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Benzalkonium ion sorption to peat and clays: Relative contributions of ion exchange and van der Waals interactions

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HIGHLIGHTS

- Sorption behavior of benzalkoniums was studied at environmental concentrations.
- Ion exchange is the main mechanism responsible for sorption to soils.
- Magnitude of the solvation energy is corelated to free energy of sorption.
- Sorption of benzalkonium ions to soils was predicted using a simple model.

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ABSTRACT

Due to their use in various domestic and industrial formulations, benzalkonium compounds have been isolated in many environmental matrices. Sorption to soil components has been shown to play a key role in their environmental fate. Whereas sorption of benzalkonium compounds to soils is attributed to cation exchange and van der Waals forces, the relative contributions of these two mechanisms at environmental levels have not been clearly defined. In this study a previously reported algal toxicity assay-based method was employed to determine the distribution coefficients (K_d) of benzalkonium compounds between water and soil components, at environmental concentrations. Cation exchange capacity corrected K_d values for organic matter and clays were all within one order of magnitude. This implies that ion exchange is the dominant mechanism of sorption for benzalkonium compounds. When the sorption data were used to compute sorption energies for four homologues of benzalkonium ions, the magnitude of the free energy change of sorption increased with size of the molecule. The increase in sorption energy could be partly explained by increased energy of hydration with addition of methylene groups to the alkyl chain. A model that predicts sorption coefficients of benzalkonium compounds to soils using organic carbon content and cation exchange capacity was also defined. When tested using an artificial soil, the model estimates were all within one order of magnitude of the experimental values.

1. Introduction

Benzalkonium compounds are widely used as an active ingredient in both domestic and industrial biocides (Flores et al., 2017; Khan et al., 2018; Sütterlin et al., 2008). They have also been traditionally added to detergents formulations and to fabric softeners as antistatics (Ruan et al., 2014; Zhang et al., 2015). In the medical and cosmetic sectors, they are part of formulations as excipients and preservatives (Choi et al., 2018; Lukáč et al., 2013; Sütterlin et al., 2007). Most of these uses result in benzalkonium ions being channeled through either the sewer system to sewage treatment plants or the storm drain. Although benzalkoniums are potentially biodegradable under aerobic conditions (Oh et al., 2014; Tezel and Pavlostathis, 2015), most sewage treatment plants do not effectively remove these compounds from wastewater and sewage sludge (Khan et al., 2017a; Zhang et al., 2011). As a result, benzalkonium ions have been reported to occur in marine sediment (Dai et al., 2018; Li et al., 2018), seawater and river sediment (Li et al., 2014). Kang and Shin (2016) reported total benzalkonium concentrations of up to 28 mg kg^{-1} in soil near cattle farms associated with

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the use of benzalkonium containing antibacterials and antifungal formulations.

Since benzalkonium compounds are surfactants and intrinsically biocidal, they present a risk to both aquatic and terrestrial organisms. The 48 h LC_{50} for *Daphnia magna* was reported to be 38 μg L^{-1}, and the lowest adverse effect level causing DNA damage was reported to be as low as 0.4 ng L^{-1} (Lavorgna et al., 2016). Sütterlin et al. (2008) studied growth inhibition by benzalkonium in *Pseudomonas putida* and *Aliivibrio fischeri* and reported EC_{50} values of 6.0 and 0.5 mg L^{-1} respectively. In another study, benzalkoniums showed acute adverse effects on *Danio rerio* and *Caenorhabditis elegans* at concentrations ranging between 0.05 and 5.0 mg L^{-1} (Sreevidya et al., 2018). From these studies, it is apparent that benzalkoniums are highly toxic to a number of organisms. It is therefore important to understand their environmental fate so as to facilitate scientifically-sound ecological risk assessment.

The environmental fate of benzalkonium compounds has been shown to be largely dependent on their sorption to sewage sludge, soils and sediments (Ferrer and Furlong, 2002; Flores et al., 2017; García et al., 1999; Khan et al., 2017b; Sütterlin et al., 2007). They are known to sorb to negatively charged surfaces through ionic interactions and also to nonpolar organic surfaces through van der Waals interactions (Ishiguro and Koopal, 2016). Sorption to sewage sludge has been shown to be a key factor affecting benzalkonium ion removal in sewage treatment plants (Zhang et al., 2011). Therefore, benzalkonium ions can be passed onto soils with the sewage sludge application on agricultural land.

