ADSORPTION OF CHLORPYRIFOS ON ORGANOCLAY COMPLEXES: INFLUENCE OF SALT CONCENTRATION

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Abstract

Chlorpyrifos is an insecticide widely used in Palestine and elsewhere to control insects in fruit and vegetables. Its application has been associated with residues in soil and plant samples, which must be controlled to minimize the hazards to human health. The objectives of this study were: 1) to investigate the adsorption behavior of chlorpyrifos on montmorillonite exchanged with different quaternary organic cations and 2) to evaluate the influence of sodium chloride (NaCl) on the adsorption reaction. Equilibrium concentration of chlorpyrifos was determined by high performance liquid chromatography (HPLC). The adsorbed amounts of chlorpyrifos on montmorillonite exchanged by quaternary phosphonium cation (e.g. tetraphenyl phosphonium, TPP) at a loading of 0.5 mmol/g were higher than obtained on clay exchanged with quaternary ammonium cation. An interesting outcome of the study is that adsorption of chlorpyrifos on clay exchanged with benzyltrimethyl ammonium (BTMA) was lower in distilled water than in saline water. Addition of NaCl dramatically increased the adsorbed amounts of chlorpyrifos on clay modified with BTMA at a loading of 0.5 mmol/g (clay-BTMA0.5) or clay alone. The binding coefficient of chlorpyrifos on clay increased about 10 fold - at a severe case of salinity as a result of salting out effect. The changes in the free enthalpy of the adsorption reaction provide evidence of physical adsorption and indicate that the adsorption reactions are spontaneous. These findings provide better understanding of the behavior of chlorpyrifos on different organoclay complexes. Thus, the addition of salt can be useful for further development of ecologically acceptable formulation to minimize the risk to the environment.

Key Words: Chlorpyrifos, adsorption, salinity, organoclays.

Introduction

Chlorpyrifos [O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) is an insecticide widely used to control Coleoptra, Diptera, Homoptera and Lepidoptra in soil or foliage in over 100 crops. Application of Chlorpyrifos has been shown to damage the environment. It has been shown that its incorporation in soils has a variety of degradation modes. It is degraded at a moderate rate DT_{50} (lab) 10-120 days (25 °C); Field DT_{50} 33-56 day (WHO, 1986).

Interaction of Chlorpyrifos with organic matter in soil has been studied. It was found that increasing cellulose concentration in sand treated with chlorpyrifos significantly reduced the mortality of *Reticulitermes hesperus* in direct exposure (Smith and Rust, 1993). Apparently, interaction of chlorpyrifos molecules with cellulose particles makes them less available. Turnbull et al. (1997) studied the fate of four pesticides including chlorpyrifos applied to agricultural land in England. Levels of the relatively particle-bound chlorpyrifos were measured in drainage water and field soil following application. Observed concentration in water was generally below 1 µg/l. Additional bioassay experiments showed that levels of chlorpyrifos lethal to *Gummarus putex* reached the stream during spring 1993. Tunceli et al. (2001) investigated several parameters that can influence the retention of chlorpyrifos on *Saccharomyces cerevisiae* immobilized on sepiolite using the column sorption method. Results showed that it was possible to achieve quantitative analysis when the pH was 6 using 100 ml of sample solution containing 20 µg of chlorpyrifos and 5 ml elute and the capacity of sorbent was 28 mg/g. Wu et al. (2002) evaluated the environmental fate of chlorpyrifos under customary field management practices during 1996 and 1997. No significant difference in clipping removal and volatilization loss were observed in both years, but significant lower cumulative leaching and lower soil concentration was observed in 1997 than in 1996.

