Modeling and predicting competitive sorption of organic compounds in soil

Isabel R. Faria and **Thomas M. Young**[*]
Agricultural and Environmental Chemistry and Department of Civil and Environmental
Engineering, University of California – Davis, One Shields Av, Davis, California 95616, USA

Abstract

Binary systems consisting of 1,2-dichlorobenzene (12DCB) + competitor were investigated over a
range of concentrations of competitor in three natural sorbents with distinct characteristics. Two
models, the ideal adsorbed solution theory (IAST) and the Potential theory (Polanyi based multi-
solute model), widely used in the prediction of multi-solute sorption equilibrium from single
solute data were used to simulate competitive sorption in our systems. The goal was to determine
which multi-solute model best represented the experimentally obtained multi-solute data in natural
sorbents of varied properties. Results suggested that for the sorbents and sorbates studied the IAST
model provided much better results. On average the IAST model provided lower errors (23%) than
the Potential model (45%). The effect of competitor structure on the degree of competition was
also investigated to identify any relationships between competition and structure using molecular
descriptors. The competitors chlorobenzene, naphthalene, 1,4-dichlorobenzene, 1,2,4-
trichlorobenzene all showed very similar degrees of competition, while benzene, phenanthrene and
pyrene were the least effective competitors towards 12DCB across all sorbents. Different sorption
sites or sorption mechanisms might be involved in the sorption of these molecules leading to a
lack of competitive behavior. A significant relationship between competitor structure and the
degree of competition was observed at environmentally relevant sorbed competitor concentrations
for the soil containing the highest fraction of hard carbon (Forbes).

Keywords

Competition; Multi-solute; Linear free energy relationships; Structure activity relationships;
Isotherm models

INTRODUCTION

In the environment contaminants often exist in mixtures with other chemicals over a wide
concentration range. The sorption/desorption behavior of hydrophobic organic compounds
(HOCs) in a single-solute system can be substantially different from that in multi-solute
systems [1–3]. The uptake of individual HOCs from aqueous solution by soils exhibiting
heterogeneous reactivity is shown to be reduced in the presence of other HOCs. The
sequestration of organic compounds in soil may be partially reversed by competitive
displacement processes where a competing chemical displaces the adsorbed chemical into
solution, taking its place in the soil matrix. This can result in a release of the formerly

unavailable chemical to the environment [4]. Competitive interactions may impact solute transport predictions and soil and groundwater remediation efforts significantly in soils manifesting nonlinear sorption behavior [1]. Previous studies [5,6] have shown that the presence of co-solutes may affect the sorption or desorption rates and the equilibrium concentration of a primary contaminant in a multi-solute system. Xing and Pignatello [7] reported the existence of competitive sorption between organic pollutants and aromatic acids; thus naturally occurring compounds may be capable of increasing the mobility and bioavailability of anthropogenic organic compounds.

The competitive effect between solutes has been attributed to the presence of rigid carbon domains which can arise in a number of ways. These *glassy* domains may consist of aromatic, low polarity natural organic matter, higher polarity organic matter bonded tightly to mineral surfaces in ways that prevent free rotation, or may be composed of black carbon such as unburned coal, kerogen, coke, soot or charcoal characterized by condensed, rigid, and aromatic structures [8]. Sorption to the rigid carbon domain is thought to be non-linear, hysteretic and to have higher organic carbon normalized sorption affinities for hydrophobic chemicals [9]. The remainder of the soil organic matter constitutes a soft, amorphous domain featuring linear and non-competitive sorption [10].

The effectiveness of a competitor in displacing a primary contaminant might be related to the physical chemical properties of the competitor. Structurally similar molecules were shown to display a stronger competitive effect [4,6,11,12]. For binary systems of 1,2 dichlorobenzene and other chlorobenzenes, competitors with structural properties closer to those of the primary solute had a competitive behavior similar to that of primary solute itself [12]. Maximum capacities for adsorption to a sediment were found to decrease with increasing sorbate molecular size, an effect thought to be caused by the difference in the accessible adsorption sites [13].

Binary systems consisting of 1,2-dichlorobenzene (12DCB) + competitor were investigated over a range of concentrations of competitor in three natural sorbents with distinct characteristics. Two models, the ideal adsorbed solution theory (IAST) and the Potential theory (Polanyi based multi-solute model), widely used in the prediction of multi-solute sorption equilibrium from single solute data were used to simulate competitive sorption in our systems. The goal was to determine which multi-solute model best represented the experimentally obtained multi-solute data in natural sorbents of varied properties. The effect of competitor structure on the degree of competition was also investigated to identify any relationships between competition and structure using molecular descriptors. Accurate modeling of multi-solute sorption is of great importance for the development of reasonable transport models, in establishing environmentally acceptable endpoints, and in predicting the risk posed to potential receptors.

