Time and temperature dependent sorption behaviour of dimethoate pesticide in various Indian soils

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A b s t r a c t. Experiments were conducted to study the sorption behaviour of dimethoate in three Indian soils at different temperatures. A kinetic study showed that adsorption equilibrium was reached within 15 h at different initial levels of pesticide concentration. Applicability of the pseudo second order kinetic model suggested that the adsorption process was complex and several mechanisms were involved. The Freundlich model explained the adsorption behaviour adequately and the isotherms were of S-type. The adsorption process was found to be strongly affected by temperature. The Gibbs free energy change, $\Delta G°$ values (from -15.81 to -16.60 kJ mol^{-1}) indicated that the process was spontaneous and exothermic in nature. The change in enthalpy of adsorption, $\Delta H°$ values (from -17.729 to -21.539 kJ mol^{-1}) suggested that relatively weak H-bond forces were the main driving forces for adsorption. Desorption was found to be concentration- and temperature-dependent with higher desorption occurring at higher temperature and concentration levels. The results signify the importance of temperature in controlling the mobility of dimethoate in water bodies.

K e y w o r d s: dimethoate, isotherms, kinetics, sorption, thermodynamics

INTRODUCTION

Dimethoate is a widely used organophosphate pesticides for control of red spider mite in cucurbits, jassids and aphids in okra (bhindi) and potato, thrips in pea, and citrus psylla and aphids in citrus and other fruits. The Environment Protection Agency (EPA) classifies dimethoate as a class II toxicity-moderate toxic compound. It is highly soluble (25 g l^{-1} in water at 21ºC) in water. Although dimethoate is quite an old pesticide, very few studies are available on its adsorption behaviour on soils (Kuisi, 2002; Vagi *et al*., 2010). Moreover, only one published study is available on desorption of dimethoate from the soil (Vagi *et al*., 2010). The presence of dimethoate residues has been reported in groundwater and soil (Vig *et al*., 2001; Batista *et al*., 2002). No work has yet been reported on adsorption as well as desorption of dimethoate on Indian soils of the Punjab region, which are characterized by low organic matter and clay content, the primary controlling factors for adsorption process. In order to describe the adsorption phenomenon, it is necessary to obtain information about the relationships at equilibrium between the amount adsorbed and the concentration of the bulk solution in contact with the adsorbent, the energies that characterize the equilibrium between the solid surface and the liquid phase, and the speed at which equilibrium is attained along with the magnitude of energies involved. Literature data concerning the kinetics of adsorption and temperature effect on sorption of dimethoate is totally absent. The kinetic study provides useful information for designing and modelling the adsorption processes. Thermodynamic studies can be useful for indication of predominant forces and reversibility of the binding forces. This can in turn help in predicting the pesticide mobility in the soil on which it is applied as well as the potential surface and groundwater contamination. Therefore, the present work was carried out to study the adsorption kinetics, effect of temperature on sorption behaviour, and leaching potential of dimethoate under laboratory conditions on three Indian agricultural soils from Punjab region (India) with different physical and chemical characteristics.

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MATERIALS AND METHODS

The technical grade standard (>99.5% purity) of dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate) was obtained from Sigma Aldrich, Bangalore (India), and was used without any further purification for the present study.

Three cultivated soils of different regions of Punjab, India, were selected and collected from the surface layer of soil (1-15 cm). The soils were air dried, stirred, crushed, and sieved to pass through 2 mm sieve to maintain a uniform particle size. The adsorption experiments were conducted on the dried soil under laboratory conditions. Drying and sieve analysis of the soils were done to obtain uniformity in the results of adsorption experiments for better comparison. Soil samples were classified based on textural analysis and according to United States Department of Agriculture (USDA) particle size classification (clay <2 µm; silt 2-50 µm and sand 50-2000 µm). Particle size distributions were performed using the hydrometer method (Bouyoucos, 1962). Soil pH was measured in water in 2:5 ratio of soil suspension using a combination glass electrode. The organic matter (OM) content of the soil was determined by a modified Walkley and Black method and organic matter was calculated by multiplying organic carbon by 1.72 (Carter, 1993). The electrical conductivity was measured in 1:5 (soil:water) soil water suspension using a conductivity meter. The heavy metals were extracted and analyzed following IS 11466:1995. (http://www.iso.org/iso/catalogue_detail.htm?csnumber= 19418). Physicochemical properties of the tested soils are presented in Table 1.

Kinetics experiments were carried out in 15 ml polypropylene centrifuge tubes at an initial dimethoate concentration of 5, 10, 15, and 20 mg l^{-1} at 30±1°C for all the soils. Pesticide dilutions were prepared in a 0.01M CaCl$_2$ aqueous solution in order to maintain constant ionic strength as it minimizes cation exchange and improves the centrifugation procedure. Each mixture consisted of 1 g of soil mixed with 10 ml of the pesticide solution in a centrifuge tube and sealed with screw caps with Teflon lining. The experiments were performed by stirring the suspensions at 100 r.p.m. for different time durations (1, 2, 4, 6, 8, 10, 15,

20, and 24 h). Thereafter, the tubes were centrifuged for 30 min at 4500 r.p.m. The supernatant was poured off for determination of the pesticide concentration.