Although several studies have reported on the sorption of benzalkonium ions to clays and other soil components, no widely accepted model is available for sorption at environmental concentrations. This is due to the fact that most studies were done at very high loading rates which are unlikely to occur in environmental samples. Sorption isotherms generated at such concentrations are not representative of partitioning behavior in the environment (Chen et al., 2013; Endo et al., 2009; Zanini et al., 2013). Of those models developed using concentrations comparable to environmental conditions, authors studied low-molecular-weight homologues which are not normally found in the environment (Droge and Goss, 2013a; Jolin et al., 2017). Thus, there is a need for models that can sufficiently describe the sorption of benzalkoniums with longer alkyl chains at environmentally relevant concentrations.

The aim of this study was to estimate the relative contributions of ion exchange and van der Waals interactions on sorption and then describe a simple model for the sorption of benzalkonium compounds to soils based on soil properties. An algal bioassay-based method described by Ndabambi and Kwon (2019) was applied to determine distribution coefficients (K_d) of benzalkoniums between water and soil components. The data were then used to calibrate separate models for sorption to organic matter and clays using the length of the alkyl chain and cation exchange capacity (CEC) of the soil as the only descriptors. The two models were combined to determine sorption of benzalkonium compounds to soils when the organic carbon content and CEC are known. The model was successfully tested on artificial soil.

2. Materials and methods

2.1. Materials

The sorbents used in this study were kaolinite (Fischer Scientific, Loughborough, United Kingdom), sodium montmorillonite (Sigma-Aldrich, St. Louis, MO, USA) and peat moss obtained from Lambert Peat Moss Inc. (Rivière-Ouelle, Canada). The peat moss was dried in an oven at 110 °C then pulverized in a blender and passed through a 74 μm analytical sieve. Kaolinite and montmorillonite were used as received from the suppliers.

The test chemicals, benzyldimethyloctylammonium chloride (BAC8), benzyldimethyldecylammonium chloride (BAC10), benzyldimethyldodecylammonium chloride (BAC12) and benzyldimethyltetradecylammonium chloride (BAC14) were purchased from Sigma-Aldrich. The test organism, *Pseudokirchneriella subcapitata* (strain number 278/4), was supplied by the Culture Collection of Algae and Protozoa in Oban, Scotland. Chemicals used to formulate culture media were also supplied by Sigma-Aldrich.

2.2. Methods

2.2.1. Formulation of artificial soil

Artificial soil (AS-1) was formulated by mixing kaolin clay and peat moss at a ratio of 90:10 respectively. Although standard methods (ASTM-International, 2002) recommend the addition of sand when formulating artificial soils, AS-1 was formulated without sand because sand does not make a significant contribution to sorption. Also, because sand is denser than kaolin and peat, higher shaking speeds would be required to keep sand from settling to the bottom of the flask. Changing the energy supplied by shaking would alter the algal growth rate, making comparisons with the earlier experiments difficult.

2.2.2. Determination of cation exchange capacity

Due to the dependence of CEC on pH, the ammonium acetate method (Tan, 2005) was adapted to determine the cationic exchange capacity of the sorbents at pH 8.10; which was the pH of the algal growth medium used for sorption tests. Sorbents were weighed in 50 mL centrifuge tubes and shaken in the displacing solution for an hour, then kept in an incubator at 25 °C overnight. The displacing solution was removed by centrifugation at 10,000×*g* for 10 min. The residue was then washed three times with 95% ethanol. After washing, the residue was collected and leached thrice with 1.0 M potassium chloride. The leachates were combined, and the concentration of ammonium ions determined using the salicylate-hypochlorite method (Tan, 2005). The chromophore was quantified at 650 nm using an Optizen POP™ UV/vis spectrophotometer (Mecasys Co., Daejeon, Republic of Korea).