MATERIALS AND METHODS

Soils sorbents and chemical sorbates

Three natural geosorbents (Yolo soil, Forbes soil and Pahokee peat) were selected as sorbents for the present study. Extensive data on the sorption of HOCs to these soils is available and they span a wide range of organic carbon contents and other properties. Yolo and Forbes soils were collected after removing the top layer of litter and collecting the 5 to 20 cm layer. These soils were collected at an agricultural field in Yolo County, CA (Yolo) and in the Tahoe National Forest in a conifer and oak forest, Placer County, CA (Forbes). Florida Pahokee peat soil was obtained air-dry from the International Humic Substance Society, Colorado School of Mines, (Golden, CO, USA). All sorbents were air-dried and crushed gently with a mortar and pestle and passed through a sieve, and the fraction <425μm

was collected for Yolo (Y) and Forbes (FB) and the fraction <2 mm for Peat (PP). All soils were γ-irradiated with 5 MRad dose of ^{60}Co (University of Michigan Phoenix Memorial Laboratory) to inhibit microbial degradation and stored at 5°C. The most relevant properties of the soils studied are shown in Table 1. Methods for the determination of OM%, OC%, soft-hard-soot carbon and other properties shown in Table 1 are described in Ju and Young [12].

Nine hydrophobic organic chemicals were used as sorbates for the present study. Five chlorinated benzenes [chlorobenzene (CB), 1,2- and 1,4-dichlorobenzene (12DCB, 14DCB), 1,2,4-trichlorobenzene (TCB), and 1,2,3,4-tetrachlorobenzene (TeCB)], benzene (BZ) and three polycyclic aromatic hydrocarbons (PAH) [naphthalene (NP), phenanthrene (PHN) and pyrene (PY)]. All sorbates used were analytical standard grade and were used as received. Benzene and NP were from Fluka (≥99% purity) and the remaining chemicals were obtained from Sigma-Aldrich Inc (≥99% purity).

Competitive sorption experiments

The competitive behavior in binary systems between 12DCB and the remaining eight sorbates was studied in competitive sorption experiments. 1,2-Dichlorobenzene was chosen as the primary solute because in this series of solutes it provided an intermediate value of hydrophobicity and molecular size. The experimental procedure followed was based on Ju and Young [12]. Experiments were carried out in triplicate in 40 mL glass tubes with Teflon® lined caps. Triplicate control reactors without sorbent were run concurrently with the experiments at each initial concentration to determine system losses. The aqueous phase in equilibrium with the sorbent contained: 555 mg/L $CaCl_2$, 200 mg/L of NaN_3 and 5 mg/L $NaHCO_3$. $CaCl_2$ was added to act as an electrolyte, NaN_3 as an inhibitor of microbial degradation and $NaHCO_3$ as a buffer. All solutions were prepared with freshly prepared deionized water (>18 MΩ; Milli-Q, Millipore, MA, USA). All the reactors were prepared leaving no headspace, and the soil and liquid amounts were determined gravimetrically.

Competitive sorption experiments were conducted at a constant initial concentration of the primary solute 12DCB and variable initial concentration of the competitors. The primary solute concentration was chosen to be low enough so that it is believed not to cause conformational change to the natural organic matter matrix [14]. Stock solutions of each solute were prepared by dissolving a known mass of chemical in acetone to a final determined volume. Seven spiking solutions containing a constant concentration of 12DCB (0.1 mg/L) and a range of concentrations of competitor were prepared for each competitor (Supplemental Data, Table S1). Solutions were prepared in acetone or methanol and a specified volume of stock solution was delivered into each reactor through the Teflon septa with a micro syringe. After mixing, the cap was quickly replaced to minimize volatile losses. The solvent did not exceed 0.1% v/v of the aqueous phase to minimize co-solvent effects. The solute initial concentrations were selected taking into consideration the solubility of the compound and the detection limit of the instruments used. The amount of sorbent used was determined so that the equilibrium aqueous phase concentrations of the two sorbates were between 15–85% of their initial concentrations.

Reactors were tumbled end-over-end at 10 rpm in the dark for 30 days (determined to be sufficient to reach sorption equilibrium for these solutes [12]) at room temperature. The reactors were subsequently centrifuged at $2053 \times g$ for 30 min and an aliquot of the aqueous phase was removed for liquid/liquid extraction. The aqueous phase was extracted with pentane (for BZ, NP and PY) or hexane (for CBs and PHN) and extracts were analyzed for both primary contaminant and competitor concentration by Gas Chromatography - Mass Spectrometry (GC-MS) (for BZ, CB, NP, PHN and PY) or Gas Chromatography - Electron Capture Detector (GC-ECD) (for the remaining CBs). The volumes of supernatant and

extraction solvent used varied according to the expected solute concentration in the supernatant. For the PAHs and BZ the volume of supernatant ranged from 10 to 12.5 mL and for pentane between 5 to 2.5 mL. For the chlorobenzenes the volume of supernatant ranged from 10 to 15 mL and for hexane between 15 to 10 mL. Details about the analytical method are provided in the supporting information. All samples were analyzed in duplicate and the average response was used to quantify the samples by means of external calibration. After injection of every eight unknown samples a known concentration sample was analyzed to check for system drift.