Huang and Lee (2001) studied the interaction among soil, chlorpyrifos, and dissolved organic matter (DOM) from poultry, swine, and cow waste-derived lagoon effluents. They found all DOM have a strong affinity for chlorpyrifos, thus a reduced sorption of chlorpyrifos by soil was observed, consequently mobility was inhibited. Rouchaud et al. (1996) found that recent organic fertilizer treatments (cow manure, pig slurry, composts, or green manure) simultaneously increase insecticide adsorption and soil persistence, indicating a mechanism of slow release of insecticide into the soil by organic matter. Roinestad et al. (1993) analyzed air born dust for possible adsorption of chlorpyrifos and found that pesticide concentration were higher in dust than in air samples. Leidy and Wright (1991) studied the effect of five adsorbents used by government and private laboratories to collect air born pesticides including chlorpyrifos. Wilcock et al. (1994) reported that 50% of the applied chlorpyrifos was lost from water within a 545 minute study due to a slower moving stream with more organically enriched sediments. Valverde et al. (1992) studied the adsorption of chlorpyrifos in soils of Almeria province (Spain) and found that adsorption isotherms may be classified as S-type of Gilles classification.

Cryer and Laskowski (1998) studied chlorpyrifos release from clay granules, and found that advection release was the dominant mechanism followed by diffusion and volatilization. Racke et al. (1993, 1994) studied the degradation and the fate of chlorpyrifos in agricultural and urban environments. They found that application of chlorpyrifos to soil resulted in large initial residue levels and increased persistence, nearly 70% of the initially applied chlorpyrifos remained in soil 18 months after application. Subsequent laboratory investigations revealed chlorpyrifos degradation half-lives ranged between 116-1576 days in five soils. Cink and Coats (1993) studied the effect of concentration temperature and soil moisture on the degradation of chlorpyrifos in an urban Iowa soil. They found that temperature did not affect degradation or mineralization of chlorpyrifos or its metabolites, whereas soil moisture greatly affected mineralization. Rouchaud and Gustin (1991) found that the rates of chlorpyrifos soil metabolism were smaller in organic fertilizer amended soil than in the untreated soil. Malek et al. (1997) found a first phase half-life of chlorpyrifos about 22 days in simulated cattle dipping vat, and bound fraction was less than 5%.

Very little information about the adsorption behavior of chlorpyrifos on clay or organoclay is available. The objectives of this work are: 1) to investigate the adsorptive behavior of chlorpyrifos on montmorillonite clay exchanged with different organic cations, 2) to evaluate the influence of NaCl concentrations on the adsorption behavior of chlorpyrifos.

Materials and Methods

Materials

The clay used was sodium montmorillonite SWy-2 (Clay) obtained from the Source Clays Repository, Clay Minerals Society, Columbia, MO. HPLC grade of methanol, benzyltrimethylammonium (BTMA), benzyltriethylammonium (BTEA), benzyltributyl-ammonium (BTBA), tetramethylammonium (TMA), tetraphenylphosphonium (TPP), methyltriphenylphosphonium (MTPP), tetrabutylphosphonium (TBP), were purchased as chloride salts from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO, USA; Aldrich Chemical Co., Milwaukee, WI, USA). The chemical structures of the organic compounds are shown in Figure 1. Analytical grade NaCl was obtained from Frutarom Laboratory Chemicals (USA). Analytical grade chlorpyrifos, purity 99.5 %, was purchased from ChemService USA. Its oral acute LD_{50} for rat is 135-163, guinea pigs 504 mg/kg body weight, the aqueous solubility is 1.4 mg/l, K_{ow} log P= 4.7, and Henry low constant is $6.76*10^{-1}$ Pa M^3 mol^{-1} (Tomlin, 2000).

Preparation of organo-clay complexes

The organo-clay complexes were prepared by addition of dry crystals of organic cation equivalent to 0.5 mmol/g clay to a 1% (w/v) aqueous suspension of montmorillonite under continuous stirring up to 3 days. The yielded organoclay complex was separated after 30-min centrifugation (6000 *g*), the precipitate was washed three times with distilled water to have free chloride ion in the washing water, freeze-dried, ground to < 50 µm and kept in plastic bottles at room temperature.