The adsorption experiments were performed according to the Organization for Economic Co-operation and Development Guideline 106 (OECD, 2000). Pesticide dilutions were prepared exactly the same way as in the kinetics experiment. Six concentrations of 1, 2, 5, 10, 15, and 20 mg l^{-1} were used for all soils. Time required for the pesticide to attain adsorption equilibrium was determined as per the kinetics study. The centrifuge tubes were gently shaken for the required time at 100 rpm at three temperatures 20±1, 30±1, and 40±1°C. Thereafter, these tubes were centrifuged for 30 minutes at 4500 r.p.m. The clear supernatant was poured off for determination of the equilibrium concentration (C_e) of the pesticide. The adsorption was performed in two replicates. One blank (without pesticide) and one control (without soil) were included in each sample batch to assure the quality control of the experiments. For the desorption study, the supernatant removed was replaced with the same volume of the 0.01M CaCl$_2$ aqueous solution. The tubes were mechanically shaken for 10 h at 100 r.p.m. as per the preliminary kinetics studies of desorption equilibrium (results of desorption kinetics are not presented) at the desired temperatures. Thereafter, the tubes were centrifuged for 30 min at 4500 r.p.m. The supernatant was poured off for determination of the pesticide concentration (pesticide desorbed).

Analysis of dimethoate extracted was performed on HPLC (Shimadzu Corporation, Japan). The chromatographic system consisted of a Shimadzu-LC 20AT pump, the stationary phase was C18, Phenomenex Luna 5 µm 100A 250 X 4.6 mm analytical column, and the detector used was SPD-20A (UV-VIS detector). An isocratic elution method in a mobile phase consisting of water: acetonitrile (60:40% v/v) at a flow rate of 1ml min^{-1} was used. The injection volume was 10 µl and the detection wavelength was 221 nm. The supernatant obtained in the kinetics, batch adsorption and desorption experiments as discussed earlier was filtered through a syringe filter (0.2 micron) before being injected into the HPLC column.

T a b l e 1. Physicochemical properties of soils under study

Soil No.	Type of soil	Textural analysis (%)			Electrical conductivity (mS cm^{-1})	pH	Organic matter (%)	Mineral content (kg ha^{-1})			
		Sand	Silt	Clay				Zn	Cu	Fe	Mn
A	Loam	40	49	11	0.095	6.7	0.57	8.5	10.6	21.9	19.4
B	Loamy sand	77	17	6	0.233	8.4	0.67	8.1	4.2	33.0	20.7
C	Sandy loam	60	35	5	0.046	8.1	0.52	8.0	11.8	22.6	16.8

Quantification of the analytes was carried out by integration of peak areas. Quantification or recovery of the pesticides in the fortified samples was performed by comparing the detector responses for the target compound in samples with those measured in calibration standards solutions, according to the equation of the appropriate calibration curve.

From the data obtained from the batch adsorption experiments, the amount of pesticides adsorbed on the soil at equilibrium (Q_e, mg kg^{-1}) was calculated as:

$$Q_e = \frac{(C_o - C_e)V}{m},$$ (1)

where: C_o is the initial and C_e is the final equilibrium concentration of the pesticide (mg l^{-1}), V is the volume of the pesticide solution (l), and m is the soil mass in contact with the pesticide (kg). C_e was found out using HPLC as discussed above.

From the desorption study, the amount of dimethoate retained by the soil (Q_e^{des}, mg kg^{-1}) was calculated as the difference between the initial adsorbed amount and the desorbed amount (C_e^{des}, mg l^{-1}):

$$Q_e^{des} = \frac{(C_e - C_e^{des})V}{m}.$$ (2)

RESULTS AND DISCUSSION

The adsorption studies were performed on the dried soils to obtain uniformity in the results and to minimize the effect of soil moisture on the adsorption process. The adsorption results of the soils under natural conditions could have been different due to the varying agricultural practices, weather and soil moisture *etc*. As studied by Calvet (1989), although soil moisture can play a role in the adsorption process, such experiments are very difficult to design. Some researchers (Hance, 1977; Yaron and Satlzman, 1972) have found that adsorption coefficients increased with a decrease in soil water content. However, the present study primarily focuses on the effect of temperature with respect to adsorption.

The graph showing the adsorption of dimethoate with respect to time for soil A (loamy soil) is presented in Fig. 1. At all the initial concentration levels, the initial rate of adsorption was very fast and more than 50 and 90% adsorption took place within the first hour and 9 h, respectively. The second phase of adsorption was very slow, but at all the concentration levels; equilibrium was reached within 15 h. The rapid initial adsorption is a surface phenomenon where vacant sites in the soil particles were filled up rapidly in the initial stages and followed a linear variation. This was followed by a slow migration and diffusion of pesticide molecules in soil (Gao *et al*., 1998). Moreover, at lower initial concentrations (5 and 10 mg l^{-1}), equilibrium was reached fast as compared to those of higher initial con-
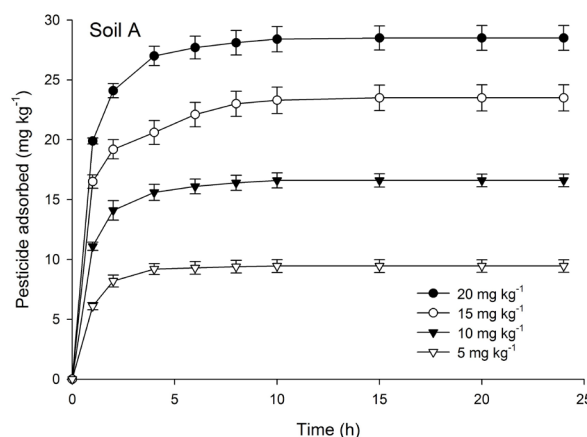

Fig. 1. Adsorption kinetics of dimethoate in soil A at different initial concentration levels and at 30°C (Error bars show standard deviation).

centrations (15 and 20 mg l^{-1}). Similar trends were observed for soils B (loamy sand) and C (sandy loam), although the amount of the pesticide adsorbed at equilibrium varied.

