

Full Length Research Paper

# The Role of Soil Clay Minerals in the Sorption and Environmental Fate of Biphenyl

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Accepted 22nd March, 2025

Only limited information is available in the literature on the role of soil mineral surfaces in the sorption of hydrophobic organic pollutants. This knowledge gap is addressed through the assessment of biphenyl sorption to kaolinite, illite and bentonite; using the batch equilibration technique with incubations lasting 6 or 21 days at  $28 \pm 2^\circ\text{C}$  in the dark. Sorption of biphenyl onto kaolinite followed the Freundlich sorption isotherm, whereas linear sorption isotherms were observed on illite and bentonite. The biphenyl sorption partition coefficient on kaolinite ranged from 0.1 to  $9.1 \text{ cm}^3 \cdot \text{g}^{-1}$  after 6 days and no sorption was observed after 21 days. This could have been caused by a completely reversible sorption or a loss of binding capacity after 21 days. The respective values of the biphenyl sorption partition coefficient on illite and bentonite ranged from  $20.3 \pm 0.3$  to  $120 \pm 8 \text{ cm}^3 \cdot \text{g}^{-1}$ . Sorption equilibrium on the internal clay surfaces was reached after 6 days, as indicated by the sorption data for illite and bentonite. Access of biphenyl molecules to the internal clay surfaces is a function of the ionic strength of soil solution and the soil organic matter is the dominant site for biphenyl sorption after 6 to 21 days.

**Key words:** Biphenyl, sorption, kaolinite, illite, bentonite.

## INTRODUCTION

Hydrophobic organic compounds have been shown to contaminate different parts of the environment. Soil sorption is important in their environmental fate and a crucial role of soil organic carbon has been well established in this context (Cornelissen et al., 2000; Tandlich, 2004). Fewer studies have focused on sorption to mineral surfaces which can be quite significant (Jaynes and Cornelissen et al., 1991a; Poulsen et al., 2000). The available literature indicates the following:

Depending on the hydrophobic organic compound, the type of soil mineral and/or the size of its surface area govern the sorption to mineral surfaces (Schwarzenbach and Westall, 1981; Keoleian and Curl, 1989; Mader et al., 1997). Other parameters influencing the sorption of hydrophobic pesticides to mineral surfaces include nature and concentration of inorganic ions, such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and

$\text{NH}_4^+$ , sorbed onto the clay mineral surfaces (Li et al., 2004a).

Biphenyl is an example of a hydrophobic pesticide. It has the following identification data: CAS number: 92-52-4; molecular formula  $\text{C}_{12}\text{H}_{10}$  and molecular weight 154.21  $\text{g} \cdot \text{mol}^{-1}$  (<http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?/.tem/~r0N2Lh:1>). It has been used as a fungicide (Sheng et al., 2001) and results of recent studies indicate it is found in commercially available fruits (EFSA, 2010). Biphenyl is also an inducer of the dioxygenase pathway involved in PCB biodegradation (Kwon et al., 2008). It is also a highly hydrophobic compound, since the log *P* value is around 4.00 (Tandlich, 2004). Biodegradation can take place from the aqueous phase, but also from the compound pool sorbed to solid particles (Tandlich et al., 2011). Based on this data, sorption to soils will be an important mechanism in the environmental fate of biphenyl. In this context, understanding the significance of clay minerals is crucial.

Several studies have been conducted on the sorption of biphenyl to clay minerals. Jaynes and Boyd (1991b) studied the sorption of biphenyl and several other aromatic hydrocarbons to vermiculite, illite, smectite and kaolinite exchanged with hexadecyltrimethylammonium and magnesium cations. Sorption occurred via partitioning

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of biphenyl into the clay mineral surfaces covered with hexadecyltrimethylammonium cations. If smectite was exchanged with magnesium, then no significant biphenyl sorption took place. De Stefanis et al. (1994) found that biphenyl molecules did not undergo specific interactions with alumina-pillared montmorillonite, mixed  $\text{Fe}^{3+}$ -alumina-pillared montmorillonite or the alumina-pillared  $\alpha$ -tin phosphate montmorillonite. All sorption isotherms were linear and the  $K_d/K$  values were independent of the concentrations of  $\text{K}^+$  or  $\text{Ca}^{2+}$  in the study of Li et al. (2004a). Certain siloxane surfaces in the structure of expandable clays carry no net charge (Li et al., 2004a), while results of theoretical calculations have indicated that oxygen atoms which are located inside the interlayer spaces in the crystal structures of clays are hydrophobic (Skipper et al., 1989). These findings provide possible sites for sorption of aromatic hydrocarbons (Jaynes and Boyd, 1991a).