The masses of 12DCB and competitor adsorbed were calculated by difference between the total solute masses added and the masses remaining in the aqueous phase at equilibrium as previously described. The average solute masses remaining in the corresponding control tube at equilibrium were used as initial aqueous loadings.

Predicting multi-component sorption

Several models have been developed to predict sorption equilibria of HOCs from liquid solution under multiple solute conditions based solely on single solute sorption isotherms. The majority of the modeling approaches for multi-component sorption systems are based on either the Potential theory or the ideal adsorbed solution theory. Either approach can be implemented using a number of single solute isotherm formulations. For sorption of HOCs to soils it is important that the selected isotherm model can capture the heterogeneous nature of sorption sites within the natural organic matter matrix [15]. Single solute isotherms for these solutes and sorbents were determined previously and used to derive best fit values of parameters for the Freundlich ($K_{F,i}$, n_i) and partition-adsorption potential models ($K_{p,i}$, $Q_{o,i}$, a_i, b_i) [16]. The IAST has been extensively used to predict multi-component sorption of HOCs on activated carbon and soil using only single solute isotherm data [1,3,4,15]. When the Freundlich isotherm model is used the IAST equation describing the sorbed phase concentration of solute 1 in the presence of co-solute 2 becomes:

$$q_{e_1}^m = \frac{V}{m}\left(C_{o_1}^m - \left(\frac{q_{e_1}^m}{q_{e_1}^m + q_{e_2}^m}\right) \times \left(\frac{n_2 q_{e_1}^m + n_1 q_{e_2}^m}{n_1 K_{F,1}}\right)^{\frac{1}{n_1}} \right)$$

(1)

where V is volume, m is mass of sorbent, $C_{o_i}^m$ is the initial concentration of solute i in a mixture and $q_{e_i}^m$ is the sorbed concentration of solute i in a mixture. Although the Freundlich model is not explicitly a dual mode model, it closely approximates a summation of multiple Langmuir isotherms [9]. Freundlich single solute parameters for each sorbate (n_i, K_F,) [16] were employed in Equation 1 and MATLAB® 7.4 (MathWorks) was used to calculate the sorbed concentrations of both the primary solute ($q_{e_1}^m$) and competitor ($q_{e_2}^m$) using a Newton Raphson algorithm and the resulting values were compared to experimental measurements.

The Potential theory or Polanyi model, initially developed to model gas-phase adsorption to activated carbon, has been modified to predict sorption of multi-component solutions by Moon and Tien [17,18]. Xia and Ball also developed a similar model to predict the sorption of chlorinated benzenes and PAH by aquitard material in binary solute systems [19]. A partition-adsorption variant of the Potential model was used to describe the single solute sorption process, with adsorption being described by the Polanyi-Manes model [20,21]. The basic equation for predicting the adsorbed phase concentrations of competing adsorbates under the Potential theory are as follows. The mole fraction of solute x_i^m in the sorbed phase of a multi-solute system is defined as:

$$x_i^m = \frac{C_{e,i}^m}{C_{e,i}^{s*}\gamma_i}$$

(2)

where γ_i is the activity coefficient of solute i in the sorbed phase ($\gamma_i = 1$ in ideal solutions), $C_{e,i}^m$ is the liquid phase concentration of i in a multi-solute solution and $C_{e,i}^{s*}$ is the hypothetical liquid phase concentration of i in a single solute system at the same ε adsorption potential density as the multi-solute system. At equilibrium $\sum_i x_i^m = 1$ and each sorbate has the same adsorption potential density ε given by

$$\varepsilon = \frac{RT}{V_s} ln\left(\frac{S_w}{C_e}\right)$$

(3)

where R is the ideal gas constant, T is Temperature (K), V_s is the molar volume of the solute and S_w is the solubility of the solute. Combining and rearranging the previous equations yields the following expression:

$$\sum_i \frac{C_{e_i}}{S_{w_i}} exp\left(\frac{V_{s_i}}{RT} \times \varepsilon\right) = 1$$

(4)

In an iterative process the previous equations were solved and the values for $C_{e,i}^*$ were determined using the method of Moon and Tien [17]. Values for $q_{e,i}^*$ were then calculated using single solute isotherm parameters [16]. Since $q_{e,i}^*$ accounts solely for the adsorption fraction, the partitioning fraction (K_pC_e) was subsequently added to calculate the total amount of sorbed solute. This approach is appropriate since no competition is expected to occur in the partitioning domain. MATLAB® 7.4 was used to solve the equations using an iterative process and calculate the sorbed concentrations of both the primary solute and competitor, which were subsequently compared to the multi-solute experimental measurements.

