a base accepts H^+. A chemical that acts as both acid and base is referred to as an amphoteric chemical. Amphoteric chemicals with acidic dissociation constant (pK_a) which is lower than its basic pK are present primarily as zwitterion at intermediate pH.

Ionogenic organic chemicals (IOCs) represent an important group of chemicals that are widely used in commerce and industry. For instance, based on an analysis of industrial chemicals that have been preregistered at the European Chemicals Agency, Franco et al. [18] suggest that a significant fraction are IOCs (51% neutral; 27% acids; 14% bases; 8% zwitterions/amphoterics). Largely in agreement with this screening effort, a more extensive review of 5,530 substances registered with the REACH legislation in 2014 [19] indicated that 50.5% were neutral, 41.1% ionizable, and 8.4% ionic. Within the pH range 4–10, 15.3% were acidic, 14.8% basic, and 16.7 amphoteric. Some of these substances are produced and applied in high tonnages per year, and detailed risk assessment on environmental fate is essential. Furthermore, a survey of more than 900 active pharmaceutical ingredients (APIs) listed in the *Australian Medicines Handbook* found that the majority of APIs were found to be ionizable (64.2%), with the remainder comprising compounds that had a high molecular weight (14.9%) or were neutral (12.4%), always ionized (4.7%), miscellaneous (2.4%), or inorganic salts (1.3%) [20, 21]. When mixtures, salts, and high-molecular-weight chemicals are removed from the list, 85% of small-molecular-weight (<1,000 Da) APIs are estimated to be IOCs. The high relevance of these APIs is of course that they are often designed to be bioactive and often have specific effects and often unintended side effects, at relatively low exposure levels. For chemicals used in personal care products, examination of a dataset of 254 chemicals [22] suggests that approximately 35% of these chemicals may be ionized within an environmentally relevant pH range. Many of such chemicals are applied on a regular basis by large fractions of the human population. Lastly, many agricultural pesticides (e.g., glyphosate), biocides (e.g., quaternary ammonium cations), herbicides (e.g., acidic 2,4-D and related structures), and fungicides (e.g., propamocarb) are IOCs. Given the propensity of IOCs used in commercial and industrial practices, it is thus prudent to develop robust tools for assessing their environmental fate, and transport, an improved understanding of which will lead to an improved assessment of environmental exposure.

The release of ionogenic organic chemicals into the environment presents risk assessors with multiple challenges. This is because the fundamental principles underlying the risk assessment of organic chemicals have been primarily developed based on relationships largely associated with the behavior of neutral organics [23]. Consequently, concerns regarding the domain of applicability with respect to the physical and chemical space defined for the tools, models, and algorithms currently used are likely to be limited and not necessarily appropriate for chemical substances that are subject to ionization at environmentally relevant pH. In addition, particularly in instances where environmental fate and behavior are influenced by changes in pH and ionic strength, models for neutral chemicals fall short.

Analogous to Karickhoff's approach for neutral chemicals described above, for ionogenic chemicals the sorption to soils much also first be systematically studied before any relationship with soil properties and chemical descriptors can be achieved. Two distinctions need to be made first:

1. If ionizable organic chemicals are mostly neutral in the common soil pH range, the sorption to soils is most likely dominated by the neutral form partitioning into

soil organic matter. Depending on the required accuracy, the K_{OW} approach or the pp-LFER approach may be applied to predict the K_{OC}. The sorption coefficient of a partially ionized chemical may be best considered as a summed contribution of both the neutral species fraction (f_N), sorbing via the K_{OC}, and the ionized species fraction ($1 - f_N$), sorbing via its own sorption coefficient.

2. Regarding the much higher densities of acidic groups in soil organic matter, relative to basic moieties, and the predominantly negatively charged surfaces of most mineral, it makes a huge difference if the ionizable chemical is speciated into an organic cation or an organic anion. Likewise, the sorption interactions for neutral chemicals with SOM will most likely strongly differ from those between SOM and ionic species. It is therefore not appropriate to aim for a single descriptor sorption model that could magically include neutral, anionic, and cationic organic structures and aim to derive specific sorption models for organic cations and organic anions, apart from their neutral species. For describing and predicting the soil sorption process of organic ions, it is critical to understand how the sorption sites in soil may look like and which properties of soil, chemical, and aqueous phase influence the sorption process.

2.2 Chemical Speciation for Ionogenic Chemicals

The critical chemical parameter describing the chemical's ability to ionize is the acid dissociation constant (pK_a). The pK_a defines at which pH 50% of the IOC is in either the neutral or ionic form by releasing an H^+ from the neutral molecule acids (AH to anion A^-) or accepting an H^+ onto the neutral molecule base (B to cation BH^+). Strictly speaking, an acid is the chemical species before releasing H+ (e.g., phenol, Ph-OH), and the corresponding anion is not an acid (e.g., phenolate Ph-O-). The same applies to bases. The equilibrium between neutral acid and dissociated form can thus be defined as:

$$[\mathrm{AH}] \leftrightarrow [\mathrm{A}^-] + [\mathrm{H}^+] \tag{5}$$

where the chemical's equilibrium speciation is defined as:

$$K_a = \frac{[\mathrm{A}^-] \cdot [\mathrm{H}^+]}{[\mathrm{AH}]} \tag{6}$$

which gives the pK_a as:

$$\mathrm{p}K_a = -\log\ (K_a) \tag{7}$$

As a function of pH, the ratio of the acid and anion is defined by the Henderson-Hasselbalch equation as:

$$\mathrm{pH} = p\mathrm{K_a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)\text{for acids, and : } \mathrm{pH} = p\mathrm{K_a} + \log\left(\frac{[\mathrm{B}]}{\mathrm{BH}^+}\right)\text{for bases} \quad (8)$$

It is conventional to consider [BH+] as acid and use "pK_a" and other relationships for bases as well. The fraction of neutral species (f_N) for simple IOCs (one acidic or basic site) can be readily calculated with a derivatization of the Henderson-Hasselbalch equation:

$$f_N = \left(\frac{1}{(1 + 10^{\alpha}(-\mathrm{pH} + pK_\mathrm{a})}\right)\text{ in which } \alpha = 1 \text{ for bases, and } -1 \text{ for acids.} \quad (9)$$

A complete, 100% ionization of an acid never happens in the strict sense, as can be demonstrated from the Henderson-Hasselbalch equation. For environmental risk assessment (ERA) purposes, strong acids/bases may be defined as those IOCs that are always >99% ionic (i.e., $f_\mathrm{N} < 0.01$). Because the environmentally relevant pH range is 4–9 (see below), strong acids are those with $\mathrm{p}K_\mathrm{a} < 2$, and strong bases are those with $\mathrm{p}K_\mathrm{a} > 11$. For ERA, very weak acids/bases are those IOCs for which the neutral form will dominate nearly all relevant partitioning interactions, which we suggest is representative of systems where the ionic fraction is <10% at pH 4–9 (i.e., very weak acids $\mathrm{p}K_\mathrm{a} > 10$, very weak bases $\mathrm{p}K_\mathrm{a} < 3$). In the case of weak acids (i.e., $\mathrm{p}K_\mathrm{a}$ between 2–9) and weak bases (i.e., $\mathrm{p}K_\mathrm{a}$ between 3–11), the pH-dependent partitioning of both the ionic and neutral species should be considered to assess environmental fate and transport in specific environmental systems.

A "permanently charged chemical" means either of the following two:

1. An IOC that has only an ionic form. A neutral form does not occur by protonation or deprotonation. Examples are quaternary ammoniums, phosphoniums, and borates.
2. An IOC that is always charged for >99.99% within the relevant pH range. In this sense, permanently charged chemicals include "truly" permanently charged chemicals and very strong acids/bases. Examples may include organic sulfate and sulfonate anions ($\mathrm{p}K_\mathrm{a} < 0$), with the detergent ingredients sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonates as important representatives, but also include perfluorinated sulfonates and carboxylates such as PFOS and PFOA ($\mathrm{p}K_\mathrm{a} < 1$).

2.3 Sorbent Speciation Driving Surface Potentials

Soils and sediments can be composed of wide varieties of sandy (>63 μm), silty (2–63 μm), and clayish (<2 μm) particles that co-occur in various distributions. The natural organic matter fraction, and dissolved organic matter fractions, can also be of structurally very different compositions, depending on weathering status and types of organic input in the system. However, to understand the sorption of IOCs to environmental substrates, several features stand out:

1. Organic matter is not just a hydrophobic phase, and certainly not just a slightly polar solvent. In all cases, the weathered material that is left poorly degraded is rich in acidic functionalities such as carboxylic acids and phenolic groups. The typical cation exchange capacity (CEC) of dissolved organic carbon (DOC) such as humic acids and fulvic acids is 0.5–5 mol charge equivalent per kg dry weight (molC/kg dw) [24] or, in alternative units for the CEC, 50–500 meq/100 g. The carboxylic acids progressively dissociate in the pH range 3–5, while the phenolates progressively dissociate in the pH range 6–9, as shown by two bumps in the pH profile of charge development (see Fig. 4, HH-21). The anion exchange capacity (AEC) of DOC, in terms of residual amine groups, is often negligible because these valuable nitrogen sources are often actively reintegrated by microorganisms, in the order of a hundredfold lower than the CEC.

    - OM charge type A. [weathered organic matter]~$C(=O)O^-$ . . .H^+ (pK_a range ~ 3–6)
    - OM charge type B. [weathered organic matter]~aromatic ring-O^- . . .H^+ (pK_a range ~ 8–10)

2. The surface area of sand particles is often negligible to that of the clay fraction, and therefore the sand fraction is often a negligible sorbent phase. Nearly all disk-like clay minerals (phyllosilicates) have a negatively charged surface (see Fig. 4), due to two features. Firstly, phyllosilicates are often reformed by weathering processes of larger mineral structures, and under specific conditions different clay minerals can form. Typically, the disks formed consist of a silica oxide layer on top of an alumina oxide layer (a 1:1 mineral) or have alumina oxide sandwiched in between two silica oxide layers (2:1). Often during clay formation, isomorphic substitutions take place in these crystal layers, e.g., Al^{3+} in place of Si^{4+} or Mg^{2+} in place of Al^{3+}. These substitutions create permanent charge defects that always create a negative surface charge on the outside of the particles. This may strongly contribute to the CEC of soils and sediments. Secondly, the external surfaces of stacked disks can have ionizable moieties. The silica oxide layer has some residual acidic hydroxyl moieties that give rise to an additional, pH-dependent, amount of negative charge that adds to the CEC. In contrast, alumina oxide is rich in hydroxyl groups that have a higher pK_a and which results in a +1 positively charged surface on the aluminum atom when a surface OH groups become protonated and detach as water molecules. This counters the surface potential influence of negative charges of dissociated silica hydroxyl moieties in 1:1 minerals and reduces the CEC in clays like kaolinite. Because the alumina layer is sandwiched in 2:1 minerals, these clays have a much higher CEC consisting of both permanent and pH-dependent charge types. The aluminum middle layer may contribute some positive charge sites at the disk edges. If the majority of the isomorphic substitutions are located in the alumina layer of 2:1 minerals, the charge defect is distributed over both silica surfaces, which creates only a rather weak attraction between stacked disks. As a result, such clays like montmorillonite are "expandable," i.e., water and ions can penetrate and diffuse into the interlayers between each disk. This creates a strongly increased CEC. Non-expandable clays such as illite are kept tightly stacked with, e.g., potassium

ions kept non-exchangeable in between the disks, resulting in lower CEC than expandable clays.