Three different kinetic models namely pseudo-first order, pseudo-second order kinetic (Ahmad, 2011), and Weber and Morris intra particle diffusion model (Weber and Morris, 1963) were applied to the adsorption data in order to study the mechanism involved in the adsorption process. The pseudo first-order equation describes adsorption in solid-liquid systems based on the sorption capacity of solids. The pseudo second-order rate equation assumed that the adsorption mechanism was dominant by chemisorptions. The pseudo first order and second order kinetic models can be expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t,$$ (3)

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e},$$ (4)

where: Q_t is the amount of the pesticide (mg kg^{-1}) adsorbed at time t (h), k_1 is the rate constant of pseudo-first order adsorption (h^{-1}), and k_2 is the pseudo-second order rate constant (kg mg^{-1} h^{-1}).

The best-fit kinetic model was selected on the basis of linear regression correlation coefficient (R^2 values) and standard error of estimate (*SEE*) value. These values along with the model constants are given in Table 2. The pseudo first order model as well as the second order model were fitted well with the experimental results although the second order rate equation gave relatively higher R^2 and very low *SEE* values. The perfect fit of the experimental data for the pseudo second order rate equation indicates the applicability of the model. This indicates that the adsorption was a complex process and several mechanisms were involved

(Peng *et al.,* 2012). Moreover, in the chemisorption process, the pseudo second order is superior to the pseudo-first order model because it deals with interaction of adsorbent-adsorbate through their valency forces (Bajeer *et al.,* 2012). Therefore, the rate-limiting step may be chemical adsorption.

The fitting of the kinetic models was checked by the coefficient of determination (R^2) and *SEE*. The *SEE* value presents a measure of agreement between the calculated and the observed values and is defined by:

$$SEE = \sqrt{\frac{\Sigma(q_{t\,exp} - q_{tcal})^2}{n-2}} . \qquad (5)$$

where: q_{texp} and q_{tcal} are the experimental and calculated adsorbed amounts of dimethoate in soil at time *t*, respectively, and *n* is the number of measurements.

The kinetic data was also subjected to Weber and Morris intraparticle diffusion model in order to explore the possibility of intraparticle diffusion on adsorption. The linear form of the model is given by:

$$Q_t = Kt^{0.5} , \qquad (6)$$

where: *K* (mg kg^{-1} h$^{0.5}$) is the intraparticle diffusion rate constant.

Intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process when the plot is linear and passes through the origin (Oladoja *et al.,* 2008). The curve obtained did not pass through the origin implying that the intraparticle diffusion was not the only operative mechanism (figure not shown). Furthermore, the plots exhibited an initial linear portion followed by a plateau. The initial curved portion of the plots are attributed to the diffusion of the adsorbate through the solution to the external surface of the adsorbent or the boundary layer diffusion of the solute molecules. The plateau could be attributed to the final equilibrium stage where intraparticles start to slow down due to the extremely low adsorbate concentration in solution. However, the plot did not pass through the origin, indicating that although intraparticle diffusion was involved in the adsorption process, it was not the rate-controlling step.

To describe the adsorption processes of dimethoate, three different non-linear isotherm models namely Freundlich, Langmuir, and Temkin were used.

Different adsorption isotherm models such as the Langmuir, Freundlich and Temkin models were used on the adsorption data. The Langmuir model is valid when the adsorption involves the attachment of only one layer of molecules to the surface and the surface has a specific

T a b l e 2. Coefficients of adsorption kinetic models, standard errors of estimate (*SEE*), and coefficients of determination (R^2) for dimethoate on different soils under study

Soil No.	Initial concentration C_i (mg l^{-1})	Pseudo first order model			Pseudo second order model			Intra particle diffusion model	
		k_1 (h^{-1})	R^2	*SEE*	k_2 (kg mg^{-1} h^{-1})	R^2	*SEE*	k (mg kg^{-1} h$^{0.5}$)	R^2
A	5	0.460	0.975	0.210	1.561	1.000	0.190	1.322	0.943
	10	0.311	0.963	0.455	0.093	0.999	0.507	1.834	0.886
	15	0.459	0.938	1.472	0.061	0.999	0.870	2.658	0.894
	20	0.428	0.966	0.641	0.053	1.000	0.228	3.357	0.839
B	5	0.447	0.995	0.220	0.146	1.000	0.502	1.585	0.869
	10	0.325	0.943	0.989	0.094	0.999	0.306	1.807	0.895
	15	0.446	0.961	0.886	0.075	1.000	0.538	2.383	0.869
	20	0.344	0.996	0.638	0.188	1.000	0.131	3.238	0.827
C	5	0.576	0.961	0.489	0.057	0.999	0.313	1.356	0.738
	10	0.452	0.987	0.529	0.306	1.000	0.243	2.299	0.827
	15	0.385	0.982	0.586	0.046	1.000	0.646	2.421	0.879
	20	0.461	0.985	0.595	0.051	1.000	0.552	2.742	0.746

number of sites where the solute molecules can be attached (Giles *et al.,* 1960). The isotherm is given by the linearized form of Eq. (7):

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0},$$ (7)

where: Q_0 is the maximum quantity of pesticides (mg kg^{-1}) per unit weight of the adsorbent to form a complete monolayer on the surface, b is a constant related to the affinity of binding sites with the pesticide (l mg^{-1}).

The Freundlich model is often used for heterogeneous adsorption (Garg *et al.,* 2008) and is given as:

$$Q_e = K_f C_e^{1/n},$$ (8)

where: K_f is the Freundlich adsorption coefficient and is related to the adsorption capacity. The exponent *n* is an adsorption constant that characterizes the adsorption intensity and energy distribution of the adsorption sites (ElShafei *et al.,* 2009).