Adsorption of chlorpyrifos on organoclays

Adsorption of chlorpyrifos on montmorillonite exchanged with either organic quaternary ammonium or phosphonium cation was measured at room temperature. 12.4 mg chlorpyrifos was dissolved in 25 ml methanol; this acts as a stock solution. 2.82 ml of the stock solution, containing 1.4 mg chlorpyrifos, was transferred to a 1 liter volumetric flask and diluted with distilled water and used to perform the adsorption experiments. To measure the adsorbed amounts, 25 ml of an aqueous solution of chlorpyrifos (0.035 mg/l) was added to 0.005 g clay or organoclay in a 30 ml centrifuge tube. The final concentration of the sorbent matrix was 0.2 g/l in all experiments. The samples were kept under continuous rotary shaking at 25 ± 1 °C for 48 hours. The supernatant was separated by centrifugation at 6,000*g* for 1 h.

Batch adsorption experiments

Batch adsorption experiments were conducted to simultaneously determine the adsorption isotherms on clay or clay-BTMA0.5. The adsorption isotherms were measured in the range of 0-1400 µg chlorpyrifos/l, the maximum solubility limit. Appropriate aliquots of an aqueous solution of chlorpyrifos 1400 µg/l were diluted in 25 ml distilled water and were added to a 0.005 g clay or organoclay in a 30 ml centrifuge tube. The samples were kept under continuous rotary agitation for 48 hours at 25 ± 1 °C. The supernatant was separated as described above. The adsorbed amounts were calculated using eq (1)

$$Q_s=(Q_i-Q_e)V/M \qquad (1)$$

Where Q_i and Q_e are the initial and equilibrium concentration in µg/l, and Q_s is the concentration in the solid phase in µg/g (the adsorbed amount). V is the volume (L) and M is the mass of adsorbent (g). Chlorpyrifos concentration in the supernatants were determined by a high performance liquid chromatography (HPLC) as described below.

Influence of different salt concentrations on the adsorption process

The influence of NaCl concentrations (0.0, 10, 40, 80, and 150 g/L) on the adsorption behavior of chlorpyrifos was measured only on clay alone (clay without organic fraction) and clay saturated with BTMA, at a loading of 0.5 mmol/g clay. In this procedure: appropriate aliquots of an aqueous solution of chlorpyrifos 1400 µg/l were diluted in 25 ml distilled water and were added to a 0.005 g clay-complex in a 30 ml centrifuge tube containing appropriate amounts of NaCl as mentioned above. The samples were vortexed for 3 min to ensure complete dissolving of NaCl and kept under continuous rotary agitation for 48 hours at 25 ± 1 °C. The supernatant was separated as described above.

HPLC measurements

Chlorpyrifos concentrations in the supernatant were determined by HP 1090 HPLC (Hewlett-Packard, Wilmington, DE) equipped with an auto-injection system and diode-array detector (DAD). The column was a 250 mm x 4.6 mm (i.d.) as described reverse-phase. Adsorbophore HS C18 (5µm, Alltech, Deefield, IL) was used, the injection volume was 25 µl and the wavelength of detection was 230 nm, the mobile phase was water:methanol 25:75. The flow rate maintained 1.0 ml min^{-1}. External calibration was used for quantification of chlorpyrifos.

Model calculations

To evaluate the adsorption mode of chlorpyrifos, the experimental data points were fitted to the Freundlich equation:

$$\log Q_s = \log K_f + 1/n \log Q_e \qquad (2)$$

Where K_f is the Freundlich constant, and 1/n is a measure of the intensity of adsorption and reflects the degree to which adsorption is a function of concentration.

K_f values were also normalized to the fraction of organic carbon in the complex to form K_{oc} and to compare it with K_{ow} (Eq 3) of chlorpyrifos to understand the mechanism of adsorption. Values are summarized in Table 1.

$$K_{oc} = (K/\%OC)*100 \qquad (3)$$

Adsorption data under the influence of NaCl were fitted to the Langmuir equation (4)

$$Q_s/Q_e = K_L(M-Q_s) \qquad (4)$$

Where K_L is the Langmuir constant, and M is the maximum adsorbed amount per unit weight.