- Clay charge type A. [isomorphic Al^{3+} in place of Si^{4+}, or Mg^{2+} in place of Al^{3+}]$^-$. . .K^+ (permanent)
- Clay charge type B. [tetrahedral silicon oxide] -O^- . . .H^+ (pK_a range ~ 3–6) (pH dependent)
- Clay charge type C. [basal octahedral aluminum oxide] Al_2-OH.H^+ (pK_a range ~ 8) (pH dependent)
- Clay charge type D. [edge octahedral aluminum oxide] $AlOH^{-0.5}$.H^+ (pK_a range ~ 10) (pH dependent)

3. Metal oxides based on iron (oxyhydroxide goethite, α-FeOOH; hematite, α-Fe_2O_3) and aluminum (gibbsite, $Al(OH)_3$) are the most common contributors to the anion exchange capacity in soils. The gibbsite surface is considered to have a positive surface potential with a pK_a of ~ 6 due to release of OH surface groups ($Al(OH)_2^+$ and $Al(OH)^{2+}$). At pH above 6, it is considerably neutralized to $Al(OH)_3$ but at elevated pH forms $Al(OH)_4^-$ (see Fig. 4 [25]). The similar protonation process of aluminum hydroxide occurs also in the 1:1 clay mineral kaolinite, although the overall net surface charge is negative due to excess dissociating silanol groups [26]. With iron oxides in water, hydroxylation occurs when Fe atoms on mineral surfaces complete their coordination with hydroxyl groups released by water molecules (Fig. 3). A hydroxyl group that coordinated with a

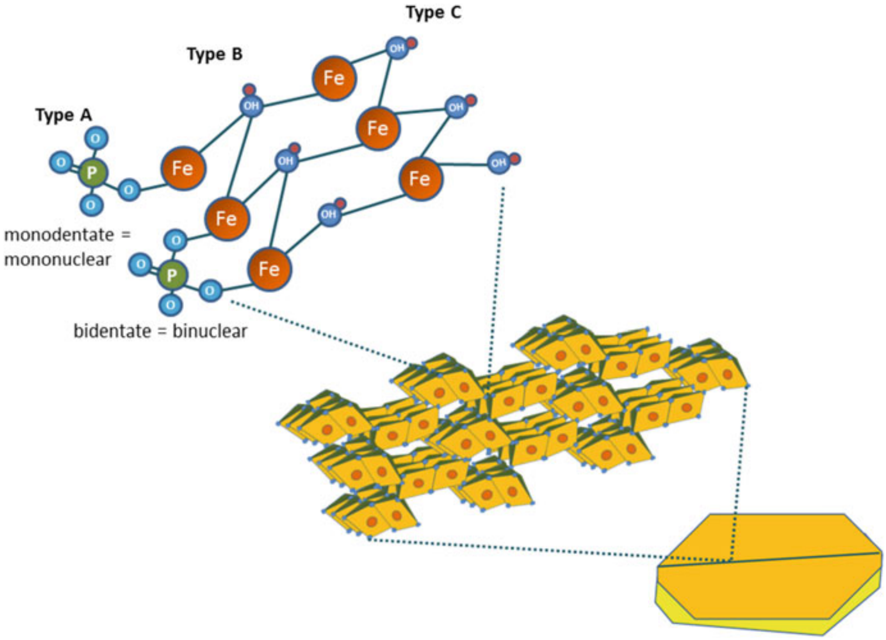


Fig. 3 Three different types of hydroxylated sites on the surface of iron hydroxide, whereby the single coordinated hydroxyl groups are replaced by phosphate in monodentate or bidentate coordination. Figure by S. Droge (2020)

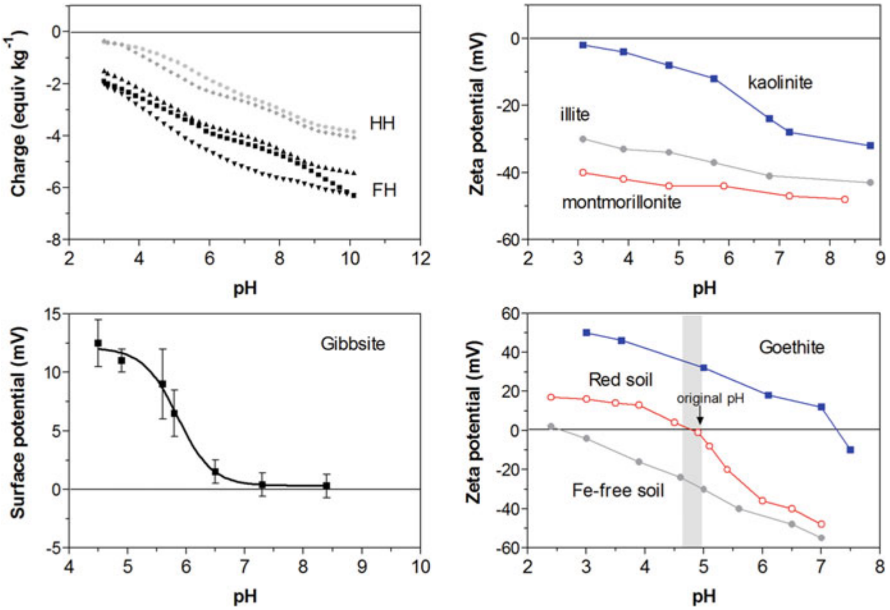


Fig. 4 pH-dependent surface charge progression on different natural substrates (*NB* charge depends also on ionic strength of the solutions): *top left* (redrawn from examples in [24]) negative charge on fulvic acids and humic acids in mol charge equivalents per kg dry weight; *top right* (redrawn from examples in [29]) the overall negative charge progression of different phyllosilicate clays in marine ionic strength solutions (0.56 M NaCl); *bottom left* (redrawn from examples in [25]) the positive surface potential progression for gibbsite (in 1 mM NaCl); *bottom right* (redrawn from examples in [28]) goethite and iron-rich/iron-depleted soil (in 1 mM NaCl)

single iron atom (type A) has a half negative charge $\equiv$Fe-OH$^{-0.5}$ which is easily protonated to get an overall +0.5 charge. In turn, this "protonated hydroxyl group" can be replaced by other inorganic anions, such as phosphate, in an inner sphere (covalent) bond. A hydroxyl group that coordinated with three iron atoms (type B) has a half positive charge $\equiv$Fe$_3$-OH$^{+0.5}$. The oxygen of the shared hydroxyl is much less electronegative than that in the type A oxide and is much less easily protonated. Goethite and hematite are thus positively charged in common soil pH, with a zero point of charge (ZPC) only at pH 7–9 [27, 28] (see Fig. 4). It depends on the number of surface iron atoms that coordinate with the hydroxyl groups how protonation occurs (type A–C). Of course, when high levels of iron oxides are mixed into soils, with a typical red coloration, the overall surface potential is lowered compared to the original goethite but may still be net positive overall at low pH (where high enough H$^+$ concentrations exist to protonate the surfaces).

- Iron oxide type A. Single iron atom coordinated hydroxyl $\equiv$Fe-OH$^{-0.5}$ (H$^+$ protonation)

- Iron oxide type B. Three iron atoms coordinated hydroxyl $\equiv Fe_3\text{-}OH^{+0.5}$
- Iron oxide type C. Two iron atoms coordinated hydroxyl $\equiv Fe_2\text{-}OH^0$
- Aluminum oxide surface groups with increasing pH: $Al(OH)^{2+}/Al(OH)_2^+/Al(OH)_3/Al(OH)_4^-$

2.4 Relevant Solvent Parameters for Ionogenic Chemicals

In a simplified view, the ionic moiety of an IOC can be thought of as being "attracted" to an oppositely charged sorbent, causing the IOC to be preferentially sorbed relative to being dissolved. The nonionic structure of an IOC can still be hydrophobic and for that reason gives the charged IOC molecules a preference to be sorbed into sorbent/onto a substrate surface rather than being fully dissolved. The ionic moiety of an IOC, however, mostly strongly prefers the molecule to be present in the aqueous phase. Not surprisingly, a dissociated acid anion has an orders of magnitude higher solubility compared to the neutral undissociated acid. The dielectric constant (symbol, ε) of a solvent is higher for more polar solvents, and this translates into a higher ability to dissolve ions. Water has an ε of 80.1, methanol 32.7, and acetonitrile 37.5. As a consequence, an ionizable acid will be more dissociated in water than in methanol. The ε of octanol is 10.3; the even less polar solvent dichloromethane has an ε of 8.5 and cyclohexane has only 2.02. In octanol, the partitioning coefficient of the neutral species is often more than a factor 1,000 higher than the dissociated anion or protonated cation. Due to the omnipresent acceptance of octanol as the prevalent descriptor of a chemical's sorption affinity to organic matter, it is often wrongly considered that ionic species of IOCs hardly sorb to environmental substrates. Organic cations have more recently been shown to sometimes sorb even as strongly as the deprotonated neutral base [15–17], while organic anions also have been shown to sorb substantially to natural colloids, soils, and sediments, as long as the nonionic structure is sufficiently hydrophobic [30–32].

The obvious fact that most environmental substrates and colloids are negatively charged particles results in that sorption of organic cations is a highly relevant process to describe in detail for adequate risk assessment purposes. An example of the higher than expected sorption of organic cations to organic matter has been presented by Sibley and Pedersen [16], who studied the parameters that influence the sorption of the base clarithromycin, a commonly used veterinary antibiotic, on dissolved Elliot soil humic acid. Clarithromycin is a base with a multiple polar moieties and a tertiary amine with a pK_a of 8.9 (see speciation diagram in Fig. 5). Illustrative for the underlying sorption process, this study clearly identified three different aspects of the aqueous solution composition that could influence the sorption affinity of ionizable bases.