The Temkin isotherm model is based on the assumption that the adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. The Temkin isotherm describes the behaviour of adsorption systems on heterogeneous surfaces. The linear form of the Temkin isotherm (ElShafei *et al.,* 2009) is given as:

$$Q_e = \frac{RT}{b} \ln(AC_e),$$ (9)

where: *R* is the gas constant (8.314 J mol^{-1} K^{-1}), *T* is absolute temperature (K), b is the Temkin constant related to the heat of sorption, and *A* is the Temkin isotherm constant (l mg^{-1}). The fitting of the isotherm models was checked by the coefficient of determination (R^2) and the standard error of estimate (*SEE*). The *SEE* value was calculated as:

$$SEE = \sqrt{\frac{\Sigma(q_m - q_e)^2}{n - 2}},$$ (10)

where: q_m and q_e are the measured and calculated adsorbed amounts of dimethoate in soil, respectively and n is the number of measurements.

The experimental data obtained from all the soils (data not shown) showed very bad fitting (R^2<0.6) to the Langmuir equation implying the inapplicability of the model. This was due to the heterogeneous nature of the soils and sediments. Table 3 gives the different constants and values of other parameters of the remaining two models. As per the R^2 value, the data was better fitted to the Freundlich model as compared to the Temkin model. In addition, the *SEE* values were relatively lower in the Freundlich model in most of the cases. Therefore, the adsorption data can be explained better using the Freundlich model at all the temperatures. This model is related to the non-ideal, reversible, and multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Bajeer *et al.*, 2012).

For all the three soils under study at the investigated temperatures, the adsorption plots are shown in Fig. 2. The adsorption mechanism can be understood from the shape of the adsorption isotherm although it does not give confirmation of the adsorbate-adsorbent interaction. The classification on the basis of the initial slope $d(Q)/dC_e$, of the adsorption isotherm has been proposed by Giles *et al.* (1960). These four categories are named as S-, L-, H-, and C- shape, based on the initial slope, which is important as it depends on the rate of change in adsorption site availability.

T a b l e 3. Adsorption isotherm model constants, coefficient of determination (R^2), and standard error of estimate (*SEE*) for dimethoate adsorption at different temperatures (two replications)

Soil No.	Temperature (°C)	Freundlich isotherm				Temkin isotherm			
		K_f (mg kg^{-1})/ (mg l^{-1})$^{1/n}$	1/*n*	R^2	*SEE*	RT/b	A (l mg^{-1})	R^2	*SEE*
A	20	2.918	1.026	0.957	2.54	10.88	1.497	0.914	4.55
	30	2.313	1.000	0.983	2.27	9.08	1.195	0.947	2.62
	40	1.586	0.999	0.949	2.08	6.79	1.123	0.939	2.03
B	20	3.278	0.997	0.954	1.75	11.30	1.369	0.948	3.47
	30	2.518	0.993	0.969	2.57	9.33	1.254	0.960	2.51
	40	1.617	1.026	0.971	1.86	7.51	1.067	0.919	2.68
C	20	2.853	0.956	0.977	2.28	9.72	1.305	0.929	4.32
	30	2.008	1.055	0.974	2.60	9.25	1.119	0.941	2.77
	40	1.457	1.077	0.978	2.23	7.54	1.034	0.952	2.10

Adsorption isotherms obtained for dimethoate were almost S-shaped on all the three soils under study. This shape is a common feature for adsorption of organic chemicals on soils with low organic matter (soils under study had organic matter < 0.67%) or clay contents (the soils under study were loam, sandy loam, and loamy sand, clay content<11%). This isotherm type indicates a low pesticide-soil affinity at low concentrations, with strong competition with the aqueous phase, and adsorption becomes easier as the pesticide concentration in the aqueous phase increases. Vagi *et al.* (2010) also found the same shape of adsorption isotherms for dimethoate on Greek soils having low organic matter content and the isotherm shape changed to the L-type as the organic matter content of the soil increased. Kaur and Sud (2010) reported S-shaped isotherms for monocrotophos and dichlorovos on Indian soils having low organic matter and clay content. Furthermore, as the solution concentration increased, the adsorption of the pesticide decreased. Similar results have been reported by many researchers (Krishna and Philip, 2008; Patakioutas and Albanis, 2002).

From Fig. 2, it can be seen that adsorption of dimethoate showed a decreasing slope with increasing temperature for all the soils under study. This is also reflected by the decreasing K_f values with an increase in temperature (Table 3), indicating that temperature strongly affected the adsorption. For example, for soil B (loamy sand), the K_f value decreased from 3.278 to 1.617 as the temperature increased from 20 to 40°C. The same trend was followed in soils A (loamy soil) and C (sandy soil). In the present study, the Freundlich constant $1/n$ values (Table 3) were around unity in most of the cases, indicating that the isotherms were almost linear with respect to the concentration in the aqueous phase. This constant is related to the sorption site energy distribution, as well as to the heterogeneous organic matter domain, where the lower $1/n$ values indicate a more heterogeneous sorption site distribution (Broznic and Milin, 2012).

As pesticides in soil are prone to leaching, the extent of adsorption measured by serves as one of the tools for predicting their mobility in the soil. Criteria given by Anderson *et al*. (1992) for soil mobility using adsorption constants are:

K_f<2 highly mobile,

2< K_f <5 mobile,

K_f >5 immobile with respect to leaching.

Therefore, dimethoate was considered to be mobile with respect to leaching in all the studied soils at lower temperature of adsorption and highly mobile at higher temperature.