Pálková et al. (2009) found that montmorillonites exchanged with tetramethylammonium or hexadecyltrimethylammonium cations sorbed biphenyl to a higher extent, than if lithium was the exchangeable cation. If the hexadecyltrimethylammonium cations were present on the clay surface, then extent of biphenyl sorption was directly proportional to the surface charge of the clay mineral. The opposite trend was observed for the montmorillonite samples exchanged with tetramethyl-ammonium and the extent of biphenyl sorption reached up to 80% of the initial biphenyl concentration. The available literature data on the biphenyl sorption to clay minerals exchanged with organic cations is relevant for the remediation technologies which involve the addition of such sorbents to soils (Zhu et al., 2009). The role of clay minerals in soil sorption has been described for structurally similar organic molecules such as naphthalene (Vianna et al., 2010), phenanthrene (Meleshyn and Tunega, 2011) and PCBs (Nolan et al., 1989). These data are useful but additional information is needed due to structural differences between these pollutants and biphenyl.

Naphthalene and phenanthrene are rigid structures and their molecules cannot undergo rotation around the single C-C bonds as it is the case for biphenyl. This could influence the site of sorption on the clay mineral as the rotation around the single C-C bond might control the ability of the biphenyl molecules to access the internal clay mineral surfaces. On the other hand, presence of strongly electronegative atoms, such as chlorines in PCBs, can lead to the formation of specific interaction between the electronegative atoms and Lewis acid sites on surface of clay minerals (Nolan et al., 1989). Nitroaromatics have been shown to undergo complex formation between weakly-hydrated inorganic cations such as  $\text{K}^+$  and the  $\text{NO}_2$  groups, while the aromatic rings of the molecule align with the clay mineral surface and interact through van der Waals forces and electrostatic interactions (Boyd et al., 2001; Johnston et al., 2001; Li et

al., 2004b). More of these interactions are likely to take place during biphenyl sorption. Most of the studies were also done only for short incubation periods around 24 h (Sheng et al., 2001). However, longer contact periods, so-called ageing can be encountered under environmental conditions (Eom et al., 2007). Therefore it is the aim of this study to elucidate the sorption mechanism of biphenyl to clay minerals by addressing the aforementioned knowledge gaps.

Kaolinite, illite and bentonite (montmorillonite) were chosen as model clay minerals.

## MATERIALS AND METHODS

### Chemicals and consumables

Kaolinite and bentonite were purchased from FLUKA and RIEDEL DE HAËN (both in Buchs, Switzerland). The following chemicals and consumables were purchased from VWR SCIENTIFIC (Milford, Massachusetts, USA): biphenyl, methanol, acetone, n-hexane, calcium chloride ( $\text{CaCl}_2$ ), sodium azide ( $\text{NaN}_3$ ), 75  $\mu\text{m}$  sieve and amberlite glass (40  $\text{cm}^3$ ) vials with screw caps and the PTFE-lined silicone septa. SPME holder for manual sampling and the PDMS fibres (film thickness of 7  $\mu\text{m}$ ); and the amberlite vials for SPME extractions (4  $\text{cm}^3$ ) were purchased from SUPELCO (Bellefonte, CA, USA). EGME was purchased from FISCHER SCIENTIFIC (Chicago, IL, USA). Helium for GC/MS was of instrument grade (purity 99.999%) and it was purchased from PRAXAIR INC. (Fargo, ND, USA). All chemicals and solvents had purity of 99% or higher. Illite for the sorption experiments was provided by the Department of Soil Science from North Dakota State University. It contained 0.97% of organic carbon and the results of X-ray diffraction analysis showed that illite accounted for 97% of this sample's weight. This sample was chosen because it was used for clay related research by the donor department and was well characterised. All clay samples were used as obtained from the manufacturer or the Soil Science Department at North Dakota State University. The particle size distribution was not examined in detail because the influence of the particle size on biphenyl sorption to clay minerals was not the aim of this study. However, to make sure that the particle size of the clay minerals was within the characteristic literature intervals scanning electron microscopy images were obtained of the air-dried minerals using a modified procedure of Tandlich et al. (2011). More detailed information can be found in Figure 2.

### The SSA and organic carbon measurements

The SSA values of clay minerals were measured using a modified version EGME adsorption method (Carter et al., 1965; Tandlich, 2004). Approximately 1.1000 g of the clay in question was weighed into an aluminium moisture can. The moisture cans were placed into a desiccator with open lids over  $\text{CaCl}_2$  overnight. After this period, the individual moisture cans were covered with lids and weighed to determine the dry weight of clay samples. The samples were then stored in a desiccator over  $\text{CaCl}_2$  until the SSA measurement. For the  $\text{CaCl}_2$ /EGME solvate preparation,  $\text{CaCl}_2$  was ground and sieved through a 75  $\mu\text{m}$  sieve and baked out at 160°C overnight. Hot  $\text{CaCl}_2$  was taken out of the oven and directly mixed into an aliquot volume of EGME to obtain the  $\text{CaCl}_2$ /EGME solvate. The solvate was immediately placed into an empty desiccator and the open moisture cans with clay samples were added. The desiccator was then evacuated at approx. 6.7 Pa using an ALCATEL PASCAL 2005 SD vacuum pump (ALCATEL INC., Palo

Alto, CA) for 45 min. After the evacuation was completed, the desiccator was sealed and the samples were allowed to equilibrate with the EGME atmosphere for 2 to 4 h, then the desiccator was re-pressurized and the aluminium cans were covered with lids and weighed. After this step, the desiccator content was again evacuated and the protocol was repeated until a constant weight of the clay samples was reached (0.0001 g precision). The total SSA values were then calculated according to Carter et al. (1965). For the determination of the external SSA values, the internal surfaces of clay minerals were collapsed by annealing the clay samples at 873 K for 2 h (Jury et al., 1991).