1. When testing the pH dependency of the sorption affinity, as shown in Fig. 5, they showed that actually the protonated cation sorbed more strongly to dissolved

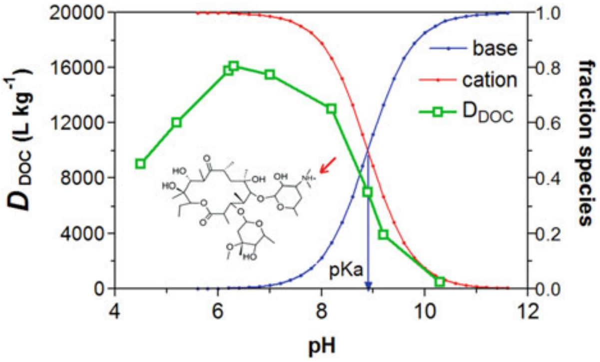


Fig. 5 pH-dependent sorption profile of clarithromycin on dissolved Elliot soil humic acid. The left *Y*-axis scales the DOC-water distribution coefficient (D_{DOC}), and the right *Y*-axis the speciation profile. The structure of clarithromycin is presented in the protonated form. Redrawn from example in [16]

organic carbon than the neutral base species, with a maximum distribution coefficient of 16,000 at pH 6, well below the basic pK_a of 8.9.

2. Furthermore, they found that when the ionic strength of the test solution was reduced by a factor 10, the sorption affinity of the protonated clarithromycin increased by a factor of 10.
3. Additionally, the sorption affinity of the protonated clarithromycin was twofold higher when the salinity was based on sodium phosphate buffer compared to a potassium buffer of equal ionic strength.

The main reason underlying this strong and variable sorption affinity of the organic cation to DOC is the abundance of negatively charged groups in DOC, such as carboxylic acids with a pK_a ~ 4–6 and phenolic acids with a pK_a ~ 8–10, that together give DOC its typical high cation exchange capacity (in the range of 0.5–5 mol charge/kg dry weight). The pH profile shown in Fig. 5 shows that the sorption affinity of the fully protonated clarithromycin increases in the pH range of 4.5–6, indicative of the increased dissociation of acidic sites on the DOC, which increases the cation exchange capacity. Another way of seeing this process is that the more abundant presence of H^+ cations in acidic solution is competing with protonated clarithromycin for the same dissociated DOC sites. It is often considered that the sorption of organic cations to DOC is an ion exchange process: the sorption of protonated clarithromycin releases a more weakly bound cation such as Na^+. K^+ cations (atomic mass 39) are larger than Na^+ cations (atomic mass 23), and K^+ consequently has a smaller hydrated radius, which translates into a higher sorptive affinity to anionic DOC sites than Na^+. At a ten times higher salinity, the solutions' cations that are competitive in binding with clarithromycin are thus also present at ten times higher levels, which would translate in the lower sorption affinity of clarithromycin.

However, this view of a mere competitive process is probably too simplistic to explain these phenomena. The sorptive capacities of DOC for metals have been described in more detail by more complex models that take into account both (competitive) electrostatic interactions at the actual sorption site (term A) and electrostatic attraction (term B) from the bulk water to the aqueous electrical double layer ("EDL") surrounding the organic DOC structure (also called diffuse water

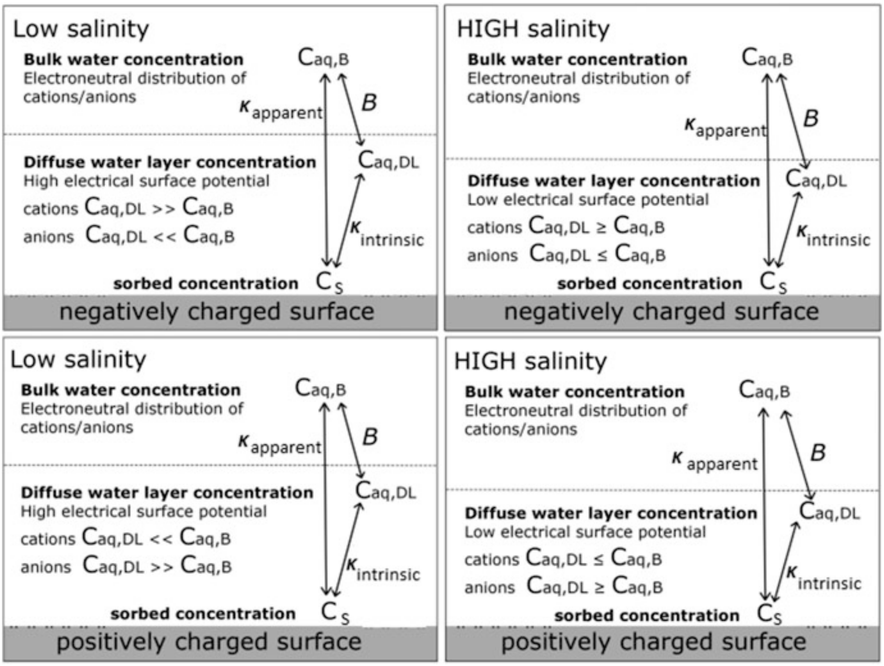


Fig. 6 Description of the sorption process between an ionic solute and a charged surface. Electrostatic attraction increases the dissolved concentration in the diffuse layer ($C_{\mathrm{aq,DL}}$) compared to the concentration in the bulk water ($C_{\mathrm{aq,Bulk}}$), by the Boltzmann factor B. The apparent sorption coefficient (K_{apparent}) should thus actually be accounting for the electrostatic attraction to identify the intrinsic sorption affinity for the surface ($K_{\mathrm{intrinsic}}$). Extended figure from [33]

layer). The sorption affinity ($K_{\text{sorbent-water}}$) of a charged compound for a charged surface can thus be approached as an apparent affinity, which combines all effects, as well as an intrinsic sorption affinity, specific for the sorption site, as in the form below:

$$\begin{aligned}\text{apparent } K = {} & \text{electrostatic attraction into EDL} \\ & + \text{interaction affinity with site}\end{aligned} \tag{10a}$$

$$\begin{aligned}&\text{intrinsic } K \\ &\quad = \text{site interaction affinity, corrected for electrostatic attraction competition}\end{aligned} \tag{10b}$$

Electrostatic attraction is described as the accumulation of oppositely charged molecules into a thin surface layer surrounding a charged surface (electrical double layer or diffuse layer) or, more relatable to dissolved organic matter, into the aqueous phase present in a wet matrix of charged organic matter structures. The *attracted* increase in a chemical's concentration in the diffuse layer is thus not due to any *interaction* with the sorption site. This electrostatic attraction can be theoretically approached iteratively by the common Boltzmann potential equation, as is done, for example, in the Donnan term for the extensively parameterized NICA-Donnan model for metals [24, 34–36] and part of the WHAM model [37]. Ionic strength and the charge density of the sorbent material, and an adjustable sorbent property descriptor *b*, determine the influence on electrostatic attraction (see for details in Box 1).

The actual, *intrinsic*, sorption affinity of an ion for the "ion exchange site" is thus not due to the electrostatic attraction but only the competitive interaction affinity at the sorption site. What we often measure in a sorption study is the summed apparent overall sorption affinity. The electrostatic attraction strongly depends on the ionic strength and can be accounted for if one tests the influence of ionic strength on the sorption affinity. The difference between apparent and intrinsic sorption affinity is theoretically approached by the Boltzmann potential. The intrinsic sorption affinity is what is needed in the competitive sorption terms of a model like NICA (non-ideal competitive adsorption refers to the sorption process being exponentially nonlinear). These have been defined for a wide range of metal cations [35] for both the carboxylate and phenolate anion sites of DOC.

Box 1 provides a more detailed description given in Chen et al. [38] on the reasoning behind the NICA-Donnan equation which could be applied to describe (part of) the sorption affinity of cationic surfactants on DOC.

Droge and Goss [15] used dynamic column studies, and Chen et al. [38] batch sorption studies, to systematically evaluate the influence of ionic strength and main inorganic salt cation type (Na^+ and Ca^{2+}) on the sorption affinity of organic cations to micronized soil organic matter and dissolved humic acids. Both studies observed that divalent inorganic cations typically control the Boltzmann potential. At equal ionic strength, sorption affinity of organic cations is an order of magnitude lower in the presence of 5 mM Ca^{2+} compared to 15 mM Na^+:

$$\text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 15 mM Na}^+ = 10 \times \text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 5 mM Ca}^{2+} \tag{11}$$

At ten times lower divalent cation concentrations, the sorption affinity of organic cations decreases only by a factor of ~3 (0.5 log units), while in ten times lower monovalent cation concentrations, the sorption affinity of organic cations decreases by a factor of ~5 (0.7 log units):

$$\text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 15 mM Na}^+ = 5 \times \text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 150 mM Na}^+ \tag{12}$$

$$\text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 0.5 mM Ca}^+ = 3 \times \text{apparent } K_{(\mathrm{DOC}-W)} \text{ in 5 mM Ca}^{2+} \tag{13}$$

As a result, even at a low hardness of 0.5 mM Ca^{2+}, sorption is stronger than that in the presence of 150 mM Na^+ (Fig. 7), so "hardness" controls the apparent $K_{(\mathrm{DOC}\text{-}W)}$