Degree of competition

To compare the impact of different competitors it is important to have an appropriate measure of how effective a competitor is at displacing a primary contaminant. The degree of competitive sorption between pairs of halogenated hydrocarbons was shown to "vary inversely with the difference in molecular free surface areas of each molecule calculated from van der Waal's radii" suggesting that degree of competition might be related to the molecular structure of compounds [6].

Recently several models have been presented to relate single solute sorption to sorbate properties using poly-parameter linear free energy relationships (pp-LFER) [22–25]. Following the approach used by others for single solute systems e.g. [22,23], molecular descriptors were used to analyze the degree of competition for each competitor according to the equation:

$$\Delta \log K_{OC} = c + sS + bB + lL + eE$$

(5)

where $\Delta\log K_{OC}$ represents the change in organic carbon normalized distribution coefficient for the primary solute (here 12DCB) from a single solute system to the case when a competitor is added at a specified concentration, E is the excess molar refraction, S is the dipolarity/polarizability parameter, B is the solute H-bond basicity and L is the logarithm of the hexadecane-air partitioning constant [26,27]. These molecular descriptors have been extensively used in multiple parameter LFERs for the prediction of single solute sorption to natural sorbents. Molecular descriptor values for all sorbates were obtained from [28]. Values of $\Delta\log K_{OC}$ were calculated plotting 12DCB K_{OC} vs. sorbed competitor concentration (q_e mg/kg OC) and by fitting a logarithmic regression to the data. At fixed sorbed competitor concentrations ($q_{e \text{ (mg/kg OC)}}$ = 1, 10, 100 and 1000) values of $\Delta\log K_{OC}$ were calculated according to the equation:

$$\Delta\log K_{OC} = \log(K_{OC,i}) - \log(K_{OC,qe}) \tag{6}$$

where $K_{OC,i}$ is the organic carbon normalized distribution coefficient for 12DCB without competitor and $K_{OC,qe}$ is the K_{OC} for 12DCB in the presence of a fixed amount of competitor. The values of q_e were chosen to cover the whole range of sorbed competitor concentrations across all the sorbates and sorbents. In some cases the selected sorbed concentrations fell outside the range of experimental concentrations and were extrapolated (usually a factor of less than 10) using the Freundlich coefficients. Sorbed concentrations were expressed on an organic carbon normalized basis so that all three sorbents could be compared.

Multiple linear regressions were performed at each of the four sorbed concentrations to determine the coefficients c, s, b and l in Equation 5 using SYSTAT® 11 (Systat Software Inc.). The descriptor E was not included in the regression because it was shown to have a negligible contribution. To our knowledge this is the first time this approach has been applied to evaluate the competitive effectiveness of various sorbates based on molecular descriptors.

RESULTS AND DISCUSSION

The multi-solute isotherms (in the presence of primary contaminant 12DCB) for all competitors were determined for Yolo, Forbes and Peat soils. Average solute losses (results shown in Supplemental Data, Table S2) determined from blank controls averaged less than 6% of the initial solute concentration indicating that losses to volatilization and sorption to glassware or Teflon® lined caps were negligible. Results for PY are not shown since aqueous concentrations at equilibrium C_e were very low and consequently values of q_e could not be determined with precision. Dissolved organic carbon (DOC) was measured in these soils in the same mass range as the loadings in the batch systems. For the amount of sorbent used and the K_{OW} of the sorbates used the DOC concentrations present in the systems (0.45–99 mg/L) were not high enough to cause a significant effect on the aqueous concentration of both the primary and competitor sorbates. Results indicate that less than 1% (0.03–0.9%) of the sorbate in the aqueous phase was DOC-complexed.

The analysis of the multi-solute sorption of the 12DCB+BZ in Yolo and 12DCB+PY in all sorbents proved to be experimentally challenging. The large differences in K_{OC} values between competitor and primary contaminant made the simultaneous determination of C_e and q_e for both chemicals quite difficult. The amount of sorbent used for those experiments was chosen so that there was enough sorption of the primary solute 12DCB that the variation of $q_{e,12DCB}$ could be measured while at the same time sorbing a sufficient amount of competitor (between 15–85%) to reliably establish q_e for the competitor. For the 12DCB

+BZ system in Yolo soil it proved impossible to find a soil/solution ratio that permitted simultaneous determination of C_e and q_e for both solutes because of the limited sorption on this soil. For the 12DCB+PY it appears that 12DCB sorption wasn't appreciably affected by the presence of the competitor PY. Since the initial concentration of PY in solution (0.004–0.05 mg/L) was low, the number of moles of PY being roughly one third that of 12DCB it is likely that even if all the PY sorbed that it might not affect 12DCB sorption significantly. Also it is possible that because of its high molecular volume PY cannot access the small pores that 12DCB can occupy, minimizing its competitive effectiveness.

