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Effect of temperature on adsorption-desorption behaviour of triazophos in Indian soils

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ABSTRACT

The present study investigated the adsorption-desorption behaviour of triazophos on Indian soils at 10, 20 and 40°C using batch equilibrium technique. Results revealed that adsorption isotherms were explained better by Freundlich model and adsorption coefficient (K_f) decreased with increase in temperature indicating that adsorption was affected strongly by temperature. Moreover thermodynamic analysis showed that triazophos adsorption onto soil was spontaneous, exothermic and might have occurred through chemisorptions, hydrogen bonding or ligand-exchange interactions. Desorption results depicted that nearly 90% of the pesticide amount adsorbed by soil was retained by it at 10°C and the amount decreased with increase in temperature. Thus, the pesticide has a potential to contaminate surface and ground water at higher temperature due to weak adsorption on tested soils and release of more adsorbed pesticide during desorption with water. At temperature below 20°C, pesticide became almost immobile and therefore soil remediation may be required. The study highlights the importance of temperature in regulating the application of triazophos in soil.

Keywords: bioavailability; degradation; leaching; thermodynamics; toxic

Pesticides are used extensively in modern agriculture to improve crop quality and productivity. However, their continued and unabated usage has raised concerns over the years due to increasing occurrence of their residues in soil and water thus posing a significant threat to our ecosystem and human health. The fate and mobility of the pesticides applied directly or indirectly to the plants, may be influenced by many processes such as volatilization, leaching, adsorption, as well as chemical and biological degradation in soil (Durovic et al. 2009). It is important to understand the adsorption-desorption mechanism of pesticides in soil and its extent since it controls other processes such as leaching into groundwater, uptake by living organisms, transport into surface waters, rate of volatilization and bioavailability of pesticides (Bhandari and Lesan 2003). Usually ignored, a very crucial parameter affecting the retention and release of the pesticide from soil is temperature. Its effect on sorption process becomes of great importance in the regions such as Punjab (India), where temperature varies widely between –2°C to 50°C during different seasons of the year and in green/poly houses where controlled environmental conditions (Ten Hulscher and Cornelissen 1996, González-Prades et al. 2002) are used for cultivation.

Triazophos [3-(*o*,*o*-diethyl)-1-phenyl thiophosphoryl-1,2,4-triazol] is a moderately toxic and broad spectrum organophosphate insecticide and formulated as emulsifiable concentrate for application to soil and plants to control aphids, jassid, fruit borer, leaf hopper, cutworms and citrus whitefly etc. (Tomlin 2009). The solubility of the pesticide varies from 30 to 40 mg/L in water with reported half-life varying from 9 to 22 days in soil (Liang et al. 2011). Among various pesticides used in agriculture in India, triazophos occupies 10th position with total annual consumption of 1164 metric tonne (Bhushan et al. 2013). The presences of triazophos residues has been reported in ground-

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water, soil, wheat grains, leaves and stem (Rani et al. 2001, Vig et al. 2001, Li et al. 2008). Therefore, it is quite obvious that there is some mobility of this pesticide through soil. Adsorption-desorption processes help us in understanding the mechanism and extent of its movement through soil and water bodies. Very few studies related to sorption behaviour of triazophos in soil are available (Zhu et al. 2010, Liang et al. 2011). No study related to effect of temperature on sorption behaviour of triazophos on Indian soils of Punjab origin, which are characterized by low organic matter and clay content, is available. The present work is an attempt to assess the effect of temperature on adsorption-desorption behaviour and leaching potential of triazophos on Indian soils.

MATERIAL AND METHODS

The technical grade standard of triazophos was obtained from the Sigma Aldrich, Bangalore (India) and other chemicals were of high pressure liquid chromatography (HPLC) grade. Three cultivated soils of different regions of Punjab, India were selected and samples were collected from the surface layer (1–15 cm). The soils were air dried, crushed and sieved to pass through 2 mm sieve. The samples were classified according to United States Department of Agriculture (USDA) particle size classification (clay: < 2 μm; silt: 2–50 μm and sand: 50–2000 μm) using hydrometer method (Bouyoucos 1962). Soil pH was measured in water in 2:5 ratio of soil solution using a combination glass electrode. The organic matter content of the soil was determined by Walkley and Black modified 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 conductivity meter. These properties are listed in Table 1.