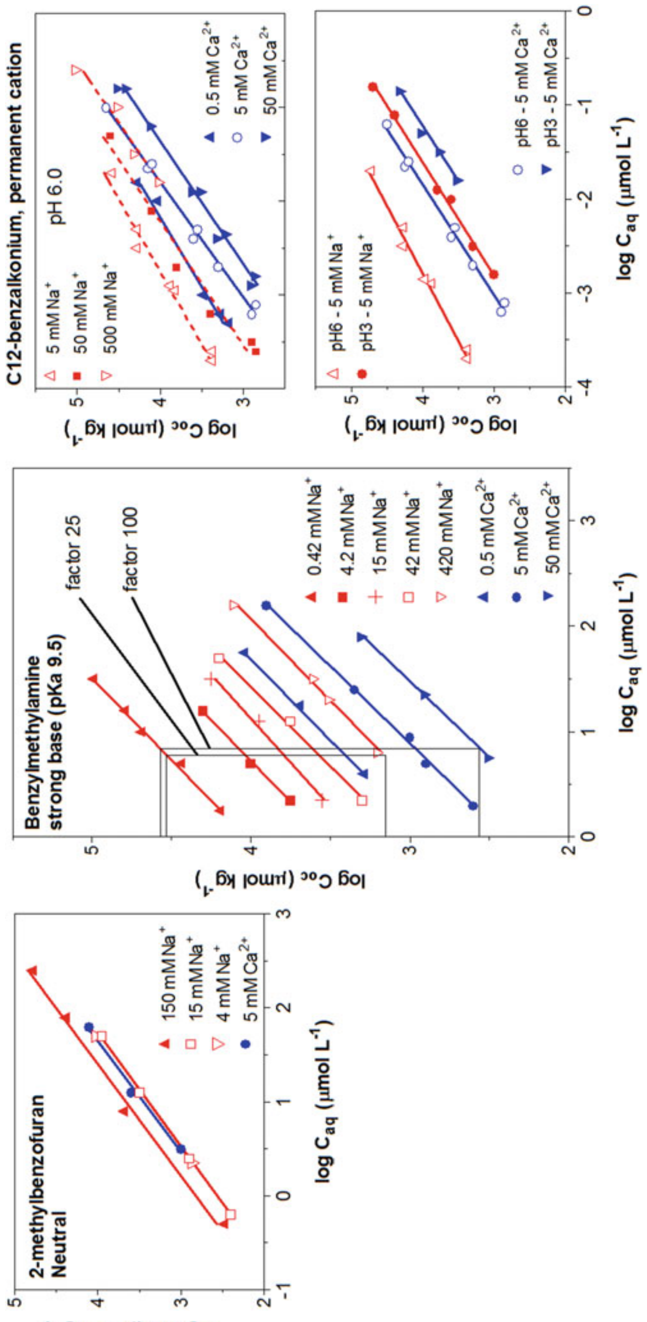


Fig. 7 Sorption isotherms in the presence of different ionic strength solutions for (left) a neutral chemical (redrawn from data in [15]), (middle) a small organic strong base at pH6 (redrawn from data in [15]), and a cationic surfactant C_{12}-benzalkonium (redrawn from data in [38])

over "ionic strength" in most environmental systems. It is important to take this into account when comparing laboratory studies performed under specific aqueous media.

Despite the obvious electrostatic repulsion that organic anionic have with negatively charged SOM/DOC and clays, with sufficiently hydrophobic structures, anionic surfactants also accumulate in organic phases of soils and sediment. Since electrostatic repulsion is reduced at higher salinity, this increases the sorption affinity. It is sometimes speculated whether the sorption of divalent cations such as Ca^{2+} forming a positive moiety $[\sim\text{carboxylate-Ca}]^{+}$ could directly bridge to sorb an organic anion solute, as increased Ca^{2+} concentrations somewhat increase organic anion sorption affinities, but this may also simply be due to the effect of surface potential screening. Tülp et al. [39] found only a small effect of the usual environmental Ca^{2+} concentration range (factor 2) on anion sorption; more importantly, this effect was independent of the anion molecular structure, i.e., there were no specific features observed that indicated specific calcium bridging for either phenolates, carboxylate, or complex anionic structure.

2.5 *Relevant Chemical Parameters for Ionogenic Chemicals*

Using a similar dynamic column setup with micronized Pahokee peat as Bronner and Goss [2] applied for 137 neutral chemicals, Tülp et al. [39] studied the sorption of 32 organic anion structures and corresponding neutral acid forms, and Droge and Goss [40] studied ~ 80 organic cations to Pahokee peat. Schenzel et al. [9] tested 25 mycotoxins and some phytoestrogens, including 2 cations and 1 anion. Zhi and Liu also used the dynamic column setup with micronized Pahokee peat to study perfluorinated chemicals, including 12 anionic and 3 amphoteric (betaine) structures [41]. All the K_{OC} values for ions obtained on Pahokee peat are listed in Table 3. This set of K_{OC} values for a single organic matter source, obtained with a similar experimental setup, is probably the most consistent sorption dataset available to investigate how structural features influence the sorption affinity. As discussed for polar organics earlier in this chapter, this allowed for the construction of pp-LFER type modeling based on the prevailing types of nonionic interactions. For ionic compounds, this is much less straightforward, since it was unknown which chemical descriptors could best be used to account for both the nonionic and ionic sorption interactions.

First of all, it still remains even unclear how ionic compounds are sorbed in the hydrated organic matter matrix. As discussed above, the first distinction to make is between electrostatic attraction/repulsion and the interaction of the ionic compound with the sorbent, which most likely for cations occurs through electrostatic interaction with the anionic moieties. The main question that still needs to be resolved is how the nonionic part of an ionic solute contributes to this sorption process: i.e., does it fully interact with the nonionic backbone of SOM surrounding the anionic moiety,

Table 3 Sorption coefficients for charged IOCs on micronized Pahokee peat

Chemical name	Log K_{OC} cation	Chemical name	Log K_{OC} cation	Chemical name	Log K_{OC} anion	Log K_{OC} acid
C_8-based cations [40] (pH 4.5, at 1 mmol/kg, 5 mM $CaCl_2$)		*>99% Cationic pharmaceuticals* [40] (pH 4.5, at 1 mmol/kg, 5 mM $CaCl_2$)		*Acidic chemicals* (fitted from pH profile, in 10 mM $CaCl_2$)		
1-octylamine	2.60	Serotonin	3.54	*Phenolic acids* [39]		
2-Phenylethylamine	2.45	Tryptamine	3.09	2,3-Dichlorophenol	n.d.	2.41
N-Benzyl-*N*-methylamine	2.31	Amphetamine	2.42	2,4,5-Trichlorophenol	n.d.	3.23
Octyltrimethylammonium	2.31	Methamphetamine	2.45	2,4,6-Trichlorophenol	1.65	2.88
Simple primary amine cations [40]		L-Adrenaline	0.90	2,3,4,6-Tetrachlorophenol	2.00	3.72
1-Hexylamine	2.11	Methylephedrine	2.16	Pentachlorophenol	2.86	4.26
1-Heptylamine	~2.35	(±)-Metoprolol	2.06	Chloroxynil	1.26	2.18
1-Octylamine	2.60	Propranolol	3.74	Bromoxynil	1.49	2.78
1-Decylamine	3.43	R-Atenolol	2.54	Bromoxynal	1.66	3.15
Benzylamine	2.30	Alprenolol	2.96	Ioxynil	1.91	3.15
4-Methylbenzylamine	2.72	Prilocaine	2.20	2-Nitrophenol	1.11	1.93
4-Butylbenzylamine	3.22	Lidocaine	2.20	4-Nitrophenol	1.11	1.98
4-Octylbenzylamine	4.06	Procaine	3.26	2,4-Dinitrophenol	1.63	2.62
2-Phenylethylamine	2.45	Atropine	3.06	Dinoseb	1.94	2.85
3-Phenylpropylamine	2.68	Scopolamine	2.27			
4-Phenyl-1-butylamine	2.95	Ropivacaine	2.40	*Carboxylic acids* [39]		
4-Chlorobenzylamine	2.84	Bupivacaine	2.50	2,4-D	1.32	n.d.
3,4-Dichlorobenzylamine	3.58	Fluoxetine	3.54	Mecoprop	1.04	n.d.
(±)-1-Aminoindane	2.54	Imipramine	3.56	2,4-DB	1.97	3.04
Naphthylamine	3.31	Codeine	2.50	2,4,5-T	1.68	n.d.
Simple secondary amine cations [40]		Clonidine	2.53	Ibuprofen	1.08	2.67
N-Benzyl-*N*-methylamine	2.31	(+/−) Verapamil	3.46	Ketoprofen	1.23	2.79

N-Benzyl-*N*-ethylamine	2.26	Nicotine (S)-(-)	2.60	Fenoprofen	1.34	2.99
N-Benzyl-*N*-butylamine	2.41			Naproxen	1.58	3.36
N-Benzylhexylamine	2.55	*Other amines with polar moieties* [40]		1-Methoxy-2-naphthoic acid	1.34	2.93
N-Benzyloctylamine	3.08	*N*-Benzylethanolamine	2.27	4-Fluoro-1-naphthoic acid	1.43	n.d.
3-methyl-*N*-methylbz.am	2.64	4-Amino-2-methylquinoline	4.10			
N-ethyl-M-toluidine	2.49	2-Phenylbenzimidazole	4.23	*Complex acids* [39]		
N-Methyl-phenethylamine	2.49	Benzimidazole	3.19	Warfarin	0.95	2.46
Dibenzylamine	3.16	Thiabendazole	3.65	Coumachlor	1.40	3.15
Simple tertiary amine cations [40]		*N*-Benzylamino-acetaldehyde diethyl acetal (2 ethers)	2.10	4′-Hydroxywarfarin	0.95	2.49
Pyridine	2.04			Coumafuryl	0.85	2.45
Quinoline	3.28	*N*-Benzyl-beta-alanine ethyl ester (ester)	2.31	Sulcotrione	0.90	n.d.
N,*N*-Diethylaniline	1.98			Mesotrione	0.90	n.d.
2-Ethylpyridine	2.19	3-Dimethylamino-propiophenone (ketone)	2.58			
2-Methylpyridine	2.08			*Anionic penicillium* (5 mM Ca^{2+}) [9]		
3,4-Dimethylpyridine	2.55	1-benzyl-3-acetamido-pyrrolidine (amide)	2.44	Citrinin	3.1	
2,6-Dimethylpyridine	1.87					
2,4,6-Trimethylpyridine	2.33	2,2′-(Benzylimino)-diethanol	2.18	*PFAS anions* (5 mM Ca^{2+}, pH 5.2–5.9) [41]		
N-Benzyldimethylamine	2.20	Acetylcholine	1.14	PFBA	1.27	
Quaternary ammonium cations [40]		Butyrylthiocholine	2.11	PFPA	1.24	
Phenyltrimethylammonium	2.12			PFHxA	1.26	
Benzyltrimethylammonium	2.24	*Cationic mycotoxins* (5 mM Ca^{2+}) [9]		PFHpA	1.35	
Benzydimethylhexylammonium	2.94	Ergocryptine	4.02	PFOA	1.54	
Benzydimethyloctylammonium	3.40	Ergocornine	3.88	PFNA	2.28	
Benzydimethyldecylammonium	3.88			PFBS	1.38	
Benzyltributylammonium	2.60	*Perfluorinated zwitterionic betaines*		PFHxS	1.47	
Benzyltripropylammonium	2.41	(5 mM Ca^{2+}, pH 5.2–5.9) [41]		PFOS	2.55	

(continued)

Table 3 (continued)

Chemical name	Log K_{OC} cation	Chemical name	Log K_{OC} cation	Chemical name	Log K_{OC} anion	Log K_{OC} acid
Benzyltriethylammonium	2.43	PFOAB	1.95	4:2 FTSA	1.42	
Difenzoquat methyl sulfate	3.16	PFOSB	2.40	6:2 FTSA	1.51	
		6:2 FTAB	2.11	8:2 FTSA	2.56	

or is it still partially/fully hydrated but strongly reduced in its entropic energy due to the sorptive interaction?