Predicting sorption in multi-solute systems

For the IAST model, previously determined single solute Freundlich coefficients and exponents of both solutes were used as inputs [16]. For PHN Freundlich isotherm parameters reported in the literature were used as initial isotherm inputs [5,29]. For a known mass of sorbent, volume of solution and initial concentration of both solutes, the equilibrium concentration of both sorbates was estimated in the sorbed phase and in the liquid phase.

The Potential model was applied in a similar fashion to estimate multi solute equilibria using the single solute Potential parameters as isotherm input data [16]. Since no single solute isotherm parameters for PHN in peat were available, parameters were calculated based on the multi-solute PHN data. Results for PY are shown but not included in average calculations because no clear effect of PY on the sorption of 12DCB was observed. Experimental data and results obtained with both models are shown in Figure 1 for Forbes soil (full set of sorbates and sorbents presented in Supplemental Data, Fig. S1).

The predictive ability of each modeling approach was quantified based on calculated and experimental K_{OC} values as described in supporting information (Supplemental Data, Eq. S1). Calculated average percent errors for all sorbates and sorbents are presented in Table 2.

Previous research has generally found that the IAST and the Polanyi theory yield similar modeling results for sorption of chemical mixtures to activated carbons and natural solids [30]. Results of the present study suggest that for the studied sorbents and sorbates that the IAST model provides much better results. On average the IAST model provided lower errors (23%) than the Potential model (45%) in all three soils. Taking into consideration that both models rely solely on single solute data to predict multi-solute data, both models can be considered satisfactory.

Sensitivity analysis for the Freundlich parameters showed that the Freundlich exponent n_i had a more significant effect on the IAST predicted results. A similar effect was reported by Xing et al [4] where IAST results were shown to be dependent on the magnitude of both $K_{F,i}$ and n_i of each compound but much more sensitive to uncertainty in n_i than in $K_{F,i}$. As pointed out by McGinley et al. [1] "the greater imprecision in sorption measurements translates into greater uncertainty in bi-solute predictions". This might explain the high deviation for BZ and NP results for both models.

The IAST was developed under the assumptions that all sorbates behave ideally, that all binding sites are accessible to each sorbate and that the system attains a thermodynamic equilibrium. Results obtained by Li and Werth [3] suggest that for microporous sorbents IAST deviations may occur due to steric effects causing deviation from ideality. Results show better IAST fits for CB, 14DCB and TCB and the magnitude of the fitting errors increase with increasing molecular weight across sorbents. Among sorbents Forbes shows the highest deviation which may be related to its higher hard carbon content where micropores are thought to be dominant.

For the Potential model only the adsorption term was modeled, with the non-competitive partitioning term later added to calculate the total sorption of the compounds. Therefore a significant part of the error in the Potential model bi-solute results may originate from inaccurate division of partitioning and adsorption in the single solute isotherm fit. The best Potential model results were obtained for the same sorbates as the IAST model with errors also increasing with increasing molecular weight across sorbents. Model fits improve with increasing concentration of sorbed competitor, which is an unexpected outcome since the adsorption effect being simulated is dominant at low concentration. Without a clear trend in predicted results it is hard to explain why some sorbates or sorbents are better described than others but overall the Potential model did not provide good results.

Competitive effect

The effect of a competing sorbate on the sorption of the primary contaminant (12DCB) present in the system at a constant initial concentration was evaluated (Forbes soil shown in Figure 2, other sorbents shown in Supplemental Data, Fig. S2). The competitive effect was assessed by comparing the ability of each competitor to reduce sorption of the primary solute as indicated by K_{OC}. The volume of competitor in the solid phase (cm^3/kg OC) at equilibrium was used as a measure of competitor uptake. Results for PY are not shown since no clear trend in 12DCB K_{OC} with increasing PY adsorbed was observed. Also included in the figure is a line showing the self-competition of 12DCB in a single solute system.

The addition of a competitor causes a clear decrease in K_{OC} of the primary contaminant 12DCB. The slopes of the BZ, TeCB and PHN across sorbents are consistently lower than the remaining sorbates indicating that these sorbates are less effective competitors. The decrease in 12DCB K_{OC} for the 12DCB+PHN systems is the lowest obtained, pointing to a lower competitive effect of PHN against 12DCB, similar to results of Ju and Young [12]. The line showing the single solute data of 12DCB indicates that 12DCB is a better competitor for itself than the remaining solutes.

The affinity of the primary and competing sorbates for a given soil determined how much sorbent was required to achieve approximately 50% sorption for both solutes. Consequently the multi-solute sorption experiments were performed using different solid to solution ratios complicating the comparison of extent of competition among the three adsorbents and across adsorbates. Comparisons among the degree of competition for all sorbates and sorbents are presented in the following section.