The free enthalpy of the adsorption reaction was calculated by equation (5) (Calvet, 1989),

$$\Delta G = -2.303\ RT \log Q_i/Q_e \qquad (5)$$

where ΔG is the free energy change (K cal mol^{-1}), R is the gas constant (1.986 cal K^{-1} mol^{-1}) and T is the absolute temperature.

Results and Discussion

The cationic quaternary ammonium or phosphonium compounds shown in Figure 1, which are solids at room temperature, are surface-active agents (surfactants) because each molecule has a non-polar hydrocarbon group and an ionic, polar component. The molecular structures of the selected compounds include an aliphatic part with alkyl-chain lengths ranging from 1 to 3 carbon atoms, and an aromatic part with one or more phenyl rings attached to the ammonium or phosphonium cation. Adsorption of BTMA, BTEA, and BTBA are described previously (El-Nahhal et al., 1998, Polubesova et al., 1997).

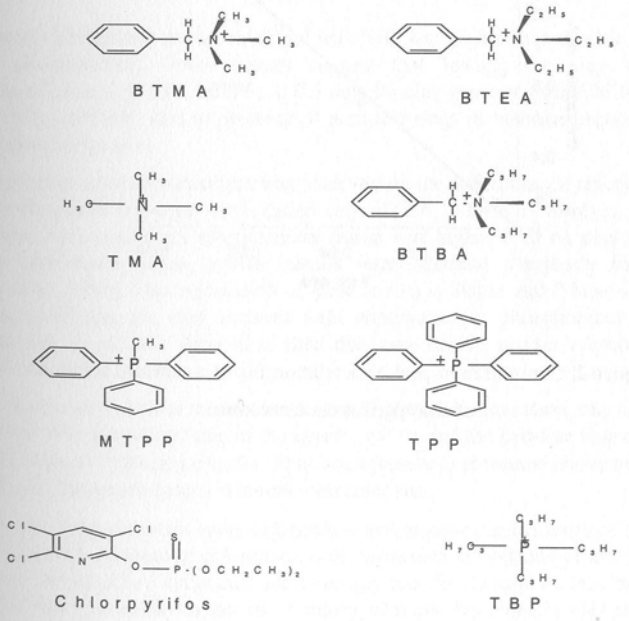

Figure 1. Chemical structure of the organic compounds used.

Standard curve of chlorpyrifos

Concentration and peak area relationship of standard concentrations of chlorpyrifos are presented in Figure 2. It is obvious that the peak area increased linearly as the concentration of chlorpyrifos increased in the solution. These findings indicate a linear relationship. Regression analysis showed a correlation coefficient (R^2) of 0.991 indicating a strong positive association. This linearity indicates the validity and the suitability of the used method and allows direct measurements of chlorpyrifos in the supernatants.

Adsorption of chlorpyrifos on clay alone and/or clay exchanged with different types of organic cations are shown in Figure 3. It is obvious that low concentration of chlorpyrifos was adsorbed on clay alone, whereas clay modified with quaternary ammonium (BTBA, BTEA, BTMA) or phosphonium cation, (TPP, MTPP, TBP) resulted in variant increases in the adsorbed amounts of chlorpyrifos. These results are due to changing the surface properties of the clay from hydrophilic to hydrophobic as a result of ion exchange reaction using organic cations. Organoclays have been shown to adsorb significant amounts of non-ionic hydrocarbon from water (Boyd et al., 1988; Jaynes and Boyd 1990, Lagaly 1994; Mortland et al., 1986; Nir et al., 2000; El-Nahhal et al., 2000).

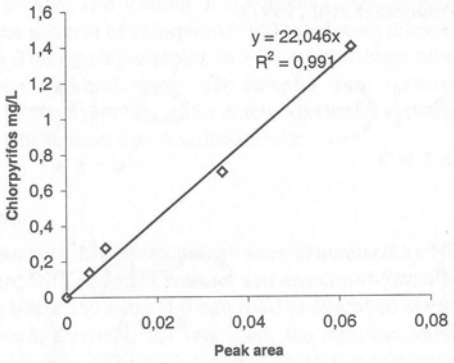

Figure 2. Concentration-peak area relationship of a standard solutions of chlorpyrifos concentration.