Although the electrostatic attraction can be deduced by the salinity effects, this attraction is equal for all monovalent organic cations [15]. As a result, as long as the same aqueous composition is applied, which is relatively easy to ensure in the chromatographic dynamic sorption setup with micronized peat, the relative differences in sorption affinity between different organic cations can still be examined to study the influence of a solute's nonionic structure. Droge and Goss [40] started their measuring series of organic cations with a wide variety of amines with a structure based on the formula $C_xH_yN^+$, thus lacking polar functionalities based on oxygen and nitrogen. Series of homologues with different alkyl chain length were included. From these series, it became apparent that a CH_2 unit in an organic cation contributes significantly less to the sorption affinity than a CH_2 unit in a neutral chemical, ~0.25 log units compared to ~0.5 log units per CH_2. Compare, for example, the alkylbenzenes in Table 2 with the alkylamine cations in Table 3. The reason for this must be due to the entirely different sorption site within the peat matrix between a neutral and a cationic chemical. The series of polar compounds tested by Bronner and Goss [2], for example, that in the selection of C_8-based chemicals in Table 2, clearly shows the influence of a single type of polar moiety on the K_{OC}, which can also be done for organic cations tested by Droge and Goss [40]. Whereas a hydroxyl group in a neutral chemical lowers the K_{OC} by ~2 log units (e.g., compare the C_8 chemical 2,2,4-trimethylpentane with 2-ethyl-1-hexanol), the organic cation *N*-benzylethanolamine has an equal sorption affinity as its "nonpolar analogue" *N*-benzyl-*N*-ethylamine (Table 3). From these examples, and also the strong influence of salinity on the sorption of organic ions, it thus also becomes clear that it is difficult to make a fair comparison between the sorption affinity of a neutral base and that of its protonated form: these species sorb to different sorption sites, which are governed by very different sorption processes, which operate by different structural contributions.

When the HPLC-measured, ion exchange-based, sorption affinity of organic cations to Pahokee peat (log $D_{OC,IE}$) was plotted against standard ways to predict K_{OC} from K_{OW} (Fig. 8 plot A, from [40]), virtually no relationships are obtained. Predicting the K_{OC} using a structural approach via EPISuite provides some trends for simple hydrocarbon structure-based cations (C_xH_yN in Fig. 8 plot D) but still a wide variation for organic cations with polar functionalities, and not relation for quaternary ammonium compounds.

Droge and Goss aimed to obtain a single consistent dataset that could identify the specific contribution of the most commonly present molecular functionalities to the relative sorption affinity to SOM. The first predictive step they suggested was to calculate the sorption affinity based on molecular size (McGowan's V_x index) and amine type (number of H on the protonated amine, *NAi*), which was defined by a set of 32 C_xH_yN cations, with average K_{OC} measured at pH 4.5–7, in aqueous solution with 5 mM Ca^{2+}:

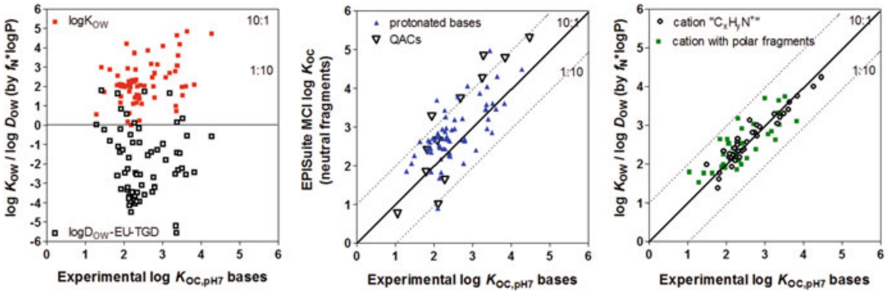


Fig. 8 Observed sorption affinities to SOM for cations (log $D_{\mathrm{OC,IE}}$) compared to predictions of (*left*) either logKow (SPARC) or logDow (following EU-TGD approach of the neutral fraction fN multiplied by logKow), which excludes the 14 quaternary ammonium compounds (QAC), (*middle*) EPISuite predictions of logKoc based on the MCI structural fragment approach obtained with neutral structures (or QAC structure), (*right*) cation fragment-based approach developed by Droge and Goss [40], using Eq. (14) with McGowans volume Vx and number of hydrogen atoms on the charged amine (NAi) for the C_xH_yN backbone of each cation, and polar fragment corrective increments as listed in Table 4 if present in the cationic structure. Based on data presented in [40]

$$\text{Log}\ K_{\mathrm{OC}}\left(\text{pH}\ 4.5-7,5\ \text{mM}\ \text{Ca}^{2+}\right)=1.53\cdot Vx+0.32\cdot NAi\\ -0.27\ \{+[\text{polar functionalities}]\}\qquad(14)$$

As shown in Table 4, the presence of a polar functional groups would then be added (as [polar functionalities] in Eq. (14)) on this V_xNAi-based prediction. For example, as listed in Table 4, in four organic cations, an amide group was present next to a phenyl ring, and on average for these four compounds, this lowered the K_{OC} by 1.4 log units compared to the V_xNAi value. Table 4 also shows that the influence of a hydroxyl unit is minor in five evaluated organic cations, as indicated in the one example of the analogue structures mentioned above. Corrective increments on the V_xNAi model were derived for 16 different functional groups. As shown in Fig. 8 plot F, certainly for many of the simple C_xH_yN but also for the majority of the polar organic cations, the K_{OC} could be predicted within a factor of 3 this way. However, with a dataset of <50 molecules to define 16 polar functionalities, this is still rather limited to validate so many features, even though many compounds contained multiple functionalities. It is furthermore questionable if K_{OC} values derived from natural soils (see below that this is unlikely) or different types of organic matter could provide more input values to this dataset specifically derived on micronized Pahokee peat. Although the correction factor for ether units had to be modified to 0, Jolin et al. found that most other corrective increments in Table 4 were successful in predicting differences between organic chemicals in their relative sorptive properties [42].

Nevertheless, the description of how molecular structure influences the IOC sorption affinity is already much more advanced for cations than the current dataset for organic anions allow for (Tülp et al. [39] provides for the largest consistent dataset). All acidic chemicals include already multiple structural features, only

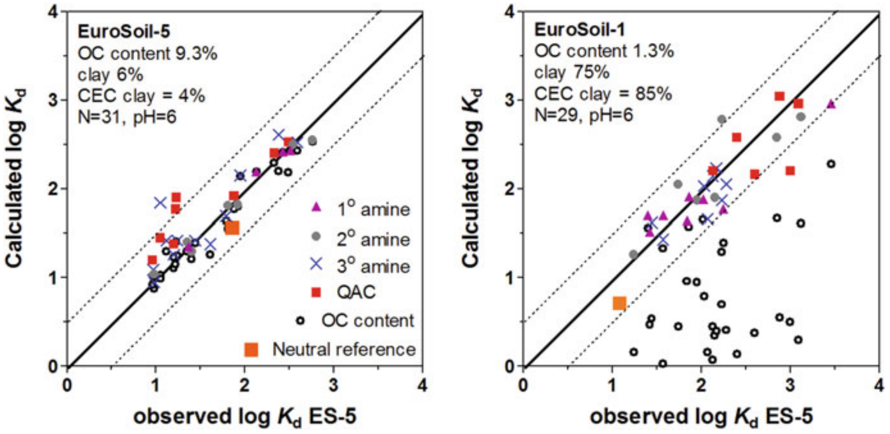


Fig. 9 Sorption coefficients for organic cations (1°, 2°, 3° amines, 4° QACs) and a neutral reference compound (N) on two reference Eurosoils and predictions with and without accounting for clay (OC content corrected only). Predictions for the soils are made using experimental sorption coefficients on reference OM (Pahokee peat) and reference clay (illite). The CEC_{soil} of Eurosoil-5 has only a minor contribution of CEC_{clay} (4%), while Eurosoil-1 has a major contribution of CEC_{clay} (85%). Based on data taken from [51]

Table 4 Empirical correction factors for polar fragments in addition to the average V_xNAi model [40]

Functional group	V_xNAi model correction factors (in log units)[b]
• Phenyl, or 3xF, or -ΞN, or S[c]	• 0
• -Cl	• +0.5 (3)
• Polycyclic aromatic ring	• +0.7 (2)
• Pyridine NH^+	• +0.7 (6)
• Aniline-NH_2	• +0.55 (1)
• -CNC- (HBDon)	• +0.6 (2)
• -CNC- (HBAcc or neutral)	• −0.1 (3)
• Benzimidazole	• +1.7 (3)
• -C-NH_2 (aniline)	• +1.2 (1)
• -OH	• −0.1 (5)
• -C(=O)NC- on phenyl	• −1.4 (4)
• -C(=O)NC- other	• −0.4 (1)
• -C(=O)OC-	• −0.8 (3)
• -COC-	• −0.6 (12)
• -C(=O)C-	• +0.1 (2)
• -C(=O)NH_2	• −0.65 (1)
• -Internal HB	• −1.3 (1)

[a] 32 CxHyN compounds

[b] 41 compounds used, no. of moieties (e.g., four ethers for verapamil) used in parentheses

[c] Phenyl was found to have negligible influence above that already covered in the V_xNAi model. 3xF, -ΞN, and S are largely neutral moieties and were assumed to be mostly covered by the size factor in V_xNAi model, and set to 0 when calculating correction factors for -COC- and benzimidazole

insight in the influence of chlorination on an aromatic ring, and a comparison between ketoprofen and fenoprofen (K_{OC} nearly equal, 17 and 22, with one having a ketone and the other an ether in between two phenyl rings) would allow for some comparison of how the neutral backbone of anionic chemicals influences their sorption affinity. In addition, chlorination on phenols not only influences the non-ionic part but also strongly influences the properties of the ionic moiety, which is reflected in the different pK_a values for the various chlorinated phenols included by Tülp et al.: pentachlorophenol has a pK_a of 4.8, while 2,3-dichlorophenol a pK_a of 7.6. Just as the affinity of the proton (H^+) to associate with the phenol unit, the charged phenolate moiety may also have a variable contribution to the sorption process in SOM. The good thing about the anion dataset is that in the same study, the K_{OC} for the corresponding neutral acids was also derived for 21 acids. This led to the surprising observation that the anionic form only had 7–60 times lower sorption affinities as the neutral forms, despite the obvious repulsion toward the sorption sites that anions probably are influenced by. This could allow for a rough K_{OW}-based calculation of the sorption affinity of anionic species (e.g., first calculating the K_{OC} for the neutral species and then subtracting an average of 1.3 log units) [43], but moreover it begs the question what process is enabling this sorptive affinity.