The amount of organic matter (OM) greatly affects the adsorption process of the pesticides in the soil especially when present in large amounts (ElShafei *et al.,* 2009), mainly because the particles of organic matter or clay provide the soil with an increased number of adsorptive sites onto which pesticides molecules can bind. Despite the complex-
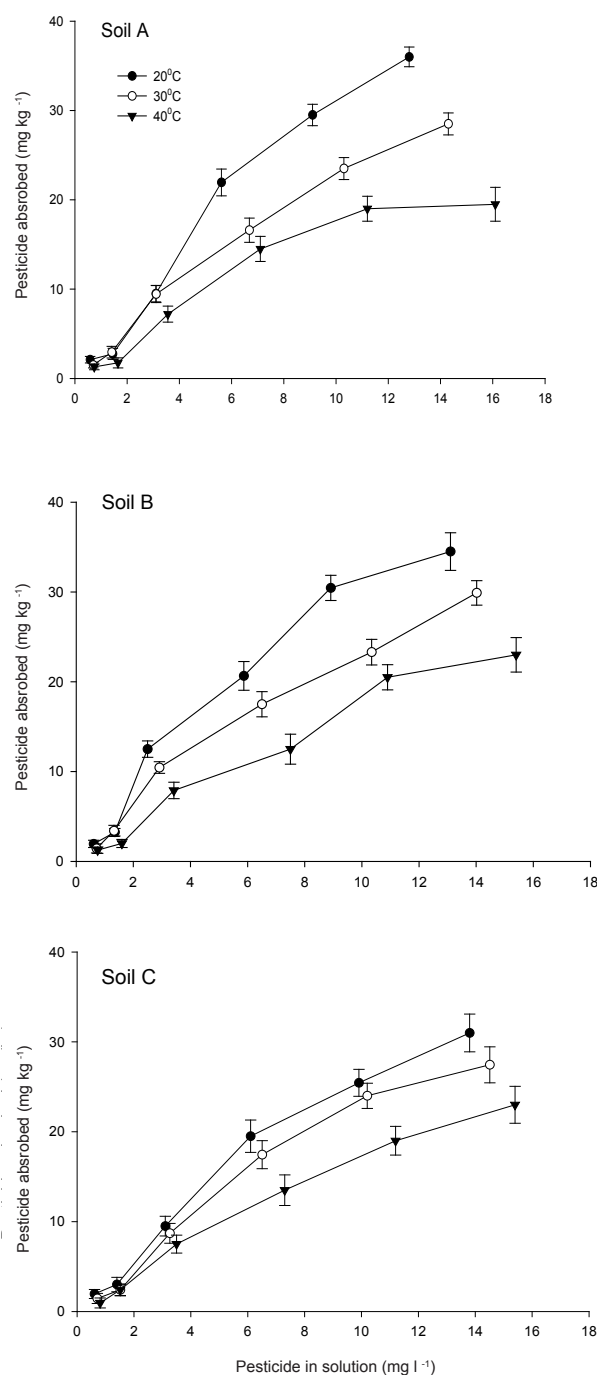

Fig. 2. Adsorption isotherm plots of dimethoate on various soils at different temperatures (error bars show standard deviation).

ity of soil organic matter compositions, it has been reported that when OM is low (<5%), adsorption of the pesticide not only may be affected by the organic matter but also other factors such as the type and nature of the pesticide, accessibility of its functional groups, inorganic constituents, and properties of the soil may have a role to play (Von *et al.,* 1991; Weber *et al.,* 1991).

The statistical correlation between K_f values and various soil properties such as OM, soil pH, electrical conductivity (EC), and silt and clay content was found at the studied temperatures. The results revealed that the K_f values were positively correlated with OM ($R^2 > 0.75$) for all the temperatures. Vagi *et al.* (2010) have reported that organic matter as well as other soil properties played a role in adsorption of dimethoate on various Greek soils having OM varying from 1.0 to 4.2%. Data from other previous studies indicate a good correlation between K_f and OM for the organophosphate pesticides in soils having OM<1.0%; the higher the organic matter, the larger the K_f value (Garg *et al.,* 2008; Islam *et al.*, 2010; Ismail *et al.,* 2002). The K_f and EC values were also positively correlated ($R^2 > 0.67$). The higher EC value of soil enhances water retention by increasing the osmotic potential of the soil, thereby increasing the contact-time for adsorption (Bajeer *et al.,* 2012). This can lead to higher adsorption by soil. ElShafei *et al.* (2009) have also reported that the higher the EC, the larger the K_f value. On the other hand, no correlation could be found between K_f and clay content. Islam *et al.* (2010) also showed an insignificant effect of clay content on adsorption of bromophos methyl and quinalphos on Greek soils. A possible reason for this may be involvement of both the mineral and organic components in sorption interaction of pesticides in soil. The values of K_f and silt content were positively correlated ($R^2 = 0.69$) only at a temperature of 20°C. No correlation could be seen at higher temperatures. Liu *et al.* (1970) found that adsorption of ametryne and diuron increased with an increase in silt content in the soil. Adsorption on soils and sediments is due to mineral and organic constituents, and it is often difficult to clearly separate their roles because these are always associated (Calvet, 1989). Therefore, in soil B (loamy sand), the K_f values were higher mainly due to higher organic matter, higher electrical conductivity, and higher iron content (Table 1) indicating possible involvement of charged ionic species present in the soil causing higher adsorption. The difference in the concentration and type of metal ions in soil influences adsorption of pesticides by competitive or non-competitive complexation of heavy metal ions with soil clay minerals and organic matter (Parr and Smith, 1974). This complexation ability is reported to be higher for Cu (due to smaller ionic size) as compared to

those of Mn and Zn ions (Lalah *et at.,* 2009; Ryan *et al.,* 1983). In soil B, the concentration of Cu is lowest and that of Mn is highest (Table 1). This might have caused a lower inhibition effect for adsorption due to lower complexation in soil B as compared to soils A and C, resulting in a higher K_f value in soil B. The K_f value showed no correlation with pH of the soil. This may be attributed to the non-ionisable nature of the pesticide. Similar results have been reported by many researchers (Islam *et al.,* 2010; Rotich *et al.,* 2004) for organophosphorus pesticides.