Degree of competition

The effect of competitor structure on the competitive effect towards 12DCB was investigated by examining the change of the K_{OC} for the primary contaminant 12DCB with increasing concentration of sorbed competitors in Yolo soil, Forbes soil and Pahokee peat. Values of $\Delta \log K_{OC}$ determined from fitted curves at fixed sorbed competitor concentrations ($q_{e \text{ (mg/kg OC)}}$ = 1, 10, 100 and 1000) are shown in Table 3. The lowest concentration of competitor (q_e = 1 mg/kg OC) used in the calculation of $\Delta \log K_{OC}$ is below the range of concentrations of the experimental data for all sorbates, nevertheless it follows the general trend.

A more effective competitor will cause a larger displacement of 12DCB resulting in a larger decrease in $\log K_{OC}$ for a given addition of competitor. The competitors CB, NP, 14DCB, TCB all show very similar degrees of competition with high values of $\Delta \log K_{OC}$ while BZ, TeCB and PHN exhibit less competition. Similar results were reported by Ju and Young [12] where no significant differences were observed for competitive effect of all CBs towards 12DCB. The high degree of competition exhibited by the solid sorbate NP contradicts the

suggestion by Xia and Ball [19] that liquid sorbates would be more effective competitors than solid sorbates. Ju and Young [12] also reported no "clear and systematic differences" between solid and liquid sorbates in terms of competitive effects. BZ, PHN and PY were the least effective competitors towards 12DCB across all sorbents, a result also observed in Figure 2. Different sorption sites or sorption mechanisms might be involved in the sorption of these molecules leading to a lack of competitive behavior.

The sorption of competitor may occur by either uptake at initially vacant sites or uptake by occupied sites in a two step mechanism in which the primary sorbate 12DCB leaves the site and is outcompeted for re-adsorption by the competitor. Benzene, with a significantly lower sorption affinity would not sorb as strongly as 12DCB, giving rise to a weak competitive behavior. Both PHN and PY with higher K_{OC} values than 12DCB have a much stronger sorption affinity for SOM, a fact that goes against the observed weak competitive effects. Structurally similar molecules have been shown to compete for sorption sites more strongly than dissimilar molecules. This result suggests that adsorption sites possess selectivity possibly dependent on "steric similarities" of the sorbates [6]. Pyrene and PHN are the largest of the molecules studied with molecular volumes of 152 and 159 cm^3/mol respectively, while the CBs and NP have volumes ranging from 101 to 127 cm^3/mol. The rigid nature of the competitive hard carbon domain may prevent these larger molecules from reaching the same micro and nanopores in which the primary contaminant is located, limiting their competitive effect.

Using calculated $\Delta \log K_{OC}$ and descriptors S, L and B a multiple linear regression was determined according to Equation 5 to examine the effect of sorbate structure on competitive effect. Results for coefficients c, s, l and b obtained for each sorbent are shown in Table 4. The coefficient of regression r^2 decreases substantially with increasing concentration for all sorbents. For Yolo and peat none of the regression models are significant at the 95% confidence level although r^2 values are relatively high for the lowest q_e point ($r^2 = 0.926$ and 0.802) while for Forbes soil both 1 and 10 mg/kg OC points generate regressions significant at the 95% confidence level ($r^2 = 0.943$ and 0.920). This difference among sorbents is possibly related to the sorbents' differing hard organic carbon content, which is highest for Forbes soil.

At the highest concentration of competitors analyzed very little correlation was observed between $\Delta \log K_{OC}$ and sorbate descriptors. Competition occurs predominantly in the hard carbon domain due to adsorption, a process likely dominant at lower concentrations, and therefore differences in degree of competition are expected to be more significant at low sorbate concentrations. For Forbes soil, results show a significant relationship between competitor sorbate structure and the degree of variation of primary contaminant K_{OC} at relevant sorbed competitor concentrations.

The regression coefficients for Forbes and peat follow the same trend where c and s increase with concentration and l and b decrease with increasing concentration, while opposite trends were found for Yolo on s, l and b. The reason for this difference in concentration effect across sorbents is not understood at this point. Further characterization of the hard carbon domain in these sorbents might assist in better understanding this result. The competitive effect might not be limited to the hard carbon domain in soil, but it is thought to occur mainly in this soil fraction. Sorbent characterization such as acidity and density of functional groups, pK_a of sorption sites and molecular structure of sorbents by pyrolysis GC-MS or solid state NMR could provide insight into the molecular composition and structure of the sorption sites. Additionally microporosity and pore size distribution of the hard carbon fraction may also be relevant pieces of information in the effort to relate degree of competition to sorbate structure in different sorbents.

At low concentrations of competitor in Forbes soil, the values for parameters s and b are much higher than those for Yolo and peat. An analysis of the magnitude of the descriptors shows that the contributions of the terms *sS* and *lL* are the most dominant (*bB* range from 0.03 to 0.39, *sS* from 0.92 to 3.02 and for *lL* from 0.68 to 2.16). This might indicate that solute H-bond basicity (H-acceptor or electron donor) interactions play a minor role in competitive effects and that solute polarizability, dipole-dipole and dispersion interactions have a more significant influence in the competitive effect, a suggestion that is in agreement with the proposed composition of the hard carbon domain as less polar and more aromatic than the amorphous soft organic carbon [31].