2.2.3. Determination of distribution coefficients

A standardized algal growth inhibition assay (OECD, 2011) was used to determine distribution of benzalkonium ions between soil components and aqueous medium. The culture medium was formulated as specified in the OECD (2011) guideline. Details on preparation procedure and the media composition were as described by Ndabambi and Kwon (2019). Algal cultures were maintained in glass conical flasks in a shaking incubator (120 rpm) at 25 °C. A light-emitting-diode lamp yielding 3000 lx was used to provide continuous lighting during culturing and the growth inhibition tests.

Growth inhibition tests were conducted in OECD media or in media containing either peat moss, clay minerals or a mixture of both. The pH of the medium was 8.1 ± 0.1. The sorbent concentration was set so as to achieve at least 80% sorption. Concentrations of kaolinite and that of the artificial soil were set at 0.40 g L^{-1} whilst montmorillonite and peat were set at 0.10 g L^{-1} each. The growth inhibition data were fitted to a four-parameter logistic model using the *drc* package in R software (Ritz et al., 2015).

3. Theory

3.1. Calculation of distribution coefficients

Distribution coefficients were calculated by dividing the sorbed concentration by the free concentration. The amount sorbed to soil components was computed as the difference between the median inhibitory concentration from OECD media ($EC_{50(\text{ref})}$) and that obtained in media supplemented with soil components ($EC_{50(\text{soil})}$) as shown in equation (1).

$$A_{sorbed} = V\left(\text{EC}_{50(\text{soil})} - \text{EC}_{50(\text{ref})}\right) \tag{1}$$

where A_{sorbed} is the amount sorbed to soil components and V is the volume of the culture medium.

To calculate the free concentration, it is necessary to account for benzalkonium ions sorbed to algal lipids. In a growing algal culture, this can be achieved by employing a toxicokinetic model for baseline toxicity (equation (2)). Details of the derivation of this model have been previously described (Ndabambi and Kwon, 2019).

$$K_d = \frac{k_u}{k_g + k_d}\frac{C_{soil}}{C_o}\left[1 - exp\left(-\left(k_g + k_d\right)t\right)\right] \tag{2}$$

where K_d is the soil water distribution coefficient in L kg^{-1}, C_{soil} is the concentration of sorbate on soil (μmol $\text{kg}^{-1}_{\text{soil}}$), C_o is the critical body burden for baseline toxicity in μmol $\text{kg}^{-1}_{\text{lipid}}$, k_u and k_d are the uptake (L $\text{kg}^{-1}_{\text{lipid}}\text{d}^{-1}$) and depuration ($\text{d}^{-1}$) rate constants respectively, k_g is the algal growth rate (d^{-1}) and t is time in days. The algal critical body burden for ionic organic compounds has been reported to be 1250 μmol $\text{kg}^{-1}_{\text{lipid}}$ (Bittermann and Goss, 2017). The uptake rate constant for algae (10^7 L $\text{kg}^{-1}_{\text{lipid}}$ d^{-1}) was adopted from a previous study (Kwon et al., 2016).

3.2. Calculation of free energy of sorption

The free energy change of sorption ($\Delta_{sorption}G$) can be calculated from sorption data using equation (3).

$$\Delta_{sorption}G = -RT \ln K_{therm} \tag{3}$$

where R is the ideal gas constant, T is the absolute temperature in K and K_{therm} is the thermodynamic equilibrium constant. K_{therm} can be calculated from the chemical activities of the sorbate in the sorbed (a_s) and aqueous (a_w) phases according to equation (4) (Zhou and Zhou, 2014):

$$K_{therm} = \frac{a_{i,\,s}}{a_{i,w}} \tag{4}$$

The activity of the sorbate in the aqueous phase was defined based on the sub-cooled liquid reference state. Since free concentrations in this study were in the micromole per liter range, well below the critical micelle concentrations of cationic surfactants (Aguiar et al., 2002; Nandni and Mahajan, 2013), the activity coefficient was assumed to be unity. Therefore, activity in the aqueous phase was calculated as:

$$a_{i,w} = xi \cong C_{i,w} \cdot V_w \tag{5}$$

where $C_{i,w}$ is the sorbate aqueous concentration in mol L^{-1} and V_w is the molar volume of water, 0.018 L mol^{-1}. For the sorbed phase, the reference state was defined as a saturated monolayer of organic cations. The activity of sorbed organic cations was calculated as:

$$a_{i,s} = \frac{C_{i,s}}{C_{i,\,s,max}} \tag{6}$$

where $C_{i,s}$ is the sorbed concentration in mol kg^{-1} and $C_{i,s,max}$ is the saturated monolayer sorbed concentration in mol kg^{-1}. Substituting activities in equation (4) using equations (5) and (6) gives:

$$K_{therm} = \frac{C_{i,s}}{C_{i,w} \bullet V_w \bullet C_{i,s,max}} \tag{7a}$$

Since $C_{i,s,max}$ is numerically equivalent to the sorbent's CEC, and the distribution coefficient, $K_\text{d} = C_{i,s}/C_{i,w}$, equation (6) can be written as:

$$K_{therm} = \frac{K_d}{V_w \bullet CEC} \tag{8}$$

Distribution coefficients computed from toxicity data were therefore, used to calculate the thermodynamic equilibrium constant according to equation (8).

4. Results and discussion

4.1. Algal growth inhibition test

The algal growth inhibition test was sensitive enough to allow determination of distribution coefficients at environmentally relevant concentrations. The dose-response curves are shown in Figs. S1–S3 in the Supplementary Material. Due to the higher sorption affinity of peat and montmorillonite—compared to kaolinite—these sorbents were used at a concentration of 0.10 g L^{-1}. This significantly reduced the scattering of light by suspended particles in the medium. Therefore, peat and montmorillonite showed only marginal reduction in algal growth rate; whilst a relatively higher reduction in growth rate was observed with kaolinite. This suggests that light scattering, not reduced bioavailability of cations, was the major cause for the reduction in growth rate.

4.2. Cation exchange capacity of sorbents

The sorbents in this study cover a range spanning three orders of magnitude. Of the three sorbents, peat had the highest CEC at 2.5 mol$_\text{c}$ kg^{-1}, followed by montmorillonite at 0.57 mol$_\text{c}$ kg^{-1} and kaolinite had the lowest value of 0.09 mol$_\text{c}$ kg^{-1}. These values are comparable with previously reported values where kaolinite clays were shown to have a CEC of 0.03–0.2 mol$_\text{c}$ kg^{-1} (Ma and Eggleton, 1999) and Canadian peats had a CEC value of about 1.25 mol$_\text{c}$ kg^{-1} (Lyon, 1995). For the artificial soil, CEC was measured to be 0.34 mol$_\text{c}$ kg^{-1}. This value was comparable to that of standard soils like the Eurosoils used in other studies (Droge and Goss, 2013a; Thomas et al., 2009). The wide range of CEC values covered by the sorbents made it possible to investigate the dependence of distribution coefficients on CEC.

4.3. Determination of distribution coefficients

The K_d values were calculated using equation (2) and the data are presented in Table 1. Sorption to clays and peat accounted for over 70% decrease in the initially spiked amount. The sorbed concentrations ranged between 20 μg kg^{-1} in the artificial soil to about 130 μg kg^{-1} for montmorillonite. These values are below or comparable to reported environmental concentrations of about 20 to 3,000 μg kg^{-1} in North American sediments (Ferrer and Furlong, 2002; Li and Brownawell, 2010), 960 μg kg^{-1} in Chinese sewage

Table 1
Distribution coefficients between water and different sorbents studied. C_{free} is the equilibrium concentration in the liquid phase (μmol L^{-1}) and K_d is the distribution coefficient (L kg^{-1}). Numbers in parenthesis are 95% confidence intervals.

Test compound	log C_{free}	log K_d (95% confidence interval)		
		Peat	Montmorillonite	Kaolinite[a]
BAC8	0.03	5.13 (5.06–5.19)	5.13 (5.03–5.20)	4.12 (3.81–4.30)
BAC10	−1.15	5.63 (5.57–5.68)	5.93 (5.90–5.97)	4.70 (4.59–4.79)
BAC12	−2.32	6.66 (6.61–6.71)	6.97 (6.94–6.99)	5.57 (5.48–5.65)
BAC14	−3.39	7.90 (7.82–7.96)	7.85 (7.84–7.87)	6.61 (6.55–6.66)

[a] Data from Ndabambi and Kwon (2019).

sludge (Ruan et al., 2014) and 1 to 28,000 μg kg^{-1} in Korean farmland soils (Kang and Shin, 2016). The calculated distribution coefficients are therefore within the environmentally applicable range.