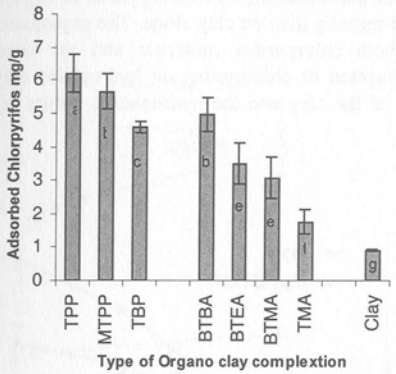

Figure 3. Adsorption of chlorpyrifos on montmorillonite exchanged with different organic cations. Bars indicate standard deviation. Columns that have the same letter are not significantly different at p =0.05 level of significance.

Adsorption of chlorpyrifos on clay modified with TPP was higher than on clay modified TBP (aliphatic phosphonium). These results suggest that loading the clay with aromatic phosphonium cation (e.g. TPP, MTPP) at 0.5 mmol/g clay generates suitable adsorption sites for chlorpyrifos, probably due to presence of aromatic rings in both the organoclay complex and chlorpyrifos (Figure 1).

Relatively similar mode of interaction was observed on the adsorption of chlorpyrifos on clay modified with quaternary ammonium cation (e.g. BTBA, BTMA). However, adsorption on clay modified with quaternary phosphonium cation was higher than on clay modified with quaternary ammonium cation, similar results were obtained previously for other cases (Lawrence et al., 1998). The explanation of these results is that N and P have similar valance state. Thus modifying the clay surfaces with ammonium or phosphonium cation would generate similar or suitable adsorption sites that may enable similar adsorbed amount of chlorpyrifos.

However, the geometry and/or the molecular size of phosphonium cation may allow for better interaction between the phenyl ring of the organic cation and the pyridine ring of chlorpyrifos molecule through π–π electron transfer. Thus adsorption was increased above that obtained by Clay-BTMA/BTEA which have a different molecular size.

In addition, π-π interactions between organoclays and organic molecules have been shown to affect the adsorbed amounts of chloroacetanilde herbicides (El-Nahhal et al., 2000), and the orientation of the adsorbed molecules due to energy transfer through molecules (Stevens and Anderson, 1996). Adsorption isotherms of chlorpyrifos on clay alone or clay exchanged with BTMA at 0.5 mmol/g are shown in Figure 4.

It is evident that a linear relationship between the adsorbed amounts and added concentration was observed on clay alone or on clay partially saturated with BTMA at a loading of 0.5 mmol/g clay. It is obvious that adsorption of chlorpyrifos is higher on clay modified with BTMA at a loading of 0.5 mmol/g than on clay alone. The explanation for these results is the hydrophobic nature of both chlorpyrifos molecule and the organoclay complex (clay-BTMA0.5). The low adsorption of chlorpyrifos on hydrophilic clay surfaces is due to the hydrated mineral surface of the clay and the hydrophobic nature of chlorpyrifos K_{ow} = 4.7 (Tomlin, 2000).

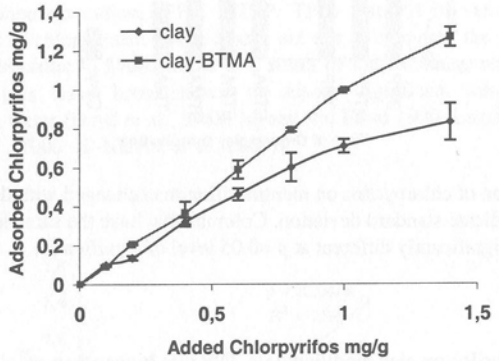

Figure 4. Adsorption isotherms of chlorpyrifos on clay and clay exchanged with BTMA at a loading of 0.5 mmol/g. Bars indicate standard devaition.