The annealing was done in a CARO muffle furnace (WEISS GALLENKAMP, Loughborough, UK) and the EGME-adsorption protocol was repeated. The second measurement yielded the external SSA. The internal SSA was calculated as the difference between the total and the external SSA values. The organic carbon content of the clay samples was determined upon combustion at 1273 K, using the PRIMACS TOC ANALYZER (SKALAR, Breda, Netherlands). Determination of the organic carbon complied with the international standards including the requirements of the U. S. EPA 9060 method requirements (Caslab, 2010).

### Sorption isotherm measurements

Air-dried and biphenyl-free clay samples were used in the sorption experiments. First, the required amount of the clay mineral; that is 1.52 g for illite and 3.80 g for kaolinite and bentonite was weighed out into a pre-cleaned amberlite glass vial (40 cm<sup>3</sup>). Aqueous phase consisted of CaCl<sub>2</sub> (5 mmol.dm<sup>-3</sup>) and NaN<sub>3</sub> (3 mmol.dm<sup>-3</sup>). Sodium azide was added to prevent biodegradation of biphenyl during sorption experiments (Xia and Pignatello, 2001). Its addition influenced the ionic strength of the aqueous phase and resulted in the accurate mass balance of biphenyl throughout sorption experiments. No other influences on the results of the study are expected. Stock solution of biphenyl was prepared by dissolution of the required amount of its crystals in methanol in a volumetric flask (50 cm<sup>3</sup>). The concentrations of the stock solution varied between 1.54 to 2.00 g.dm<sup>-3</sup> and it was stored at 277 K if not in use. A fresh stock solution was prepared once a week. For each clay mineral, 11 different initial concentrations of biphenyl from 15 to 4500 ng.cm<sup>-3</sup> were then prepared by spiking 38 cm<sup>3</sup> of the aqueous phase with different volumes of the methanolic stock solution or relevant dilutions of it. The spiked aqueous phase was added to the clay minerals inside the amberlite vials. The contents of the 40 cm<sup>3</sup> vials were mixed thoroughly to achieve complete visible wetting of the clay mineral. The vials were then closed with polypropylene caps with the PTFE-lined silicone septa. The final concentration of methanol in all aqueous phases was always below 0.1% (v/v).

The accuracy of spiking was equal to 103 ± 6 % of the target biphenyl concentration, and it was verified using liquid-liquid extraction (Haluška et al. 1995). The *X* values were equal to the mass of the clay particles divided by the volume of the aqueous phase. The respective values used in the sorption experiments are shown in Table 1. The 40 cm<sup>3</sup> vials with the clay-aqueous phase suspensions and biphenyl were placed onto an orbital shaker and incubated in a dark room at 200 rpm. The temperature was controlled at 301 ± 2 K and the incubations lasted for 6 or 21 days. These equilibration periods were chosen because to date only a 24 h equilibration periods were studied (Sheng et al., 2001) and data for longer equilibration periods are missing in the literature. All experiments were performed in triplicate. The pH values of the aqueous phase were monitored periodically throughout the sorption isotherm experiments and were equal to 7.00 ± 0.16. Blank samples of clay suspensions and biphenyl solutions without clays additions were incubated as controls under identical conditions as the sorption isotherm samples.

### Measurement of *Q<sub>L</sub>* and *S*

Measurement of *Q<sub>L</sub>* in the batch equilibration method usually involves separation of the soil particles and the aqueous phase by centrifugation which can however, lead to changes in the established sorption equilibrium (Pawliszyn, 1997). This is because centrifugation inputs new energy into the system, which can lead to an increase in the temperature in the samples from the isotherm experiment. Since the sorption partition coefficient is a distribution constant, it is affected by temperature (Zhao et al., 2003). Increase in temperature can, thus result in the disruption of the established sorption equilibrium. Such disruption in turn causes that the *K<sub>d</sub>*/*K* values are influenced by the sample extraction process. To avoid this, a headspace SPME extraction technique was developed and used for the determination of the *Q<sub>L</sub>* values of biphenyl. In this SPME technique, a small subsample of the clay-aqueous phase suspension is withdrawn after the incubation period. The subsample is placed into a small vial with a headspace and the vial is then closed. As a result, biphenyl molecules that are freely dissolved in the aqueous phase of the subsample, that is account for *Q<sub>L</sub>*, evaporate and are extracted from the vial headspace. The biphenyl concentration in the headspace is directly proportional to *Q<sub>L</sub>*, that is the GC/MS response in headspace SPME in this study is directly proportional to *Q<sub>L</sub>* and the sorption equilibrium established is not disturbed (Pawliszyn, 1997).