The distribution coefficients increased with alkyl chain length from 8 to 14 carbon atoms (Table 1). On a weight basis, the distribution coefficients for peat and montmorillonite were similar, differing at most by only 0.3 log units. However, there is no apparent explanation why the K_ds were comparable. Organic matter is expected to sorb organic cations through both ionic interactions and van der Waals forces (Ishiguro and Koopal, 2016). This would result in a higher K_d for peat when compared with montmorillonite. Since K_ds for the two sorbents were comparable, the contribution of van der Waals forces to overall sorption seems to be negligible. Compared with kaolinite (Table 1), K_ds for peat and montmorillonite were at least one order of magnitude higher. The higher K_d for montmorillonite can be attributed to its specific surface area, typically one to two orders of magnitude larger than that of kaolinite (Schwarzenbach et al., 2016).

Unlike most studies that normalize K_ds of peat to organic carbon content (Droge and Goss, 2012; Endo et al., 2009; Tülp et al., 2009), K_ds are given on a weight basis in this study. Normalizing sorption to carbon content is often construed as depicting organic carbon as some kind of ‘hydrophobic solvent’ into which non-polar organic compounds are absorbed (Webster, 2014). Therefore, when the notation is used with organic cations it gives an inaccurate impression that van der Waals interactions between nonpolar components are the dominant mechanism behind the observed sorption. As has been previously postulated (Droge and Goss, 2013a; Ishiguro and Koopal, 2016; Zanini et al., 2013) and discussed in section 4.4—at environmentally relevant concentrations— van der Waals interactions do not play a significant role in organic cation sorption to peat.

4.4. Cationic exchange capacity corrected distribution coefficients

Assuming that at the concentration range studied, sorption mechanism was mainly due to charge-charge interactions between the benzalkonium ion and negative surface charges of sorbents, the distribution coefficients were normalized to the sorbents’ CEC. The CEC corrected distribution coefficients ($K_{d(CEC)}$; L mol_C^{-1}) are plotted against the number of carbon chains in the alkyl chain on Fig. 1. For all the four benzalkonium homologues studied, the CEC corrected distribution coefficients increased in the order peat < kaolinite < montmorillonite. The differences between peat and kaolinite were below 0.5 log units, whilst those between kaolinite and montmorillonite were all within 0.6 log units. This variation in CEC corrected K_ds, for clays, is comparable to what was reported by Droge and Goss (2013a) between the clay minerals kaolinite and illite. Whereas the difference between peat and montmorillonite was within one order of magnitude in this study, other studies on organic cations have reported differences of one to two log units (Droge and Goss, 2013b; Miao and Bi, 2018). The reason behind the lower K_d for organic matter is not obvious. One possible reason for lower CEC corrected K_d might be that not all cation exchange sites on peat are available for sorption of large organic cations. Especially, sorption to cation exchange sites that exist within micropores might be energetically less favorable due to hydrophobic exclusion of the organic cation, imposed by the surrounding anions. This might also be responsible for the unexpected results reported by Droge and Goss (2013c) where an increase in solution pH led to a decrease in sorption coefficients. Although they did not measure the CEC at the higher pH, it is expected to have been higher than at the lower pH due to additional dissociation of acidic groups. The additional dissociation increases the hydrophilicity of organic matter, making sorption of organic cations less favorable.