The contribution of organic matter to sorption capacity can be quantified by a new parameter, organic matter partition coefficient, K_{OM}. The K_{OM} value can be calculated by Eq. (11):

$$K_{OM} = K_f/f_{OM}, \tag{11}$$

where: f_{OM} is the organic matter in the soil (g g^{-1}).

The data related to K_{OM} and log (K_{OM}) is presented in Table 4. The K_{OM} of soil B was higher than for the other two soils studied for the pesticide. Pesticides with a K_{OM} value below 500 are considered mobile with respect to leaching (Swann *et al.,* 1983). According to this, dimethoate can be classified as mobile, as its adsorption was generally weak in the soils under study (OM<0.67, having sandy loam, loam, or loamy sand texture). Values of K_{OM} reported by Vagi *et al* (2010) predicted that dimethoate was mobile in some Greek soils. Many other researchers have also predicted the mobility of organophosphorus pesticides in the soil on the basis of the K_{OM} value (Islam *et al.,* 2010; Rotich *et al.,* 2004; Vagi *et al.,* 2010). The experimental results showed that the adsorption capacity of dimethoate increased with an increase in organic matter of the soil. In general, the values of K_{OM} of the present study are almost the same as those reported in literature. The log K_{OM} values of the present study varying from 2.38 to 2.74 are in agreement with those reported in literature (Vagi *et al.,* 2010).

The K_{OM} and $\Delta G°_{OM}$ can be related by Eq. (12):

$$\Delta G°_{OM} = -RT \ln K_{OM}, \tag{12}$$

where: $\Delta G°_{OM}$ is the organic matter normalized free energy change in adsorption (kJ mol^{-1}).

The $\Delta G°_{OM}$ values obtained in the present study are also listed in Table 4. All the values were negative indicating that the process was spontaneous and thermodynamically

T a b l e 4. Values of K_{OM}, log(K_{OM}), and $\Delta G°_{OM}$ for adsorption of dimethoate on various Indian soils at different temperatures

Soil No.	K_{OM} (kg l^{-1})	log(K_{OM})	$\Delta G°_{OM}$ (kJ mol^{-1})	K_{OM} (kg l^{-1})	log(K_{OM})	$\Delta G°_{OM}$ (kJ mol^{-1})	K_{OM} (kg l^{-1})	log(K_{OM})	$\Delta G°_{OM}$ (kJ mol^{-1})
		20°C			30°C			40°C	
A	511.93	2.71	-15.20	405.79	2.61	-15.13	278.25	2.44	-14.65
B	489.25	2.69	-15.09	375.82	2.57	-14.94	241.34	2.38	-14.28
C	548.65	2.74	-15.37	386.15	2.59	-15.00	280.19	2.45	-14.67

favourable. The values changed from -15.20 to -14.65, -15.09 to -14.28, and -15.37 to -14.67 kJ mol^{-1} as the temperature changed from 20 to 40°C for loamy (A), loamy sand (B), and sandy loam (C) soils, respectively. Therefore, an increase in temperature can result in a decrease in adsorption. Furthermore, the negative ΔG°_{OM} values indicated that physical adsorption was carried out by involving weak forces of attraction between pesticide molecules and soil surface.

Thermodynamic considerations of the adsorption process are necessary to conclude whether the process is spontaneous or not. The thermodynamic parameters such as ΔG°, ΔH°, and ΔS° provide additional information regarding energetic changes involved during the temperature-dependent sorption (Broznic and Milin, 2012). The Gibbs free energy change ΔG° was calculated as:

$$\Delta G^{\circ} = -RT \ln K_d. \tag{13}$$

The partitioning coefficient K_d of the pesticide toward a soil is an important parameter for examining the contaminant migration through the soil to the groundwater. If the K_d value is low, the soil has little or no ability to slow the contaminant movement. For a K_d value of zero, it will travel at the rate of infiltration of water. High K_d values signify that the substrate does not leach and site remediation may be possible.

As suggested by Roth et al. (2012), K_d (l mol^{-1}) in batch experiments is calculated as:

$$K_d = \frac{MQ_e}{C_e}, \tag{14}$$

where: M is the molecular weight of the pesticide (229.63).

Defining the K_d as above implies that the adsorption of the pesticide is a linear isotherm model. However, this is an approximation at a low initial pesticide concentration and adsorption on soil often deviates from linearity.

As K_d is concentration dependent (the adsorption process is not linear), thermodynamic calculations are obtained by plotting lnK_d versus C_e and extrapolating to zero.

The other thermodynamic parameters can be calculated by Eq. (15):

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}, \tag{15}$$

where: ΔH° and ΔS° are the changes in enthalpy and entropy of adsorption.

The ΔG^{o} value is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Reactions occur spontaneously at a given temperature if ΔG^{o} is a negative quantity. The values of three different thermodynamic parameters ΔG°, ΔH°, and ΔS° for dimethoate are presented in Table 5. The ΔG° values ranged from -15.34 to -16.60 kJ mol^{-1} for all the studied soils. The absolute values decreased with an increase in

temperature of adsorption indicating that the adsorption decreased with the rise in temperature. The change in the ΔG° value may be due to the increase in the degree of freedom, which might have enhanced desorption rather than adsorption at higher temperatures.