The Henry's law constant of biphenyl was found to be independent of *Q<sub>L</sub>* and so calibration of the GC/MS response was obtained by the external standard method using solution of biphenyl in the aqueous phase. After the sorption experiments, individual 40 cm<sup>3</sup> vials were taken as samples for the measurement of *Q<sub>L</sub>* and *S<sub>L</sub>* and placed in a fume hood. They were quickly opened and 2.5 cm<sup>3</sup> of the aqueous phase was quickly removed and immediately pipetted into a 4 cm<sup>3</sup> amberlite vial. Both vials that is volumes 4 and 40 cm<sup>3</sup> were then promptly sealed with screw caps and the PTFE-lined septa. Care was taken not to contaminate the neck of the 4 cm<sup>3</sup> vial with the aqueous phase sample. The 40 cm<sup>3</sup> vial was put aside and kept away from direct sunlight until a liquid-liquid extraction was performed for mass balance calculations. The *S* values for biphenyl were calculated using mass balance from the SPME and the liquid-liquid extraction. Septum of the 4 cm<sup>3</sup> amberlite vial was pierced and the SPME fibre was immersed into the vial headspace (immersion depth 0.6 cm, exposure time 5 min). After the SPME extraction, the SPME fibre was retracted and biphenyl was immediately desorbed at 593 K in the injector of the 3800 GC-SATURN 2000 MS (VARIAN INC., Palo Alto, CA) for 3 min. Helium was used as the mobile phase and the GC instrument was operated in the constant flow mode at 1.0 cm<sup>3</sup>.min<sup>-1</sup>.

The temperature program for the DB-5 column was as follows:

Initial temperature 373 K, ramp to 435 K at 2.5 K/min, ramp to 553 K at 20 K/min.

The injector temperature was set to 593 K, while the detector was set to 553 K. Content of each 40 cm<sup>3</sup> vial was extracted using the method of Haluška et al. (1995). The biphenyl concentration was quantified using GC/MS as mentioned in the previous paragraph. Reproducibility of all GC/MS analyses was 5% or less.

### Mathematical analysis of data and molecular calculations

Sorption isotherms were fitted using Freundlich or linear isotherms using the Microcal Origin software package (version 6.0; MICROCAL SOFTWARE, INC., Northampton, MA, USA). Values of *K<sub>d</sub>* were determined as the first derivative of *S* according to *Q<sub>L</sub>*, using non-linear or linear regression analyses. To assess whether the biphenyl molecules could fit into the interlayer space of illite and bentonite, its molecular dimensions in a flat conformation were

**Table 1.** Sorption parameters of biphenyl on kaolinite, illite and bentonite as mentioned in Equations 1 to 4.

Clay	Period <sup>b</sup> (days)	$C_L \cdot 10^2$ (ng.cm <sup>-3</sup> )	$S \cdot 10^2$ (ng.g <sup>-1</sup> )	$K_d$ (cm <sup>3</sup> .g <sup>-1</sup> )	$X$ g.cm <sup>-3</sup>	$K$
Kaolinite <sup>a</sup>	6	0.20-36.0	0.00-13.8	9.1 ± 0.7	0.10	0.91 ± 0.07
Illite	6	0.30-17.5	11.0-800	42.7 ± 1.8	0.04	1.71 ± 0.08
	21	0.28-9.20	25.0-990	120 ± 8	0.04	4.80 ± 0.32
Bentonite	6	0.32-17.0	4.00-32.5	20.3 ± 0.3	0.10	2.03 ± 0.03
	21	0.65-16.0	9.60-350	23.0 ± 1.1	0.10	2.30 ± 0.11

<sup>a</sup> Only the maximum values of  $K_d$  and  $K$  are shown. <sup>b</sup> Incubation period during sorption experiments.

calculated using the SYBYL computer package (version 6.7, TRIPOS INC., St. Louis, Missouri, USA). The paired  $t$ -test was used to compare  $K_d$  and  $K$  values and it was performed using the Microsoft Excel software package (Microsoft Inc., Johannesburg, South Africa).

## RESULTS

The total SSA values were equal to  $68 \pm 4$  m<sup>2</sup>.g<sup>-1</sup> for kaolinite, to  $212 \pm 6$  m<sup>2</sup>.g<sup>-1</sup> for illite and to  $738 \pm 1$  m<sup>2</sup>.g<sup>-1</sup> for bentonite. The average internal SSA values were as follows: 0.34 m<sup>2</sup>.g<sup>-1</sup> for kaolinite, 87 m<sup>2</sup>.g<sup>-1</sup> for illite and 552 m<sup>2</sup>.g<sup>-1</sup> for bentonite. Concentrations of soil organic carbon were below 0.001% (w/w) in kaolinite and bentonite. The illite samples contained 0.97% of organic carbon. According to the X-ray diffraction analysis, illite accounted for 97% of this sample's weight. For the six-day incubation period on kaolinite, the  $C_L$  values ranged from 20 to 3600 ng.cm<sup>-3</sup> and sorption followed the Freundlich sorption isotherm as shown in Equation 1 and Table 1:

$$S = \frac{K C_L^N}{1 + K C_L^N} \quad ; \quad R^2 = 0.994 \quad (1)$$

The  $S$  values ranged from 100 to 13800 ng.g<sup>-1</sup>. The  $K_d$  values were calculated as the first derivative of  $S$  according to  $C_L$  as shown in Equation 2:

$$K_d = \frac{dS}{dC_L} = \frac{K N C_L^{N-1}}{1 + K C_L^N} \quad ; \quad = 2.39 \cdot 10^{-5} \quad (2)$$

The  $K_d$  values increased from 0.1 to 9.1 cm<sup>3</sup>.g<sup>-1</sup> as the  $C_L$  values increased from 20 to 3600 ng.cm<sup>-3</sup>. There was no statistically significant difference between the initial biphenyl concentrations in the aqueous phase at day 0 and the  $C_L$  values on day 21 (the paired  $t$ -test at 5% level of significance with  $p$ -value  $\leq$  0.02). Therefore no biphenyl sorption onto kaolinite was observed after 21 days, and the  $K_d$  values decreased from 0.1 to 9.1, to 0 cm<sup>3</sup>.g<sup>-1</sup> between 6 and 21 days of incubations. After 21

days of incubation, fully reversible desorption or complete loss of binding capacity for biphenyl could provide an explanation for this observation. For the case of biphenyl sorption to illite and bentonite, the sorption isotherms of biphenyl were linear ( $R^2$  values ranged from 0.942 to 0.998) as shown in Equation 3 and Table 1:

$$S = d \cdot L \quad (3)$$

The  $C_L$  values ranged from 28 to 1750 ng.cm<sup>-3</sup>, while the  $S$  values ranged from 400 to 99000 ng.g<sup>-1</sup> (Table 1). The  $K_d$  values range from  $20.3 \pm 0.3$  cm<sup>3</sup>.g<sup>-1</sup> for bentonite after 6 days to  $120 \pm 8$  cm<sup>3</sup>.g<sup>-1</sup> on illite after 21 days. Different  $X$  values had to be used for different clay minerals, to minimize standard deviations of measured  $S$  and  $C_L$  values.  $K_d$  has been shown to vary with the changes in the  $X$  (U. S. EPA, 1999). Therefore, the sorption affinity of biphenyl for individual clay minerals can only be compared between the individual clay minerals once the influence of  $X$  has been eliminated. This can be done using the  $K$  values and were calculated according to Equation 4:

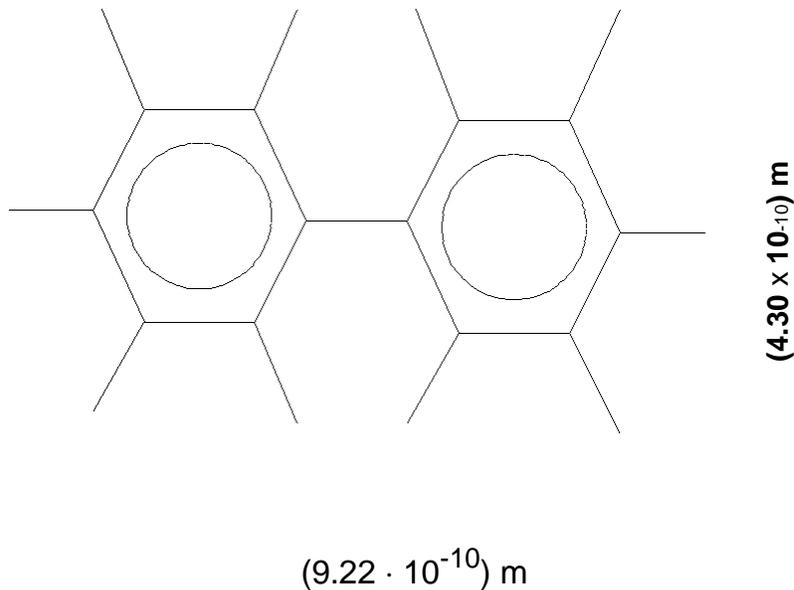
$$K = \frac{S}{C_L} \quad (4)$$

The results are shown in Table 1. After 6 days the relative sorption affinity of biphenyl for bentonite that is  $K$  was 19% higher than towards illite and 223% higher than for the maximum affinity for kaolinite. After 21 days, there was a 280% increase in the  $K$  value for illite, but only

13% increase in the  $K$  value for bentonite, compared to 6 days of incubation. The increase in  $K$  on bentonite was not statistically significant (the paired  $t$ -test at 5% level of significance;  $0.001 \leq p$ -value  $\leq$  0.002). Results of molecular calculation provide the estimated dimensions of the biphenyl molecule which are shown in Figure 1.