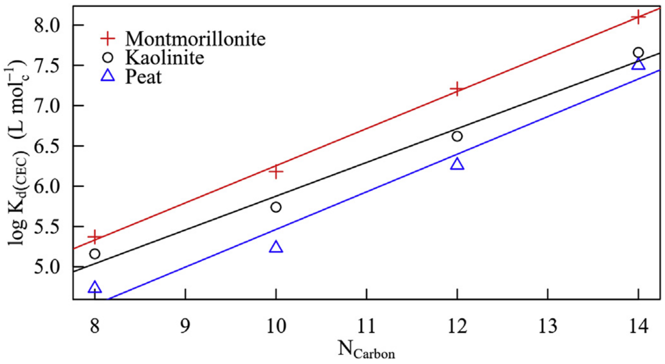

Fig. 1. CEC normalized distribution coefficients ($K_{d(CEC)}$, L mol_c^{-1}) plotted against the number of carbon atoms in the alkyl chain. Lines represent best-fits using linear regression ($r^2 > 0.97$).

4.5. Role of hydrophobicity in sorption

Studies have shown that sorption of organic cations to soil surfaces is due to either ion exchange or specific interactions with organic matter (Ishiguro and Koopal, 2016). For clays, sorption has been shown to be exclusively due to ion exchange for sorbed concentrations below 80% of the clay’s cation exchange capacity (Zanini et al., 2013). Above this level, sorption is due to van der Waals interactions between the nonpolar components of the organic cations—leading the formation of a double layer (de Paiva et al., 2008; Zanini et al., 2013). In the present study, however, sorbed concentrations were below 10% of the sorbent’s cation exchange capacity. Thus, sorption should be exclusively due to ionic interactions. Whereas it was expected that sorption to peat would be enhanced by van der Waals forces between the hydrophobic chains of organic cations and the nonpolar surfaces of peat, the experimental results do not show any evidence of such interactions. The sorption free energy for peat was comparable to that for montmorillonite (Fig. 2) where van der Waals interactions can be excluded as there are no organic surfaces. It is, therefore,

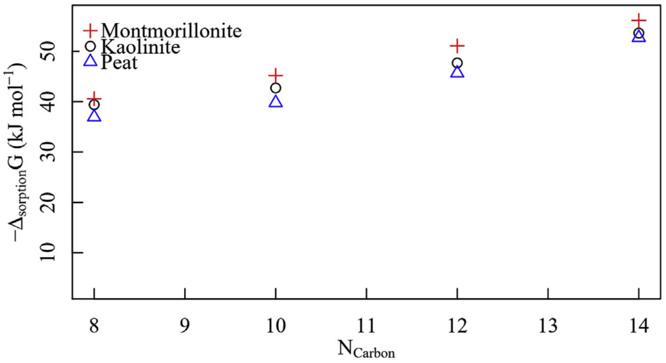

Fig. 2. Sorption energy increases with increase in alkyl chain. Accounting for alkyl chain hydrophobicity reduces the sorption free energy by at least 20 kJ mol^{-1} and changes the gradient from 2.5 to 1.8.

reasonable to conclude that even for soil organic matter, at environmentally relevant concentrations sorption is mainly due to ionic interactions.

Fig. 1 shows an increase in K_d with the carbon chain length of the sorbate. Since van der Waals interactions with the sorbent are negligible at the low loading rates used in this study, the observed effect can be attributed to hydrophobic exclusion of the benzalkonium ions from the aqueous phase. The higher excess free energy of hydrating larger organic ions makes their precipitation at the sorbent's surface more favorable (Elsherbiny et al., 2012; Kronberg et al., 1995; Teppen and Aggarwal, 2007; Wang et al., 1998). This phenomenon has also been described for monovalent alkali metal ions. Metal ion sorption coefficients to clays increase with ionic radius due to the lower hydration energies of the smaller metal ions (Lavikainen et al., 2015; Rotenberg et al., 2009; Teppen and Miller, 2005). Sorption of cesium to smectites has been shown to be endothermic but cesium can displace sodium from clays because of the more favorable hydration energy of sodium ions (Rotenberg et al., 2009).