The approach used to investigate competitive effectiveness is promising, offering insight into the process of competitive sorption between sorbates in different sorbents, however there are limitations to the study. Sorbates used in this study were relatively few and limited to planar hydrophobic compounds with very similar core structures which meant that the molecular descriptors used varied relatively little between sorbates and in some cases were highly correlated with each other. Although the sorbents used presented a high variation in organic carbon, they did not vary drastically in hard organic carbon content. Since competition is believed to take place in the hard organic carbon domain a greater variation in the hard carbon content of the sorbents might help to better elucidate the role of this parameter.

Future research to understand the role of sorbent and sorbate structure in determining the degree of competition should include: sorbents with higher variations in hard organic carbon content, further characterization of the hard carbon domain of the sorbents as mentioned previously, as well as inclusion of sorbates with a broader range of characteristics as reflected by the independent variation of the molecular descriptors. The integration of this type of information into the described method has the potential to extend the applicability of this approach to other sorbents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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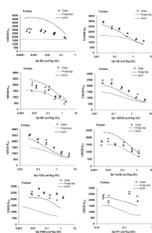
Figure 1.
Multi-solute experimental data (1,2-dichlorobenzene + competitor), Ideal adsorbed solution theory (IAST) model and Potential model results for sorbates benzene (BZ), chlorobenzene (CB), naphthalene (NP), 1,4-dichlorobenzene (14DCB), 1,2,4-trichlorobenzene (TCB), 1,2,3,4-tetrachlorobenzene (TeCB), phenanthrene (PHN) and pyrene (PY) as competitors in Forbes soil.
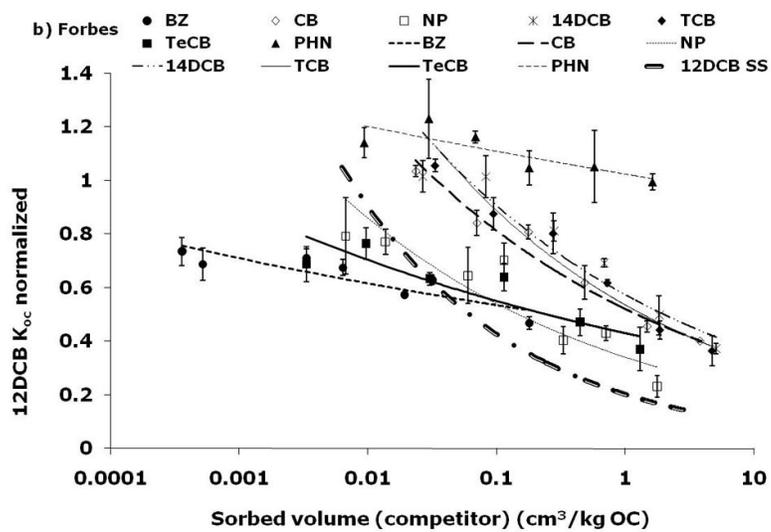
Figure 2.
Competitive effect shown for all sorbates in Forbes soil. Refer to Figure 1 legend for other definitions.

Table 1

Sorbent properties

	OM (%)	OC (%)	soft-hard-soot C ratio (%)[a]	H (%)[b]	O (%)[b]	N (%)	SSA (m²/g)[b]	Pore volume (mL/g)[b]
Yolo	2.93 (3.80)[a]	1.20 (1.08[a];1.20[c])	39.3-60.0-0.6	0.48	2.05	0.14[c]	18.3	0.03
Forbes	6.93 (13.90)[a]	4.80 (5.52[a];4.30[c])	33.2-66.3-0.5	1.20	6.29	0.19[c]	46.7	0.08
Pahokee peat	76.02 (89.88)[a]	47.20 (51.80)[a]	49.8-50.0-0.2	3.73	31.51	3.09[d]	1.0	0.01

Organic matter (OM), Organic carbon (OC), Hydrogen (H), Oxygen (O), Nitrogen (N), Specific surface area (SSA)

[a]Xing and Pignatello[12]

[b]Weber et al. [10]

[c]Watanabe et al. [32]

[d]Ju and Young [11]. Numbers in parenthesis are shown for comparison with obtained values.

Table 2

Comparison of ideal adsorbed solution theory (IAST) and Potential multi-solute models.