## DISCUSSION

All three minerals used in this study are crystalline clays (Brady and Weil, 2008). Kaolinite consists of 1:1



**Figure 1.** Molecular dimensions of the biphenyl molecule as calculated using the SYBYL computer package version 6.7.

arrangement of one tetrahedral aluminosilicate sheet with  $\text{Si}^{4+}$  cations and one octahedral aluminosilicate sheet with  $\text{Al}^{3+}$  cations. These sheets are stacked on top of each other and the adjacent layers undergo hydrogen bonding between an OH group from one layer and an O atom from the next layer (Brady and Weil, 2008). Due to this H-bonding the crystal structure of kaolinite does not expand when wetted with water. The internal specific surface areas of kaolinite thus constitute a negligible part of the total specific surface area (Jury et al., 1991). As a result, sorption of organic chemical compounds can only take place on the external surface of kaolinite (Gianotti et al., 2008). The sorption affinity for cations is relatively low for kaolinite as indicated by the cation exchange capacities from -1 to -15 cmol/kg (Brady and Weil, 2008). The particle diameter of kaolinite particles ranges from 0.5 to

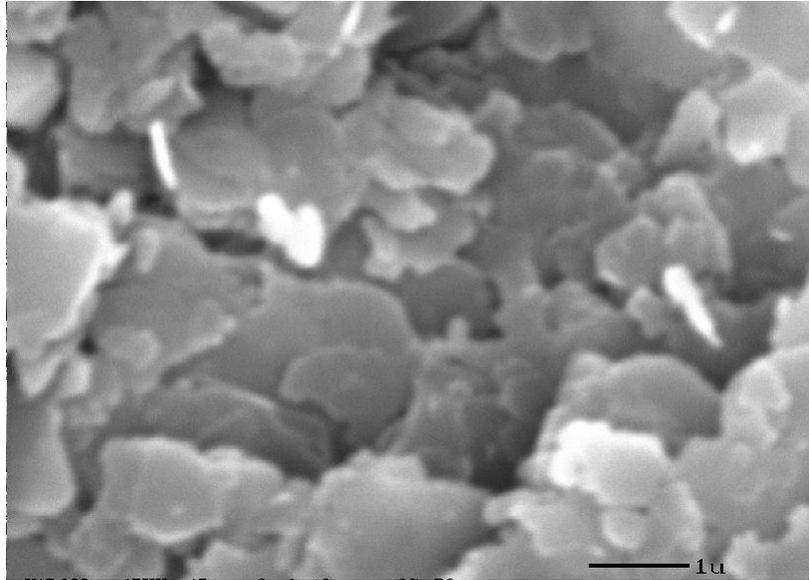
1.0  $\mu\text{m}$  and they are mostly hexagonal in shape (Brady and Weil, 2008). This was proven for the sample of kaolinite used in this study as shown in Figure 2. Illite and bentonite belong to the 2:1 crystalline clay minerals which have one octahedral sheet sandwiched between two tetrahedral aluminosilicate sheets; and their particle diameters range from 0.01 to 2.0  $\mu\text{m}$  (Brady and Weil, 2008). The cation exchange capacities vary from -10 to -40 cmol/kg for illite and -80 to -150 cmol/kg for bentonite (Brady and Weil, 2008). This indicates that both minerals have a higher surface concentration of negative charge per kg of clay than kaolinite that is they have a higher affinity for sorption of cations.

Bentonite is a member of the smectite group of clays (Brady and Weil, 2008). High values of the cation exchange capacities result from the isomorphous substitution of  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral sheets, and

$\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheets in the smectite group of clays. Layers are held together by weak non-covalent interactions between O-O atoms and cations and oxygen atoms, respectively. This leads to among other things the exposure of large internal surfaces for adsorption of  $\text{H}_2\text{O}$ , cations and possibly organic compounds. The structure of bentonite undergoes swelling upon water adsorption. Illite is a member of the nonexpanding 2:1 clays of the fine-grained mica family (USGS, 2001; Brady and Weil, 2008). In contrast to bentonite, the negative charge on the surface of illite originates from the isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sheets only. The high cation exchange capacities lead to the sorption of the  $\text{K}^+$  cations in hexagonal spaces which are located between the O atoms in the tetrahedral clay sheets. Close association of the potassium cations and the oxygen atoms results in the strong attractive forces between the sheets, thus preventing expansion of the illite particles upon water adsorption (Brady and Weil, 2008). Internal surface are available for adsorption of organic molecules, water and cations, but the total specific surface area is intermediate between kaolinite and bentonite (Jury et al., 1991). The total SSA values for clay minerals fall inside the following intervals (Jury et al., 1991; Kahr and Madsen, 1995; Li et al., 2004a; Brady and Weil, 2008): kaolinite 5 to 43  $\text{m}^2 \cdot \text{g}^{-1}$ ; illite 78 to 200  $\text{m}^2 \cdot \text{g}^{-1}$  and bentonite 630 to 800  $\text{m}^2 \cdot \text{g}^{-1}$ .