One possible reason for the unexpectedly strong apparent affinity of organic anions has in recent years been identified as (negative) charge-assisted hydrogen bonds or (−)CAHB. These (-)CAHB were first studied on the more simplified surfaces of functionalized black carbon [44] and carbon nanotubes[45]. More recently, (-)CAHB were discussed to also contribute significantly to OM cohesion itself [46], proving an important feature of the forces holding organic supramolecular structures together. The (−)CAHB can be exemplified by structures where an anionic sorption site approaching proton (H^+) connects two dissociated organic moieties, together still rendering a negatively charged group, for example, between two carboxylate structures:

$(\sim CO_2...H...O_2C\sim)^-$

or mixed moieties such as carboxylate and phenolate:

$(\sim CO_2...H...O\sim)-$,

It appears that the (-)CAHB forms between weak acids with similar proton affinity (similar pK_a) and is shorter, more covalent, and much stronger than ordinary hydrogen bonds. This may explain some of the observed K_{OC} differences between the anion-acid couples Tülp et al. [39] used, but since natural organic matter has many types of acidic sites with a wide variety in pK_a, the organic anions may always find optimal binding spots to form (-)CAHB with.

For the anions it was concluded [39] that the K_{OC} values of both the neutral and anionic species increased with increasing molecular size and decreased with increasing polarity. At a constant concentration of 10 mM Ca^{2+} over a pH profile, the investigated anions sorbed between a factor of 7 and 60 less than the corresponding neutral acid. A log unit lower Ca^{2+} concentration decreased the sorption affinity of the anions by 0.26 ± 0.05 log units. This was mainly explained as a reduced electrostatic repulsion at lower salinity.

Perfluorinated anions have been studied in sorption experiments too, but mostly with natural soils of widely different compositions and in various solution chemistries. As a result, widely ranging sorption values have been derived, and it is often not clear whether K_{OC} values can be obtained from such data because other soil components may have contributed to the sorption processes [47]. Campos Pereira et al. made a systematic summary of both literature reviews and own spiked experiments, taking the effect of solution chemistry on the net charge of OM into account [48]. Only in 2019 was the dynamic column setup used to determine the K_{OC} for PFAS structures on micronized Pahokee peat, from a separate batch as used by Bronner and Goss. No linear trends were observed, however, between perfluorinated chain length and K_{OC}, with minimal differences between C_4 and C_6 compounds. Also remarkable is the minor difference between perfluorinated carboxylates and analogue sulfonates (log K_{OC} (PFOS) $-$ log K_{OC} (PFNA) $= 0.27$), whereas recent studies on phospholipid binding indicated a much larger difference (0.84 log units). This may reflect to the smaller effect of the hydration shell surrounding the charged anion group in binding to organic matter compared to that in phospholipids.

2.6 Relevant Sorbent Phases in Soils for Organic Cations

As discussed above, organic anions may be electrostatically attracted to positively charged surfaces such as mineral oxides and may coordinate to acidic sites on soil organic matter via (-)CAHB. Black carbon phases such as soot particles and biochar may also preferentially (ad)sorb acids in soils [49]. There is still no good model to distinguish between the sorption components in soil for organic acids.

For organic cations, a systematic sorption dataset has been established on three clay minerals, obtained in the same dynamic column sorption setup as used for micronized peat [50]. Similar effects of ionic strength were observed as for peat, indicating similar effects of dissolved ions on the surface charge, which induces electrostatic attraction. Differences between kaolinite (1:1), illite (2:1, non-expanding), and montmorillonite (2:1, expanding) clays could be reduced to within a factor of 3 when sorption coefficients are normalized to their CEC (log $K_{\mathrm{clay,cec}}$). Apparently, the type of surface charge site does not make a large difference for sorption to these different clays. Ideal for modeling purposes, the log K_{OC} of organic cations to Pahokee peat, normalized to the CEC of peat, is within a factor of 10 of log $K_{\mathrm{clay,cec}}$ for many organic cations. The polar amide moiety next to a phenyl ring reduced the clay sorption coefficient by 11.5 log units compared to a V_xNAi approach derived for clay, which compares well to the -1.4 log units for peat discussed above. Particular differences were observed however, in how the nonionic part and ionic group of organic cations influence sorption to clay relative to that in peat. For example, quaternary ammonium cations sorbed relatively more strongly to clays than to peat, while primary amines preferentially sorbed to peat compared to clays.

As a result of specific factors influencing sorption of organic cations to clay minerals and soil organic matter, these two sorbent phases should be accounted for separately in a soil sorption model. Droge and Goss [51] suggested a simple summed contribution model, based on the soil CEC and fraction organic matter to define the key soil parameters and the sorption affinities to reference organic matter (Pahokee peat) and reference clay (e.g., illite):

$$\mathrm{Log}\ K_d(\mathrm{soil}) = \log\ K_{\mathrm{OC,cation}} \cdot f_{\mathrm{oc}} + \log\ K_{\mathrm{clay,cec}} \cdot \mathrm{CEC}_{\mathrm{clay}} \tag{15}$$

where $\mathrm{CEC}_{\mathrm{clay}}$ represents the contribution of clay minerals to the soil CEC ($\mathrm{CEC}_{\mathrm{soil}}$), which is derived according to:

$$\begin{aligned}\mathrm{CEC}_{\mathrm{clay}} &= \mathrm{CEC}_{\mathrm{soil}} - \left(f_{\mathrm{OC,soil}} \cdot f_{\mathrm{OC,SOM}} \cdot \mathrm{CEC}_{\mathrm{SOM}}\right) \\ &= \mathrm{CEC}_{\mathrm{soil}} - \left(f_{\mathrm{OC,soil}} \cdot 3.4\right)\end{aligned} \tag{16}$$

in which $f_{\mathrm{OC,soil}}$ has units kg OC/kg dry soil, $\mathrm{CEC}_{\mathrm{SOM}}$ is fixed at ~2 $\mathrm{mol_C}$/kg organic matter [52], and $f_{\mathrm{OC,SOM}}$ is fixed at the standard 1.7 kg organic matter/kg OC conversion factor [53]). The practical approach of this model is twofold: (1) it applies soil parameters for which standardized protocols exist already and which are well reported soil properties, and (2) it requires independently measured sorption coefficients on reference soil components, which can be further standardized. Jolin et al. [42] found that the value of 3.4 $\mathrm{mol_C}$/kg organic carbon may be somewhat high for typical soil organic matter types other than peat and suggested a value of 1.75 $\mathrm{mol_C}$/kg which provided a better fit to their set of soil sorption coefficients according to Eqs. (15) and (16). Still, Droge and Goss cross-validated the model of Eqs. (15) and (16) on two natural reference soils, one enriched in clay ($\mathrm{CEC}_{\mathrm{clay}} = 85\%$ of $\mathrm{CEC}_{\mathrm{soil}}$) and one enriched more in organic matter ($\mathrm{CEC}_{\mathrm{clay}} = 4\%$ of $\mathrm{CEC}_{\mathrm{soil}}$) [51]. Again, using the dynamic column setup, soil sorption coefficients were determined in controlled aqueous conditions, for a set of ~ 30 organic cations for which sorption coefficients on reference SOM and clay were determined. In the OM-enriched soil, sorption coefficients were explained by the f_{OC} and reference SOM log K_{OC} within 0.4 log units. In the clay-enriched soil, however, soil sorption coefficients were underestimated by a factor of 10–1,000 for most chemicals when only using f_{OC} and reference SOM log K_{OC}. However, when including the $\mathrm{CEC}_{\mathrm{clay}}$ approach and reference log $K_{\mathrm{clay,cec}}$ values, nearly all soil sorption coefficients were predicted within a factor ±3.

The $\mathrm{CEC}_{\mathrm{clay}}$ approach is obviously a simplified model compared to the heterogeneous complexity of natural soils, where organic matter and clay minerals are also closely interacting. Nonetheless, it delivers adequate predictions that do take into account that organic cations bind to different surfaces, governed by surface-specific interaction rules. The V_xNAi model is obviously less effective in accurately predicting sorption affinities to natural soils than using experimental sorption coefficients to reference soil components but still provides a more realistic alternative compared to octanol-water-based approaches.

An evaluation of Eqs. (15) and (16) on 30 soils from across the USA covering six different classes of soils [54] confirms the strong contribution of the clay fraction to the total soil CEC. Binding to clay, therefore, will play a dominant role in the overall soil sorption affinity of organic cations. This leads to important insights in dealing with the soil sorption affinities of (strong) bases:

1. Deriving K_{OC} values for organic cations from soil sorption data will lead to strongly overestimated binding affinities to organic matter (e.g., in comparisons with sewage sludge)
2. Applying only the sorption affinities of organic cations to organic matter (or organic matter-enriched sorbent such as sewage sludge) can potentially result in substantive underestimation of the sorption affinities of organic cations to soils.

It is important to note that as an alternative to the V_xNAi model, the K_{OC} for a largely protonated basic IOC in soil could be derived as a proxy from sewage sludge sorption data [55, 56]. A first estimation of the sorption affinity to clay would be a similar sorption affinity between clay and OM normalized by CEC. Finally, the impact of Al^{3+} on both electrostatic attraction and competitive interaction in acidic soils may be stronger than that of Ca^{2+} and may lead to further refinement of K_d predictions [42].

2.7 *Sorption of Amphoteric IOCs*

Amphoteric pesticides (e.g., imidazolinones) typically exhibit a behavior that combines the processes previously described for acids and bases. A number of general rules can thus be drawn. For instance, sorption of amphoteric pesticides is generally positively influenced by organic carbon content and clay content (or CEC) and negatively influenced by pH [57]. In general, compounds with protonated basic functional groups at pH relevant to the environment strongly sorb to environmental matrices, due to strong electrostatic attractions (consistent with Fig. 10).

Nevertheless, zwitterions tend to be complex molecules and may also interact through mechanisms that cannot be extrapolated to other molecules. A remarkable example is that of the herbicide glyphosate, whose phosphonate group can bind directly to oxides through ligand exchange, resulting in the formation of inner sphere complexes [57]. A detailed study on the interactions between ciprofloxacin and soil and peat and aquatic humic substances also illustrates the variety and complexity of interactions that zwitterions may engage with environmental matrices [58]. Given the limited availability of datasets to build regression and/or fragment-based models, it is thus recommended to proceed on a case by case evaluation for those compounds on which positive and negative charges may coexist at environmentally relevant pH. The small set of perfluorinated betaines [41] provides some experimental data on the effect of speciation on K_{OC} but needs to be evaluated in more detail.