Competitor	Yolo		Forbes		Peat	
	IAST	Potential	IAST	Potential	IAST	Potential
BZ	--	--	58.4	35.2	19.8	180.5
CB	8.6	17.3	17.4	33.1	7.6	66.1
NP	62.6	76.9	34.8	19.4	23.9	59.0
14DCB	18.8	30.1	21.7	37.1	15.6	31.4
TCB	10.4	15.8	20.4	35.7	12.9	34.4
TeCB	21.3	34.1	33.2	19.9	10.5	44.5
PHN	21.6	40.4	23.5	55.5	20.9	32.3
PY	55.3	60.4	20.8	48.9	39.9	64.6
Average *	**23.9**	**35.8**	**29.9**	**33.7**	**15.9**	**64.0**

benzene (BZ), chlorobenzene (CB), naphthalene (NP), 1,4-dichlorobenzene (14DCB), 1,2,4-trichlorobenzene (TCB), 1,2,3,4-tetrachlorobenzene (TeCB), phenanthrene (PHN), pyrene (PY), -- data not available

*
average does not include PY model results.

Table 3

Calculated values for the change in organic carbon normalized distribution coefficient for the primary solute 1,2–dichlorobenzene ($\Delta\log K_{OC}$) with increasing sorbed concentration of competitor (q_e) for all sorbates in Yolo, Forbes, and peat sorbent.

Yolo	$\Delta\log K_{OC}$			
q_e (mg/kg OC)	1	10	100	1000
CB	−0.121	−0.016	0.122	0.326
NP	−0.025	0.070	0.192	0.363
14DCB	−0.115	−0.020	0.102	0.271
TCB	−0.095	0.007	0.140	0.333
TeCB	−0.058	0.004	0.076	0.163
PHN	−0.003	0.022	0.049	0.078
PY	−0.357	−0.270	−0.162	−0.018
Forbes				
q_e (mg/kg OC)	1	10	100	1000
BZ	−0.030	0.024	0.085	0.157
CB	−0.138	−0.039	0.090	0.274
NP	−0.097	0.008	0.148	0.355
14DCB	−0.192	−0.098	0.024	0.193
TCB	−0.158	−0.058	0.070	0.254
TeCB	−0.091	−0.019	0.066	0.173
PHN	−0.036	−0.006	0.027	0.063
PY	0.070	0.060	0.050	0.041
Peat				
q_e (mg/kg OC)	1	10	100	1000
BZ	−0.007	0.032	0.074	0.121
CB	−0.107	−0.014	0.103	0.265
NP	−0.002	0.084	0.191	0.334
14DCB	−0.105	−0.017	0.094	0.245
TCB	−0.147	−0.057	0.057	0.212
TeCB	−0.080	−0.006	0.084	0.197
PHN	−0.029	0.016	0.066	0.122

Yolo		Δlog K_{OC}			
	q_e (mg/kg OC)	1	10	100	1000
PY		0.941	0.145	−0.119	−0.283

Sorbed concentration of competitor expressed as mass of contaminant per mass of soil organic carbon (q_e (mg/kg OC)). Sorbate acronyms defined in Table 2.

Table 4

Multiple linear regression results for Yolo soil, Forbes soil and Pahokee peat.

Yolo		q_e (mg/kg OC)			
		1	10	100	1000
coef	c	−0.094	0.136	0.446	0.915
	s	−0.713	−0.985	−1.341	−1.867
	l	0.111	0.126	0.143	0.163
	b	0.666	0.814	1.018	1.344
S.E.	c	0.104	0.158	0.258	0.432
	s	0.646	0.980	1.603	2.681
	l	0.082	0.125	0.204	0.341
	b	0.421	0.640	1.047	1.750
r^2		0.926	0.626	0.572	0.760
S.E.		0.021	0.032	0.052	0.087
Forbes		1	10	100	1000
coef	c	0.010	0.075	0.149	0.229
	s	−1.765*	−1.204*	−0.355	1.098
	l	0.245*	0.162*	0.038	−0.174
	b	1.356*	0.934*	0.319	−0.683
S.E.	c	0.042	0.034	0.016	0.239
	s	0.363	0.295	0.918	2.07
	l	0.051	0.041	0.128	0.289
	b	0.211	0.172	0.534	1.205
r^2		0.943*	0.920*	0.248	0.236
S.E.		0.020	0.017	0.052	0.117
Peat		1	10	100	1000
coef	c	−0.013	0.020	0.055	0.090
	s	−0.715	−0.156	0.635	1.858
	l	0.091	0.015	−0.094	−0.264

Yolo		q_e (mg/kg OC)			
		1	**10**	**100**	**1000**
	b	0.861	0.430	−0.174	−1.098
S.E.	c	0.073	0.081	0.113	0.179
	s	0.629	0.701	0.979	1.548
	l	0.088	0.098	0.137	0.216
	b	0.366	0.408	0.570	0.901
r^2		0.801	0.606	0.249	0.355
S.E.		0.035	0.039	0.055	0.087

Multi-linear regression coefficients (c, s, l, b), Standard error (SE), q_e (mg/kg OC) defined in Table 3,

*
Significant at 95% confidence interval