The adsorption data were fitted to the Freundlich equation (2). The resultant Freundlich adsorption coefficients are normalized to the fraction of organic carbon in the clay complex as in equation (3), which gives the value of K_{oc} (Table 1). A comparison between K_{oc} and K_{ow} values showed significant differences. This data indicate that chlorpyrifos interact with the organoclay surfaces via adsorption forces such as ionic bonding, dipole-dipole interaction, hydrogen bonds and or energy transfer bonds due to the presence of π-bonds in the chemical structure.

Furthermore, calculation of the free energy of the adsorption reaction using equation (5) provides additional evidence of physical adsorption rather than partitioning, indicating that the fraction of organic carbon is not the key issue in the adsorption process; similar results were observed for other cases (El-Nahhal, 2002). It seems that the chemical structures of both organic cation and chlorpyrifos have a strong influence on the adsorption process.

Influence of NaCl concentrations on adsorption of chlorpyrifos on clay or clay-BTMA0.5 is shown in Figure 5. It is obvious that adsorption of chlorpyrifos on clay partially saturated with BTMA at 0.5 mmol/g, sharply increased as the concentration of NaCl jumps from 0 to 10 g/l in the equilibrium solution. A relatively linear increase of the adsorbed amount of chlorpyrifos was also observed as NaCl concentration continues to increase. These results indicate positive

and strong association between the adsorbed amount of chlorpyrifos and the concentration of NaCl. Furthermore, adsorption on clay was also influenced by NaCl concentration, indicating a positive association.

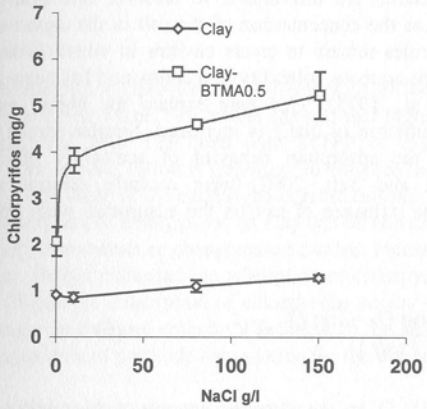

Figure 5. Adsorption of chlorpyrifos on clay and clay-BTMA0.5 under different salt concentration. Bars indicate standard deviation

However, influence of NaCl concentrations on the adsorption behavior is more pronounced at a lower concentration of NaCl. This can be pronounced as the salt influence on the adsorption behavior. The influence of NaCl on the adsorption behavior may be explained as follows:

1) Reduction of the clay surface negative potential thus enables more adsorption of chlorpyrifos as shown in the case of clay alone.
2) Reduction of the hydration state of the clay surfaces at a micro-scale level in the surfaces. This effect may be referred to as generation of hydrophobic sites in the clay surfaces. Thus it allows to adsorb more hydrophobic molecules.
3) A salting out effect on the adsorption process similar to that of partitioning nonionic compound into two phases, one of them being water. Thus addition of salt may decrease the solubility of chlorpyrifos in water and thus increase its partitioning in the non-polar phase, (the organoclay complex). It was observed that the predominant ionic species found in natural water always decrease the aqueous solubility of non-polar compounds (McDevit and Long, 1952; Godon and Thorne, 1967).

This effect is commonly referred to as salting out phenomena which one can qualitatively picture as the ion produced during the dissolution of a salt tightly binds water into hydration shells, which has long been recognized to reduce the volume of aqueous solution even macroscopically by a process known as electrostriction (Schwarzenbach et al.,1993). These tightly bound water molecules are unavailable to dissolve into non-polar organic solute molecules. Consequently, as the concentration of the salt in the aqueous solution increased, less and less water molecules remain to create cavities in which to accommodate organic solute. This reduction in the aqueous solubility of a compound has been shown to increase its adsorption (Carringer et al., 1975). This may explain the higher adsorbed amounts of chlorpyrifos as the concentration of NaCl is increased. Similar results on the influence of NaCl concentrations on the adsorption behavior of acetochlor (El-Nahhal, 2002), and Phenanthrene (El-Nahhal and Safi, 2002) were recently demonstrated. However, the experimental results of the influence of salt on the adsorption were fitted very well to the following equation:

$$\frac{[salt]\log Q_0 - \log Q_s}{[salt]} = K_s \qquad (6)$$

K_s is the salting constant, Q_o, Q_s are the adsorbed amounts of chlorpyrifos in µg/g from distilled water and at a salinity level respectively, [salt] is the concentration of NaCl in µg/g during the adsorption process. This indicates the validity of the relationship. This mathematical model may have an important practical value in predictions of adsorption of pollutants from saline water, and/or in the sea or its sediments.