The ΔH° value in the range of 4 to 8 kJ mol^{-1} indicates the existence of van der Waals interactions, whereas H-bonds are main interactions in the range of 8 to 40 kJ mol^{-1} (Broznic and Milin, 2012). The ΔH° values associated with chemical sorption are usually higher than 40 kJ mol^{-1}. In the present study, the ΔH° values were negative and varied from -23.39 to -32.95 kJ mol^{-1}. This shows that the adsorption process was exothermic in nature and occurred through a bonding mechanism indicating the participation of amino and carbonyl groups in dimethoate with other O- and N-atoms present in soil colloids. The results of the study also indicated that the interactions between dimethoate and soils were stronger at lower temperatures. The small negative values of ΔS° (from -25.7 to -55.9 J mol^{-1} K^{-1}) suggested decreased randomness on the solid/solute interface during the adsorption of dimethoate on the studied soils.

Leaching is a downward movement of a substance with water through the soil. The main factors that influence the leaching of a pesticide in the soil are adsorption of the pesticide on soil surface, water solubility of the pesticide, the volume of water flow, and soil texture (Crisanto et al., 2000). The desorption data was also fitted to the Freundlich isotherm model using Eq. (16):

$$Q_e^{des} = K_f^{des}(C_e^{des})^{1/n}, \tag{16}$$

where: K_f^{des} and n are Freundlich desorption isotherm constants. The extent of hysteresis can be obtained for every

T a b l e 5. Values of thermodynamic parameters obtained for dimethoate adsorption on studied soils at different temperatures

Soil No.	Temperature (°C)	ΔG°	ΔH°	ΔS°
		(kJ mol^{-1})		
A	20	-16.60		
	30	-15.93	-32.95	-55.90
	40	-15.48		
B	20	-16.27		
	30	-16.19	-27.73	-38.70
	40	-15.50		
C	20	-15.85		
	30	-15.59	-23.39	-25.70
	40	-15.34		

set of adsorption and desorption isotherms using the hysteresis coefficient H (Cox *et al.,* 1997). The H value was calculated as:

$$H = \frac{1/n_{des}}{1/n_{ads}} \quad , \qquad (17)$$

Desorption isotherms of dimethoate on the studied soils at different temperatures are shown in Fig. 3. The related Freundlich coefficients and R^2 values along with the hysteresis coefficients are given in Table 6. Desorption isotherms looked similar to those of adsorption isotherms although the values of Freundlich coefficients differed significantly. As compared to the adsorption isotherm coefficients, the K_f values increased and the $1/n$ values decreased in desorption isotherms. The Freundlich isotherm m was fitted better to the desorption process than to the adsorption process as indicated by the R^2 value (Tables 3 and 6). As shown in Table 6, the K_f values decreased as the temperature increased from 20 to 40°C in all the soils indicating that temperature strongly affected the desorption process. The $1/n$ value ranged between 0.702 and 0.825 in the studied range of temperatures. This value indicated that 17.5 to 30% deviation from linear function took place in the fitted isotherms. In order to find out differences in adsorption and desorption isotherms, the hysteresis coefficient H was calculated. The hysteresis phenomenon is characterized by differences in the slopes of adsorption and desorption isotherms. A lower H value indicates that the adsorption-desorption phenomenon is more pronounced with high nonlinearity and therefore the desorption rate is slower in relation to the adsorption rate (Broznic and Milin, 2012). In the present study, as evident from Table 6, the hysteresis existed and the H value ranged between 0.712 and 0.828. In general, this phenomenon was less pronounced at 40°C as compared to 20 and 30°C.

Mass balances for dimethoate were made by using the data collected from adsorption and desorption studies and the results are presented in Table 7. The percent mass balance indicated that during the adsorption process, nearly 60% of the initial pesticide amount remained free in all the studied soils even at 20°C and this amount increased further as the temperature increased. This indicates the chances of surface water contamination through run off and groundwater contamination in all the studied soils. The percent dimethoate desorbing with water increased with the increasing initial concentration level as well as with temperature in all the soils although the extent of the release of the pesticide varied. Therefore, irrespective of the soil, temperature affected the desorption process significantly. The higher
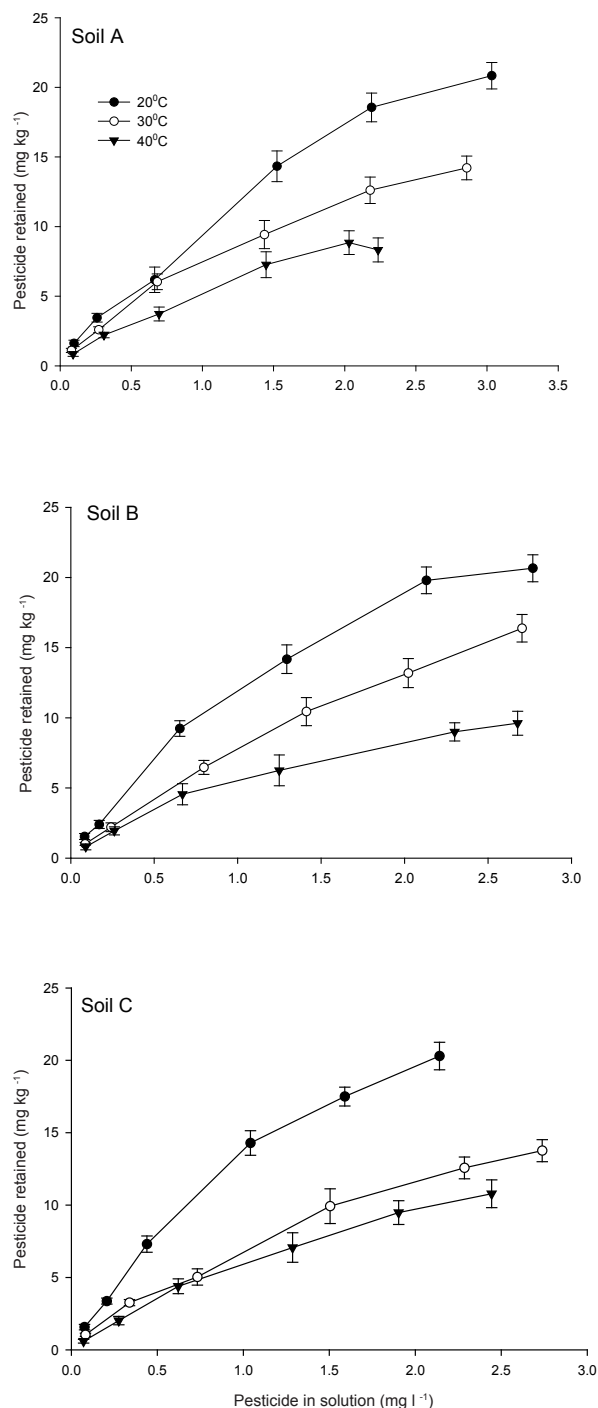