For sorption of an organic cation to a negatively charged surface, $\Delta_{sorption}G$ is the sum of charge-charge interactions ($\Delta_{ionic}G$) and hydrophobic effects ($\Delta_{hydrophobic}G$) of the solute in the aqueous phase. The first term can be quantified by $zF\Psi$; where z is the charge of the ion, F is Faraday's constant and Ψ is the surface potential in volts (Schwarzenbach et al., 2016). $\Delta_{ionic}G$ will therefore, vary depending on the valency of the cation and the surface potential of the sorbent. The $\Delta_{hydrophobic}G$ is best described by the solute's free energy of hydration—defined from the ideal gas reference state (Abraham and Blandamer, 2002; Sedov and Solomonov, 2012a, 2010; Solomonov and Sedov, 2008; Teppen and Aggarwal, 2007). If the hydration energy of the sorbate is known, $\Delta_{ionic}G$ can be obtained by subtracting the hydration energy from the free energy change of sorption. However, for cationic surfactants, aqueous solubility is not clearly defined (Hodges et al., 2019). Therefore, their hydration energies cannot be reliably determined. In this study, the hydration energies of alkanes corresponding to benzalkonium ion alkyl chains are used to estimate the hydrophobic effect. Fig. 2 illustrates how benzalkonium sorption free energy increases with length of the alkyl chain. Notably, an additional methylene group leads to a decrease of about 2.5 kJ mol^{-1} in sorption free energy. However, for homologous organic compounds—including alcohols, amines and alkanes—an additional methylene group results in only about 0.73 kJ mol^{-1} increase in excess free energy of hydration (Plyasunov and Shock, 2000; Sedov and Solomonov, 2012b). The difference between the two can be attributed to the increased polarizability of the larger organic cation. Using linear interaction energy modelling, Samaraweera et al. (2014) suggested that increased polarizability due to addition of a methylene to a hydrocarbon group bonded to the nitrogen atom leads to a decrease of about 1–4 kJ mol^{-1} in $\Delta_{ionic}G$.

4.6. Prediction of benzalkonium ion sorption to soils

The cation exchange capacity of natural soils is due to the presence of both clays and organic matter. Since the nature and density of cation exchange sites on clays and organic matter are different, it can be assumed that their electrostatic energies are different. Hence, any model that seeks to predict sorption of organic ions to soils must consider the difference in sorption affinity of the two sorbent phases. Where the sorbed concentration is low enough such that sorption is solely due to ionic interactions, the distribution coefficient for a soil can be estimated by:

$$K_d = K_{d(CEC)}^{clay} \cdot CEC_{soil}^{clay} + K_{d(CEC)}^{org} \cdot CEC_{soil}^{org} \tag{7b}$$

where $K_{d(CEC)}^{clay}$ and $K_{d(CEC)}^{org}$ are the cation exchange capacity normalized distribution coefficients for clays and organic matter respectively, K_d is the distribution coefficient for the soil in L kg^{-1} and, CEC_{soil}^{clay} and CEC_{soil}^{org} are the respective fractions of soil cation exchange capacity contributed by clays and organic matter in mol$_c$ kg^{-1}. Since soils are often characterized with reference to the organic carbon content rather than total organic matter, the second term in equation (7) can be computed based on the fraction of organic carbon. The fraction of organic carbon of the peat used in this study has been reported to be 0.49 (Kim and Kwon, 2020). Using this estimate and the CEC of peat (2.5 mol$_c$ kg^{-1}), it is possible to separate the contributions of organic matter and clays to the total CEC of the soil (CEC_{soil}^{tot}). Equation (7) can then be written as

$$K_d = K_{d(CEC)}^{clay} \cdot \left(CEC_{soil}^{tot} - CEC_{soil}^{org}\right) + K_{d(CEC)}^{org} \cdot CEC_{soil}^{org} \tag{8b}$$

Values for the CEC-normalized distribution coefficients for clays and peat were derived using a simple linear regression of experimental data. To simplify the model and to avoid the need of having to differentiate between the different types of clay minerals, data for kaolinite and montmorillonite were combined into a single model. Whereas the two clay minerals are likely to have different surface potentials—hence different sorption energies, combining the data in one model can be justified since the CEC-normalized distribution coefficients for the two sorbents were within 0.5 log units of each other. Using a separate model for each clay type would require cumbersome characterization of natural soils, without any significant increase in accuracy of the predicted values. The models for clays and peat are given in equations (9) and (10), respectively.

$$\log K_{d(CEC)} = 0.440(\pm 0.042) \times N_{Carbon} + 1.66(\pm 0.47) \tag{9}$$

$$\log K_{d(CEC)} = 0.467(\pm 0.059) \times N_{Carbon} + 0.793(\pm 0.67) \tag{10}$$

where N_{Carbon} is the number of carbon atoms in the alkyl chain of the benzalkonium ion. The correlation coefficients were 0.95 and 0.97 for clays and peat, respectively.