However, a quantitative description of the influence of dissolved salts on aqueous solubilities was provided previously (Setschenow 1889) which probably has the same influence.

$$\text{Log } (S_o/S_s)=K_s[\text{salt}] \qquad (7)$$

Where S_o and S_s are the saturated solutions of the chemical in distilled water and at a salinity level respectively, [salt] is the total salt concentration and K_s is Setschenow or salting constant, a bulk constant relating the effectiveness of a particular salt or combination of salts to salt out a given compound. This model shows the salt effect on the partitioning of a certain chemical between two phases.

Influence of salt concentration on the free energy and the binding coefficient of chlorpyrifos adsorption reaction calculated from eq (5) are shown in Table 2.

It is obvious, that the magnitude of ΔG is increased as the concentration of NaCl increased in the aqueous phase in the adsorption experiment. However, the value of ΔG decreased about 4 times on the adsorption on clay alone, whereas it decreased about 12 times on the adsorption on clay-BTMA0.5 indicating high influence of salt on the adsorption process.

In addition, the value of binding coefficient based on the Langmuir equation (4) increased about 10- and 60-fold on the adsorption on clay or clay-BTMA0.5, respectively. These findings indicate a strong and positive association between salt concentration and adsorption process. The calculated value of ΔG was always negative, indicated either chlorpyrifos adsorbed on the surface of organoclay or the organoclay has undergone an expansion to accommodate chlorpyrifos molecules.

Moreover, the value of ΔG was increased proportionally as the concentration of NaCl increased (Table 2). These findings indicate that the adsorption reaction is spontaneous and further enhanced by the addition of salt.

Concluding Remarks

This study reveals the adsorption behavior of chlorpyrifos on different organoclay complexes from distilled and hyper-saline water. The results showed that higher adsorbed amounts were obtained on clay modified with TPP than with MTPP or BTMA (0.5 mmol/g clay). Exchanging the clay with organic cation is important to enhance the interactions between the chlorpyrifos molecules and those of the exchanged organic cations (Figure 3). The conclusion of this work is that adsorption of chlorpyrifos on clay can be enhanced by modifying the clay surfaces with quaternary ammonium or phosphonium cations. Increased NaCl concentration in the equilibrium system further enhanced the adsorption of chlorpyrifos beyond that obtained from distilled water (Figure 5). Adsorption of chlorpyrifos occurs via physical adsorption as observed by the changes in the free enthalpy (Tables 1 & 2). These findings may provide better methods for preparation of pesticide formulation for the use in different environments.

Table 1. Changes of the free energy of adsorption reaction as affected by fraction of organic carbon on the organclay complex.

System	K_{oc}	ΔG Kcal mol^{-1}
Clay-TPP0.5	555.9±5.42	-3.7407±(-1.0002)
Clay-MTPP0.5	998.61±6.22	-4.0874±(-1.0817)
Clay-TBP0.5	1561.8±24	-4.3521±(-1.8808)
Clay-BTBA0.5	1217.24±17.75	-4.2045±(-1.5927)
Clay-BTEA0.5	1533.61±13.99	-4.3413±(-1.5614)
Clay-BTMA0.5	1417.82±16.3	-4.2948±(-1.6519)
Clay-TMA0.5	4450.8±128.5	-4.9718±(-2.8738)
[a] K_{ow}	50118.72	-6.40485

K_{ow} =octanol-water partition coefficient, [a] data from Tomlin (2000).