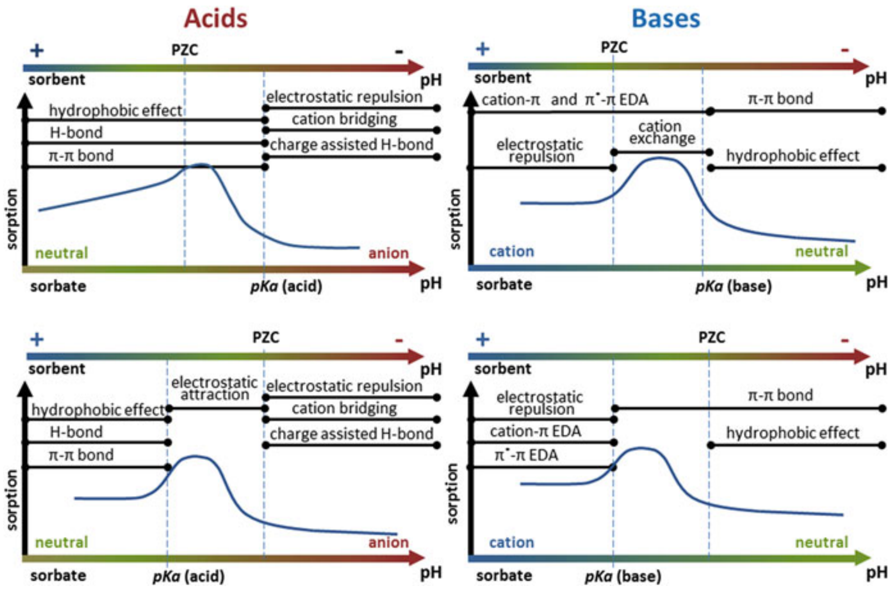


Fig. 10 Sorptive interactions governing the sorption processes of acids and bases in different pH ranges, under a situation with either the solute pK_a above the sorbent PZC (top row) or with the solute pK_a below the sorbent PZC (bottom row). Negative charge is red, positive charge is blue, neutral is green. The *X*-axis displays the sorbate speciation; the sorbent speciation is the arrow above. Adapted from a figure presented in [49]

Kah et al. [49] have reviewed the sorption processes of IOCs to various carbonaceous surfaces and provided an schematic overview of the governing sorptive processes for each IOC type in relation to its speciation properties (pK_a) relative to the speciation of the sorbent surface (pH where the surface has a point of zero charge (PZC), i.e., positive at lower pH, negative at higher pH). As, for example, shown in Fig. 10, an acid with a pK_a above the PZC is only dissociated when the surface is negative, while an acid with a pK_a below the PZC is partly negative while the surface is still positive. This overview sketches the summarized findings of this chapter on IOCs: neutral acids sorb more strongly than their corresponding dissociated anions on negatively charged sorbents, while neutral bases may sorb more weakly than their corresponding protonated cations on negatively charged sorbents. There are multiple scenarios possible to describe amphoteric chemicals that relate to the relative positions of the basic pK_a and acidic pK_a and the PZC of the sorbent. Typically, sorption of amphoteric compounds has a maximum near the neutral sorbent PZC.

Box 1 Assumptions in the NICA-Donnan Sorption Model for Organic Ions [38]

The higher cation concentration in the aqueous Donnan phase ($C_{i,D}$) compared to bulk medium phase ($C_{i,B}$) is thus not related to sorption to specific sites but is due to "indifferent accumulation." The difference in ion concentrations results in a Donnan potential (ψ_D). This potential ψ_D quantitatively accounts for the electrostatic attraction of all cations from bulk solution to the Donnan volume. The concentration ratio between Donnan phase and bulk phase is quantified by the Boltzmann factor (B) [59],

$$B = C_{i,D}/C_{i,B} = \exp\left(\frac{-z_i F\psi_D}{RT}\right) = \exp\left(\frac{-z_i e\psi_D}{kT}\right) \tag{17}$$

where z_i is the valency of the cation, F the Faraday constant, R the gas constant, and T the absolute temperature.

The first important assumption in the NICA-Donnan model approach is that the aqueous Donnan phase volume V_D depends on ionic strength (I, mol/L), which in a simplified form can be described by an empirical constant b [24, 34]:

$$\mathrm{Log} V_D = b(1 - \log I) - 1 \tag{18}$$

Maintaining electroneutrality requires that the enhanced cation concentration equals the charge density of the organic matter Q (mol charge/kg) in V_D (in L) [34, 36]:

$$Q/V_D = -\sum z_i(C_{i,D} - C_{i,B}) = -\sum z_i(B \cdot C_{i,B} - C_{i,B}) \tag{19}$$

By incorporating Eq. (17) in Eq. (19), ψ_D can be determined via $C_{i,B}$ and V_D, if Q and b are known (e.g., listed in Milne et al. [24] for humic acids). B can then be derived to calculate concentrations in the Donnan phase for each test condition. Note that Q depends on the number of unbound sorption sites, and therefore the Donnan potential ψ_D changes with higher specifically sorbed ion concentrations. Sorbed organic cation concentration on HS can then be replotted against $C_{i,D}$ instead of $C_{i,B}$. Such plots should explicitly reflect the specific ion binding, while the electrostatic effect caused by background salts is omitted.

Since V_D is related to b, $C_{i,D}$ is also dependent on b. Therefore, by adjusting b, the sorption isotherms obtained at different salt concentrations would merge to one "master curve" (MC) if the salt ions do not bind specifically to AHA [36, 60].

(continued)

Box 1 (continued)

The second important assumption in the NICA-Donnan model approach is that inorganic monovalent cations, except protons, do not bind specifically to ion exchange sites but only balance electroneutrality and thereby influence the Donnan potential (ψ_D).

In study of Chen et al. [38] with the cationic surfactant C_{12}-benzalkonium, the Donnan approach enables the isotherms measured at 5, 50, and 500 mM Na^+ successfully merging into one MC (Fig. 4 in Chen et al. [38]), resulting in an ion-specific log K_F (4.15 ± 0.05) where b is exclusively set to 0.59. The b is typically around 0.5 based on proton binding studies for different HA [24], but the fitted value agrees well with the value (0.63) obtained in the study using the same purified AHA as in this work [60]. The effect of Na^+ we observe on sorption of C12-BAC is thus only the result of variable electrostatic attraction, and just fitting a single b value (which corresponds to earlier findings for AHA) can explain this effect of Na^+.

One of the weak points of the second assumption in relation to tests with organic cations is that it does not explain why the sorption of organic cation clarithromycin to HA was more efficiently reduced for in solutions of K^+ compared to equal concentrations of Na^+ [16]. Such differences between the effect of various monovalent cations on sorption of organic cations were also found for polymers [61, 62], which suggests that specific sorption of some monovalent ions may not be negligible.

The third important assumption in the NICA-Donnan model approach is that divalent/multivalent cations and protons have a sufficiently high sorption affinity to both carboxylic groups on HS to compete with cationic surfactants, which is described with the non-ideal competitive ion binding (NICA) term. Monovalent organic cations appear to sorb much more strongly than most monovalent inorganic cations [63, 64], as a result of which organic cations also bind specifically to negatively charged sites in humic acids. The sorption affinity of organic compounds can therefore be regarded as the product of the (Boltzmann factor)$*$(intrinsic sorption coefficient), where the intrinsic sorption coefficient is influenced by the concentration of competing ions.

Most sorption studies that wanted to understand the specific sorption affinities of divalent metals and apply NICA-Donnan have all tested under high background monovalent electrolyte concentrations, so that ionic strength was always constant and therefore also the Boltzmann factor was constant. In the study design of Chen et al. [38], Ca^{2+} influences both the electrostatic (Donnan) effect and the competition effect. The Donnan approach does not attain the same MC at different Ca^{2+} concentration using the same b, as shown in Fig. S5 of Chen et al. [38]. This is likely the reason why the MC for the Ca^{2+} data is lower than the MC for Na^+ data. The difficulty when applying the NICA-Donnan model for Ca^{2+} data is that Boltzmann factors are different for

(continued)

Box 1 (continued)

each different medium composition, which also affects the sorbed H^+ concentrations. However, different Boltzmann factors appeared to have only a minor influence when determining the Donnan parameter b with the Na^+ data, but it complicates calculations with the calcium data. This requires that the full NICA-Donnan is run for Ca^{2+} data, not only the Donnan model, which can be readily done with ECOSAT software.

A fourth important NICA-Donnan assumption is that sorption, and therefore also competition, occurs at two collections of sorption sites in HA: carboxylic acids and phenolic acids, which have a specific affinity distribution. At pH 6 and pH 3, however, phenyl groups are almost fully protonated and therefore hardly matters for cation binding in the test system of Chen et al. [38]. Thus, for a system at pH 6, the NICA equation [36] was simplified to include only carboxylic acids and considers specific sorption of H^+, cationic surfactant, and Ca^{2+}, namely

$$Q_i = \frac{n_i}{n_H} \cdot Q_{\max,H} \cdot \frac{\left(\overline{K}_i \cdot C_{i,D}\right)^{ni}}{\sum_i \left(\overline{K}_i \cdot C_{i,D}\right)^{ni}} \cdot \frac{\left[\sum_i \left(\overline{K}_i \cdot C_{i,D}\right)^{ni}\right]^p}{1 + \left[\sum_i \left(\overline{K}_i \cdot C_{i,D}\right)^{ni}\right]^p} \tag{20}$$

where K_i is the median value for the “intrinsic” sorption coefficient for ion i to carboxylic acids (based on $C_{i,D}$, following from the MC); n_i the stoichiometry index of i, relative to n_H for protons; $Q_{\max,H}$ (Q in equation the total number of reference sorption sites; and p is the width of the affinity distribution for carboxylic acids for a specific HS, thereby accounting for sorption site heterogeneity.

The first quotient at the right-hand side defines the maximum ion exchange capacity of i, the second quotient is the fraction of covered sites occupied with i, and the third quotient indicates the total number of sites bound to an ion.