The internal SSA for bentonite accounts for 81 to 87% of the total SSA value (Brady and Weil, 2008). Therefore the SSA values measured in this study for kaolinite and illite are higher than the literature values, while the values for bentonite are comparable to previously reported data.

This is probably caused by the use of the EGME



**Figure 2.** Scanning electron microscopic images of kaolinite particles.

method which has been shown to provide higher SSA values for some minerals than other methods (Arnepalli et al., 2008). Sorption of biphenyl on kaolinite followed Freundlich isotherm with  $N$  equal to 2.57. Sorption of biphenyl to clay minerals has not been studied extensively and so there are no reports on the Freundlich isotherm sorption behaviour in the literature. This type of isotherm was reported for sorption of PCBs on soot and coal (Januten et al., 2010), and hydrocarbons which are structurally similar to biphenyl on clay minerals (Chen et al., 2008). Therefore some of this data is used to evaluate the sorption of biphenyl to kaolinite after 6 days.

Naphthalene is an aromatic hydrocarbon with a similar structure to that of biphenyl. It has fused aromatic rings which are not linked via a C-C sigma bond. Its logP is equal to 3.29 (Chen et al., 2008) that is of similar hydrophobicity as biphenyl. Sorption experiments of naphthalene on bentonite from MilliQ water and 0.5 M KCl led to Freundlich isotherms with  $N$  ranging from 0.7960 to 1.1675; and  $K_d$  varying between 0.939 and  $1.598 \text{ cm}^3 \cdot \text{g}^{-1}$  (Chen et al., 2008). The authors explained these values through the dissolution of the naphthalene molecules in the interfacial water film attached to the bentonite particles during naphthalene sorption (Chiou et al., 1985). Thus this is indicative of sorption to external clay mineral surfaces. The  $K_d$  values for biphenyl on kaolinite have similar values as reported by Chen et al. (2008), namely between 0.1 to  $9.1 \text{ g} \cdot \text{cm}^{-3}$ . This indicates that sorption of biphenyl took place on the external surface of the kaolinite particles. The wider  $K_d$  interval for biphenyl in this study probably indicates that biphenyl had a higher affinity for the external surfaces of clay minerals than naphthalene. At the same time, the  $N$  value for biphenyl measured in this study exceeded the values reported for naphthalene. This observation is explained

as follows:

Skopp (2009) showed that Freundlich sorption isotherm can be derived using the fractal kinetics to describe the rate of sorption and desorption as shown in Equation 6:

$$\frac{dC_L}{dt} = -L_1 \cdot C_L^{N_1} + L_2 \cdot S^{N_2} \quad (5)$$

After sorption equilibrium has been reached, left-hand side of Equation 5 is equal to zero and thus the Freundlich isotherm takes the form of Equation 6:

$$S = K_f \cdot C_L \quad N = \frac{L_1 \cdot \frac{1}{N_1}}{L_2 \cdot \frac{N_2}{N_1} \cdot C_L} \quad (6)$$

Comparing the right-hand side of Equation 1 and 6, it can be concluded that  $N$  is equal to the ratio of  $N_1$  and  $N_2$ . It can be seen that if  $N_1$  is greater than  $N_2$ , then the sorption is kinetically of a higher order than desorption. As a result, the Freundlich isotherm is concaved up, that is the  $N$  value is greater than 1.00. This was the situation for the biphenyl sorption on kaolinite after 6 days when  $N$  had a value of 2.57. After a 24 h equilibration period, Sheng et al. (2001) reported that the  $K_d$  value for biphenyl was equal to  $6.40 \text{ cm}^3 \cdot \text{g}^{-1}$  on the potassium-saturated smectite and equal to  $791 \text{ cm}^3 \cdot \text{g}^{-1}$  on a muck sample (an organic soil). Li et al. (2004a) studied the sorption of three pesticides, including biphenyl, onto smectite exchanged with different proportions of  $\text{K}^+$  and  $\text{Ca}^{2+}$ . Following a 24 h equilibration period on smectite,  $C_L$  for biphenyl ranged from 0 to  $2250 \text{ ng} \cdot \text{cm}^{-3}$ , while the  $S$  values ranged from 0 to  $19700 \text{ ng} \cdot \text{g}^{-1}$  (Li et al., 2004a).

The  $C_L$  intervals observed for biphenyl in this study were comparable to those of Li et al. (2004a) for illite and bentonite sorption after 6 days and bentonite sorption after 21 days. At the same time, the  $S$  intervals were wider and reached higher maximum values in this study. Intervals for  $C_L$  and  $S$  for kaolinite after 6 days of incubation were comparable to those of Li et al. (2004a), while the maximum value of  $K_d$  for kaolinite after a 6 day incubation was comparable to the data of Sheng et al. (2001). The sorption to kaolinite was reversible and followed the Freundlich sorption isotherm. Reversibility of the sorption is contradictory to the observations made for organic compounds with similar hydrophobicity, for example 2,4,6-trichloroaniline with the logP value of 3.77 (Gianotti et al., 2008). All values of  $K_d$  for sorption to illite and bentonite (a smectite clay) were higher than those measured by Sheng et al. (2001). The discussion of the effects of inorganic cations on biphenyl sorption takes into account the following facts. The total ionic strength of the aqueous phases was equal to 0.018 M in this study and it was calculated using Equation 7:

$$I_c = \frac{1}{2} \cdot \sum_i (C_i \cdot z_i^2) \quad (7)$$

Ionic strength was equal to 0.100 M in the study of Sheng et al. (2001) and to 0.250 M in the study of Li et al. (2004a). The  $K_d$  values and the  $S$  intervals on kaolinite from this study and on smectite from the literature were comparable, while higher  $K_d$  and higher  $S$  values were measured for illite and bentonite in this study compared to the literature. These facts indicate that high concentrations of inorganic cations probably block the access of biphenyl molecules to the internal surfaces of the clay minerals. Such a conclusion is further supported by the observation that the extent of biphenyl sorption on smectite was independent of the concentration and chemical nature of the cations exchanged onto the surface of the smectite, if the ionic strength was 6 to 12 times higher than in this study (Li et al., 2004a).

Values of  $K$  for biphenyl sorption to illite and bentonite after 6 days, along with the lack of statistically significant difference between the  $K$  values on bentonite after 6 and 21 days of incubation, indicate that the apparent sorption equilibrium was established on the internal clay surfaces after 6 days. This is contrary to the literature data (Sheng et al., 2001). Molecular dimensions of biphenyl in a flat conformation were equal to  $4.30 \cdot 10^{-10}$  by  $9.22 \cdot 10^{-10}$  m (Figure 1). Therefore biphenyl molecules in their planar conformation would easily fit into the interlayer spaces in the crystal structures of illite and bentonite, since these range from  $10 \times 10^{-10}$  m for illite (Vali and Hesse, 1990) to  $12.3 \times 10^{-10}$  m for bentonite (Li et al., 2004a). Taking discussion above into account, biphenyl sorption onto clay minerals will be governed concentration of inorganic cations in soil solution, the type of clay mineral and

access to the internal surface areas. The influence of the total SSA of the clay mineral onto biphenyl sorption will be limited. Soil organic carbon becomes the dominant phase for biphenyl sorption in soil between 6 and 21 days. This is indicated by the  $K_d$  value for illite after 21 days of incubation which is of the same order of magnitude as the  $K_d$  value for biphenyl sorption to muck (Sheng et al., 2001).

The difference in numerical values is caused by the higher concentration of organic carbon in the muck sample, namely 49.3%, and the illite sample, that is 0.97%. The results of this study should be considered preliminary and the findings will have to be verified for other types of clay minerals.

## ACKNOWLEDGEMENTS

The authors would like to thank the United States Environmental Protection Agency (grant number R82-6652-011) for financial support of the study. Although the research described in this article has been funded by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

**Abbreviations:** **C<sub>i</sub>**, Concentration of the particular inorganic ion in the aqueous phase during the sorption experiments ( $\text{mol} \cdot \text{dm}^{-3}$ ); **C<sub>L</sub>**, freely dissolved biphenyl concentration ( $\text{ng} \cdot \text{cm}^{-3}$ ); **EFSA**, European food safety authority; **EGME**, ethylene glycol monoethyl ether; **GC/MS**, gas chromatography with mass spectrometric detection; **I<sub>c</sub>**, ionic strength of the aqueous phase during sorption experiments ( $\text{mol} \cdot \text{dm}^{-3}$ ); **K**, dimensionless partition coefficient; **K<sub>a</sub>**, the effective sorption coefficient ( $\text{cm}^3 \cdot \text{g}^{-1}$ ); **K<sub>f</sub>**, Freundlich sorption coefficient ( $\text{cm}^3 \cdot \text{g}^{-1}$ ); **L<sub>1</sub>**, fractal rate constant of adsorption ( $\text{day}^{-1}$ ); **L<sub>2</sub>**, fractal rate constant of desorption ( $\text{ng} \cdot \text{cm}^{-3} \cdot \text{day}^{-1}$ ); **Log P**, logarithm of the 1-octanol/water partition coefficient (dimensionless); **N**, Freundlich exponent (dimensionless); **N<sub>1</sub>**, fractal order of adsorption uptake in equation 6 and 7 (dimensionless); **N<sub>2</sub>**, fractal order of desorption uptake in Equation 6 and 7 (dimensionless); **PDMS**, polydimethylsiloxane; **PTFE**, polytetrafluoroethylene; **S**, sorbed concentration of biphenyl ( $\text{ng} \cdot \text{g}^{-1}$ ); **SPME**, solid-phase microextraction; **SSA**, specific surface area; **X<sub>s</sub>**, the solid/liquid ratio for clays in the sorption isotherm experiments ( $\text{g} \cdot \text{cm}^{-1}$ ); **Z<sub>i</sub>**, charge of a particular inorganic ion in the aqueous phase during sorption experiments.

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