Table 2. Changes of the free energy of the adsorption reaction as affected by NaCl concentration.

[NaCL] %	Clay		Clay-BTMA0.5	
	K	ΔG	K	ΔG
0	4.06±1.8	-0.4539±0.143	9.02±3.6	-0.2947±0.154
1	4.69±0.61	-0.5293±0.0776	29.72±4.1	-0.6515±0.04
8	6.82±0.08	-0.9397±0.009	41.67±8.1	-0.736±0.111
15	47.03±5.43	-1.973+0.537	625.5±58.1	-3.5155±0.09

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VON "TYPISCH NORMALEN" ZU CIS-VACANTEN DIOKTAEDRISCHEN 2:1 ALUMOSCHICHTSILICATEN

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Die Eigenschaften von Tonen werden bekanntlich durch das Gefüge und den Mineralbestand, d.h. insbesondere durch ihren Tonmineralbestand, bestimmt. Die technologischen Anwendungsmöglichkeiten der Tone sowie die diagenetische oder hydrothermale Umwandlung von Smectiten in Illite sind im Allgemeinen abhängig von der Struktur und der Kristallchemie der Tonminerale. Aus diesem Grund ist die Klassifikation und Nomenklatur der Schichtsilicate immer wieder ein aktuelles Problem in der Tonmineralogie (Warshaw & Roy 1961, Güven 1988, Zwyagin 2001). Die Beschreibung der Kristallstruktur sowie eine eindeutige Namensgebung der Minerale ist unerlässlich.

Ziel der Präsentation ist es, die für die eindeutige Nomenklatur der dioktaedrischen Smectite notwendigen Strukturmerkmale zu identifizieren.

Dioktaedrische Smectite sind 2:1 Schichtsilicate. Sie bestehen aus einer rhythmischen Folge von Schichtpaketen, die aus zwei Tetraederschichten und einer Oktaederschicht aufgebaut sind.

Durch Substitutionen der Tetraeder- und Oktaederionen entsteht ein Ladungsdefizit in den Schichtpaketen, das durch Kationen zwischen den Schichtpaketen in der sogenannten Zwischenschicht ausgeglichen wird. Unterschiedliche Minerale werden durch die Art und Anzahl der Substitutionen und damit durch die resultierende Schichtladung sowie deren Lokation definiert.

Sind 2/3 der Oktaederplätze mit dreiwertigen Aluminiumkationen besetzt, spricht man von dioktaedrischen Dreischichtsilicaten. Aufgrund der Verteilungsmöglichkeiten dieser Kationen in der Oktaederschicht unterscheidet man cis-vakante und trans-vakante Mineralvarietäten.

Smectite besitzen im Gegensatz zu Illiten eine turbostratische Fehlordnung. Dies ist der Grund, weshalb die Struktur der Oktaederschicht der Smectite nicht ohne weiteres mittels Röntgendiffraktometrie erkannt werden kann. Die hkl-Reflexe fehlen in den Diffraktogrammen der Smectite.

Erst Drits et al. (1995) haben bewiesen, dass die Struktur der Oktaederschicht mit der Dehydroxylierungstemperatur aller dioktaedrischen 2:1 Alumosilicate korreliert. Bis zu diesem Zeitpunkt war bekannt, dass Illite eher bei 500 °C dehydroxylieren, während Montmorillonite in den meisten Fällen bei 700 °C dehydroxylieren. Sie wurden als normale (typische) Illite und Montmorillonite bezeichnet (Cole 1955, Mackenzie 1957). Minerale, die ein entgegengesetztes Dehydroxylationsverhalten oder Doppelpeaks zeigten, wurden anormaler (atypischer) Illit bzw. Montmorillonit genannt. Nachfolgende Klassifikationen (Grim & Kulbicki 1961, Schultz 1969) lassen deshalb das Dehydroxylierungsverhalten und damit die Struktur der Oktaederschicht unbeachtet, wobei diese bereits nicht mehr gänzlich unbekannt war. Güven (1988) beschreibt in einem Review die Struktur der Oktaederschicht.