References

1. Goss KU, Schwarzenbach RP (2001) Linear free energy relationships used to evaluate equilibrium partitioning of organic compounds. Environ Sci Technol 35(1):1–9
2. Bronner G, Goss KU (2011) Predicting sorption of pesticides and other multifunctional organic chemicals to soil organic carbon. Environ Sci Technol 45(4):1313–1319
3. Bronner G, Goss KU (2011) Sorption of organic chemicals to soil organic matter: influence of soil variability and pH dependence. Environ Sci Technol 45(4):1307–1312
4. Weber EJ, Spidle DL, Thorn KA (1996) Covalent binding of aniline to humic substances. 1. Kinetic studies. Environ Sci Technol 30(9):2755–2763

5. Lee LS, Nyman AK, Li H et al (1997) Initial sorption of aromatic amines to surface soils. Environ Toxicol Chem 16(8):1575–1582
6. Droge STJ, Yarza-Irusta L, Hermens JLM (2009) Modeling nonlinear sorption of alcohol ethoxylates to sediment: the influence of molecular structure and sediment properties. Environ Sci Technol 43(15):5712–5718
7. Karickhoff SW (1981) Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10:833–846
8. Droge STJ, Paumen ML, Bleeker EAJ et al (2006) Chronic toxicity of polycyclic aromatic compounds to the springtail *Folsomia candida* and the enchytraeid *Enchytraeus crypticus*. Environ Toxicol Chem 25(9):2423–2431
9. Schenzel J, Goss KU, Bucheli T et al (2012) Experimentally determined soil organic matter-water sorption coefficients for different classes of natural toxins and comparison with estimated numbers. Environ Sci Technol 46:6118–6126
10. Abraham MH (1993) Hydrogen-bonding. 31. Construction of a scale of solute effective or summation hydrogen-bond basicity. J Phys Org Chem 6(12):660–684
11. Endo S, Goss KU (2014) Applications of polyparameter linear free energy relationships in environmental chemistry. Environ Sci Technol 48(21):12477–12491
12. Stenzel A, Goss KU, Endo S (2013) Experimental determination of polyparameter linear free energy relationship (pp-LFER) substance descriptors for pesticides and other contaminants: new measurements and recommendations. Environ Sci Technol 47(24):14204–14214
13. Stenzel A, Endo S, Goss KU (2012) Measurements and predictions of hexadecane/air partition coefficients for 387 environmentally relevant compounds. J Chromatogr A 1220:132–142
14. Ulrich N, Endo S, Brown TN et al (2017) UFZ-LSER database v 3.2.1 [Internet], Leipzig, Germany, Helmholtz Centre for Environmental Research-UFZ. http://www.ufz.de/lserd. Accessed 30 Nov 2018
15. Droge STJ, Goss KU (2012) Effect of sodium and calcium cations on the ion-exchange affinity of organic cations for soil organic matter. Environ Sci Technol 46(11):5894–5901
16. Sibley SD, Pedersen JA (2008) Interaction of the macrolide antimicrobial clarithromycin with dissolved humic acid. Environ Sci Technol 42(2):422–428
17. Karthikeyan KG, Chorover J (2002) Humic acid complexation of basic and neutral polycyclic aromatic compounds. Chemosphere 48(9):955–964
18. Franco A, Ferranti A, Davidsen C et al (2010) An unexpected challenge: ionizable compounds in the REACH chemical space. Int J Life Cycle Assessm 15(4):321–325
19. Arp HPH, Brown TN, Berger U et al (2017) Ranking REACH registered neutral, ionizable and ionic organic chemicals based on their aquatic persistency and mobility. Environ Sci Process Impacts 19(7):939–955
20. Manallack DT (2007) The pK_a distribution of drugs: application to drug discovery. Persp Med Chem 1:25–38
21. Manallack DT, Prankerd RJ, Yuriev E et al (2013) The significance of acid/base properties in drug discovery. Chem Soc Rev 42(2):485–496
22. Gouin T, Van Egmond R, Price OR et al (2012) Prioritising chemicals used in personal care products in China for environmental risk assessment: application of the RAIDAR model. Environ Pollut 165:208–214
23. European Centre for Ecotoxicology and Toxicology of Chemicals (2014). Environmental risk assessment of ionisable compounds. Technical Report 123. ECETOC AISBL, Brussels, Belgium
24. Milne CJ, Kinniburgh DG, Tipping E (2001) Generic NICA-Donnan model parameters for proton binding by humic substances. Environ Sci Technol 35(10):2049–2059
25. Gan Y, Franks GV (2006) Charging behavior of the gibbsite basal (001) surface in NaCl solution investigated by AFM colloidal probe technique. Langmuir 22(14):6087–6092
26. Tombácz E, Szekeres M (2006) Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite. Appl Clay Sci 34(1-4):105–124

27. Zeltner WA, Anderson MA (1988) Surface charge development at the goethite/aqueous solution interface: effects of CO2 adsorption. Langmuir 4(2):469–474
28. Yan M, Sun C, Dong J et al (2015) Electrochemical investigation on steel corrosion in iron-rich clay. Corros Sci 97:62–73
29. Liu Y, Alessi DS, Flynn SL et al (2018) Acid-base properties of kaolinite, montmorillonite and illite at marine ionic strength. Chem Geol 483:191–200
30. Westall JC, Chen H, Zhang WJ et al (1999) Sorption of linear alkylbenzenesulfonates on sediment materials. Environ Sci Technol 33(18):3110–3118
31. Higgins CP, Luthy RG (2006) Sorption of perfluorinated surfactants on sediments. Environ Sci Technol 40(23):7251–7256
32. Higgins CP, Luthy RG (2007) Modeling sorption of anionic surfactants onto sediment materials: an a priori approach for perfluoroalkyl surfactants and linear alkylbenzene sulfonates. Environ Sci Technol 41:3234–3261
33. Droge STJ (2016) Dealing with confounding pH-dependent surface charges in immobilized artificial membrane HPLC columns. Anal Chem 88(1):960–967
34. Kinniburgh DG, Van Riemsdijk WH, Koopal LK et al (1999) Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf A 151(1–2):147–166
35. Milne CJ, Kinniburgh DG, Van Riemsdijk WH et al (2003) Generic NICA-Donnan model parameters for metal-ion binding by humic substances. Environ Sci Technol 37(5):958–971
36. Koopal LK, Saito T, Pinheiro JP et al (2005) Ion binding to natural organic matter: general considerations and the NICA-Donnan model. Colloids Surf A 265(1–3):40–54
37. Tipping E (2002) Cation binding by humic substances. Cambridge University Press, Cambridge
38. Chen Y, Hermens JLM, Droge STJ (2013) Influence of organic matter type and medium composition on the sorption affinity of C12-benzalkonium cation. Environ Pollut 179:153–159
39. Tülp HC, Fenner K, Schwarzenbach RP et al (2009) pH-Dependent sorption of acidic organic chemicals to soil organic matter. Environ Sci Technol 43(24):9189–9195
40. Droge STJ, Goss KU (2013) Ion-exchange affinity of organic cations to natural organic matter: influence of amine type and nonionic interactions at two different pHs. Environ Sci Technol 47:798–806
41. Zhi Y, Liu J (2019) Column chromatography approach to determine mobility of fluorotelomer sulfonates and polyfluoroalkyl betaines. Sci Total Environ 683:480–488
42. Jolin WC, Goyetche R, Carter K et al (2017) Predicting organic cation sorption coefficients: accounting for competition from sorbed inorganic cations using a simple probe molecule. Environ Sci Technol 51(11):6193–6201
43. Kah M, Brown CD (2008) Log D: lipophilicity for ionisable compounds. Chemosphere 72 (10):1401–1408
44. Ni J, Pignatello JJ, Xing B (2011) Adsorption of aromatic carboxylate ions to black carbon (Biochar) is accompanied by proton exchange with water. Environ Sci Technol 45 (21):9240–9248
45. Li X, Pignatello JJ, Wang Y et al (2013) New insight into adsorption mechanism of ionizable compounds on carbon nanotubes. Environ Sci Technol 47(15):8334–8341
46. Ni J, Pignatello JJ (2018) Charge-assisted hydrogen bonding as a cohesive force in soil organic matter: water solubility enhancement by addition of simple carboxylic acids. Environ Sci Process Impacts 20(9):1225–1233
47. Li Y, Oliver DP, Kookana RS (2018) A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). Sci Total Environ 628–629:110–120
48. Campos Pereira H, Ullberg M, Kleja DB et al (2018) Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon – effect of cation composition and pH. Chemosphere 207:183–191
49. Kah M, Sigmund G, Xiao F et al (2017) Sorption of ionizable and ionic organic compounds to biochar, activated carbon and other carbonaceous materials. Water Res 124:673–692

50. Droge STJ, Goss KU (2013) Sorption of organic cations to phyllosilicate clay minerals: CEC-normalization, salt dependency, and the role of electrostatic and hydrophobic effects. Environ Sci Technol 47(24):14224–14232
51. Droge STJ, Goss KU (2013) Development and evaluation of a new sorption model for organic cations in soil: contributions from organic matter and clay minerals. Environ Sci Technol 47 (24):14233–14241
52. Lyon WG (1995) Swelling of peats in liquid methyl, tetramethylene and propyl sulfoxides and in liquid propyl sulfone. Environ Toxicol Chem 14(2):229–236
53. Hallsworth EG, Wilkinson GK (1958) The contribution of clay and organic matter to the cation exchange capacity of the soil. J Agr Sci 51(1):1–3
54. Carrasquillo AJ, Bruland GL, Mackay AA et al (2008) Sorption of ciprofloxacin and oxytetracycline zwitterions to soils and soil minerals: influence of compound structure. Environ Sci Technol 42(20):7634–7642
55. Gulde R, Helbling DE, Scheidegger A et al (2014) PH-dependent biotransformation of ionizable organic micropollutants in activated sludge. Environ Sci Technol 48(23):13760–13768
56. Hyland KC, Dickenson ERV, Drewes JE et al (2012) Sorption of ionized and neutral emerging trace organic compounds onto activated sludge from different wastewater treatment configurations. Water Res 46(6):1958–1968
57. Kah M, Brown CD (2006) Adsorption of ionizable pesticides in soils. In: Anonymous reviews of environmental contamination and toxicology. Springer, New York, pp 149–217
58. Aristilde L, Sposito G (2013) Complexes of the antimicrobial ciprofloxacin with soil, peat, and aquatic humic substances. Environ Toxicol Chem 32(7):1467–1478
59. Kinniburgh DG, Milne CJ, Benedetti MF et al (1996) Metal ion binding by humic acid: application of the NICA-Donnan model. Environ Sci Technol 30(5):1687–1698
60. Ishiguro M, Koopal LK (2011) Predictive model of cationic surfactant binding to humic substances. Colloids Surf A 379(1-3):70–78
61. Murakami F (1980) Quantitative structure-retention relationships in cation-exchange chromatography. J Chromatogr A 198(3):241
62. Bauerlein PS, Ter Laak TL, Hofman-Caris RCHM et al (2012) Removal of charged micropollutants from water by ion-exchange polymers – effects of competing electrolytes. Water Res 46(16):5009–5018
63. Polubesova T, Nir S (1999) Modeling of organic and inorganic cation sorption by illite. Clays Clay Miner 47(3):366–374
64. Gondar D, López R, Antelo J et al (2012) Adsorption of paraquat on soil organic matter: effect of exchangeable cations and dissolved organic carbon. J Hazard Mater 235–236:218–223