The K_ds for artificial soil were estimated using equation (8). The predicted values are plotted against experimental values, determined using an artificial soil composed of clay and peat (Fig. 3). The proposed model fitted the data very well; all the predicted values were within 0.5 log units of the experimental values. The model is expected to be suitable for predicting sorption to soils whose

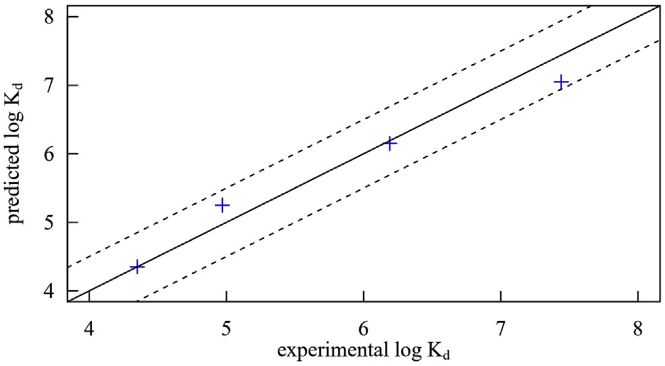

Fig. 3. Sorption data for the artificial soil as predicted by equation (8). The continuous line represents 1:1, whilst the dotted lines represent ±0.5 log units.

organic matter content closely resembles peat. However, predictions might not be reliable where soils contain high proportions of black carbon—whose sorption capacity has been shown to differ from that of peat and other commonly used organic sorbents (Carter et al., 2016; Tuikka et al., 2016; Zhi and Liu, 2018).

The model presented here can be used to provide better estimates of sorption coefficients for hydrophobic cationic organic compounds in various environmental systems. Since van der Waals interactions are of limited significance in sorption of benzalkonium compounds to soil surfaces, classical sorption models based on the octanol/water partition coefficient are not reliable in defining their sorption behavior especially at low and environmentally relevant concentrations. Environmental quality standards derived from aquatic toxicity tests can be translated into either soil or sediment quality standards using the appropriate distribution coefficient computed from this model. Also, the model can be applied in estimating removal efficiency for engineering systems that rely on sorption to mineral solids and soils. Where sewage sludge is applied as an amendment to agricultural land, the model can be used to estimate the mobility and bioavailability of benzalkonium compounds in the soil.

5. Conclusions

At environmentally relevant concentrations, sorption of benzalkonium compounds to soils and soil components was found to be dominated by the sorbent's CEC. This is evident from the similarity between CEC corrected K_ds which differed by less than one log unit among the three sorbents tested. The length of the alkyl chain was another major determinant of the magnitude of the K_d. Although intuition suggests that the hydrophobic surfaces on organic matter should make sorption of large organic ions to peat more energetically favorable, this does not seem to contribute much to the sorption of benzalkonium ions to soil components. Instead, similar to clays, sorption to peat was predominantly due to ion exchange. This suggests that the popular notation of expressing sorption of organic ions to organic matter with reference to organic carbon content would be of limited value, especially at the environmentally relevant concentration range. Relative contributions of ion exchange and van der Waals interactions should be investigated for a variety of ionic organic chemicals to develop a universal model for predicting their distribution at lower concentration range. A model was proposed to predict K_d of benzalkonium ions between water and soils using the soil's CEC and fraction of organic carbon. It successfully predicted experimental K_d values to within 0.5 log units. The model can be used to estimate soil/water distribution coefficients for benzalkonium compounds when modelling the environmental fate of cationic organic compounds.

CRediT authorship contribution statement

Mlamuli Ndabambi: Conceptualization, Methodology, Investigation, Writing - original draft. **Jung-Hwan Kwon:** Conceptualization, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

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