Fig. 3. Desorption isotherm plots of dimethoate on various soils at different temperatures. Error bars show standard deviation.

temperature can cause more surface water contamination partly by free pesticide remaining in water during adsorption and partly by higher release of the adsorbed pesticide during desorption.

T a b l e 6. Freundlich desorption coefficients along with coefficients of determination (R^2) and hysteresis index (H) for dimethoate desorption at different temperatures

Soil No.	K_f	$1/n$	R^2	H	K_f	$1/n$	R^2	H	K_f	$1/n$	R^2	H
						Temperature (°C)						
		20				30				40		
A	9.528	0.766	0.994	0.747	7.106	0.728	0.995	0.728	5.067	0.739	0.994	0.740
B	10.800	0.782	0.988	0.784	7.493	0.822	0.998	0.828	5.124	0.731	0.989	0.712
C	12.410	0.789	0.991	0.825	6.810	0.741	0.825	0.702	5.661	0.825	0.994	0.766

T a b l e 7. Mass percent balances for adsorbed, free or non-adsorbed and desorbed with water dimethoate in soils under study at different temperatures

Soil No.	Initial concentration level (mg l⁻¹)	Adsorbed amount (mg kg⁻¹)	Free or not adsorbed (%)	Desorbed with water (%)	Adsorbed amount (mg kg⁻¹)	Free or not adsorbed (%)	Desorbed with water (%)	Adsorbed amount (mg kg⁻¹)	Free or not adsorbed (%)	Desorbed with water (%)
						Temperature (°C)				
			20			30			40	
A	1	2.10	58.00	23.11	1.50	70.00	26.31	1.30	74.00	35.17
	2	4.75	52.50	27.22	3.95	60.50	34.32	3.75	62.50	41.04
	5	9.50	62.00	34.96	9.45	62.20	36.12	7.20	71.20	48.26
	10	21.95	56.10	34.71	16.60	66.80	43.23	14.50	71.00	49.91
	15	29.50	60.67	37.09	23.50	68.67	46.34	19.00	74.67	53.44
	20	36.00	64.00	42.12	28.50	71.50	50.13	19.50	80.50	57.31
B	1	1.95	61.00	21.15	1.44	71.18	29.82	1.25	75.00	35.76
	2	3.25	67.50	26.15	3.40	66.00	35.33	3.25	67.50	40.23
	5	12.50	50.00	26.12	10.45	58.20	38.14	7.90	68.40	42.35
	10	20.65	58.70	31.34	17.50	65.00	40.32	12.50	75.00	49.97
	15	30.45	59.40	34.98	23.30	68.93	43.40	20.50	72.67	56.10
	20	34.50	65.50	40.12	29.90	70.10	45.21	23.00	77.00	58.21
C	1	1.95	61.00	19.52	1.45	71.00	28.32	0.95	81.00	37.54
	2	4.40	56.00	23.45	4.95	50.50	34.14	3.40	66.00	40.61
	5	9.50	62.00	23.12	8.70	65.20	42.12	7.50	70.00	41.43
	10	19.50	61.00	26.70	17.45	65.10	43.12	13.50	73.00	47.65
	15	25.45	66.07	31.24	24.00	68.00	47.62	19.00	74.67	50.10
	20	31.00	69.00	34.53	27.45	72.55	49.87	23.00	77.00	53.13

CONCLUSIONS

1. Sorption behaviour of dimethoate pesticide in various Indian soils show that the experimental kinetic data revealed that equilibrium was reached within 15 h in all the soils under study and the adsorption process could be described by the pseudo second order kinetic model.

2. The equilibrium adsorption isotherms belonged to the Freundlich model and were S-shaped, describing the reversible, non-uniform, and multilayer adsorption over the heterogeneous surface. The desorption process could also be explained by the Freundlich isotherm model and was strongly affected by temperature and pesticide concentration levels.

3. The decrease in the Freundlich coefficient K_f with the increase in temperature indicated that the adsorption process was strongly affected by temperature. The K_f was positively correlated with organic matter content and electrical conductivity of soil.

4. Thermodynamic analysis showed that the adsorption process was spontaneous and exothermic in nature. Relatively weak H-bond forces were the main driving forces in the adsorption process.

5. The surface as well as groundwater resources are vulnerable to dimethoate contamination partly due to low adsorption by soil and partly due to higher release of adsorbed pesticide especially at higher temperature.

6. The information obtained can be useful in development of models for predicting the dimethoate behaviour in soil and aqueous media as well as controlled application thereof in order to minimize environmental contamination.

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