Table 1. Properties of soils under study

Soil type	Textural analysis (%)			Electrical conductivity (mS/cm)	pH	Organic matter (%)
	sand	silt	clay			
Loam (A)	40	49	11	0.09	6.7	0.57
Loamy sand (B)	77	17	6	0.23	8.4	0.67
Sandy loam (C)	60	35	5	0.04	8.1	0.52

Experimentation. The batch adsorption experiments were performed according to OECD guidelines (OECD 2000) at 10 ± 1, 20 ± 1 and 40 ± 1°C. Pesticide dilutions were prepared in 0.01 mol/L $CaCl_2$ aqueous solution in order to maintain constant ionic strength (Vagi et al. 2010). Each mixture consisted of 2 g of soil and 10 mL of the pesticide solution in centrifuge tube. Five concentrations of 1, 5, 10, 15 and 20 mg/L were used. Tubes were shaken for 24 h as per the preliminary kinetic study at 100 rpm and thereafter centrifuged for 30 min at 4500 rpm. The clear supernatant was poured off for determination of equilibrium concentration (C_e) of pesticide as discussed later. The adsorption-desorption experiments were replicated thrice. 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 0.01 mol/L $CaCl_2$ aqueous solution. The tubes were shaken for 15 h at 100 rpm at the desired temperatures and were centrifuged for 30 min at 4500 rpm. The supernatant was poured off for determination of concentration of pesticide (pesticide desorbed, C_e^{des}).

Instrumentation. Analysis of triazophos present in the supernatants obtained from adsorption and desorption experiments was performed on the HPLC (Shimadzu, Japan). System consisted of LC 20AT pump, C18, Phenomenex Luna 5 μm 100A 250 X 4.6 mm analytical column, and UV-VIS detector (SPD-20A, Japan). Isocratic elution method in a mobile phase consisting of water:acetonitrile (20:80% v/v) at a flow rate of 0.8 mL/min was used. Injection volume was 10 μL and detection wavelength was 270 nm. The supernatant obtained in adsorption and desorption experiments was filtered through a syringe filter (0.2 micron) before being injected into the HPLC column.

Quantification of the analytes was carried out by integration of peak areas. Quantification 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. The retention time was found to be 16.04 min. The calibration curve was found to be linear in the range of 1–25 mg/L concentration of triazophos with detection limit of 0.15 mg/L. The recovery efficiency of triazophos at concentration of 20 mg/L was found to be 93 ± 5.1% in soil.

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The amount of pesticides adsorbed on the soil was calculated using the equation:

$$Q_e = (C_o - C_e)V/m$$

Where: Q_e – amount of pesticide adsorbed at equilibrium (mg/kg); C_o – initial concentration of pesticide (mg/L); V – volume of pesticide solution (L); m – mass of soil (kg).

From the desorption study, the amount of pesticide retained by the soil was calculated as:

$$Q_e^{des} = Q_e - C_e^{des}V/m$$

Where: Q_e^{des} – amount of triazophos retained by soil (mg/kg) during the desorption process; C_e^{des} – equilibrium desorption concentration of triazophos (mg/L).

RESULTS AND DISCUSSION

To describe the adsorption processes of triazophos, two isotherm models namely Freundlich's and Temkin's were used. The Freundlich model is often used for heterogeneous adsorption and is given as:

$$Q_e = K_f C_e^{1/n}$$

Where: K_f – Freundlich adsorption coefficient related to adsorption capacity; *1/n* – adsorption constant that characterizes adsorption intensity and energy distribution of adsorption sites (ElShafei et al. 2009).

The Temkin isotherm model is based on the assumption that adsorption energy decreases linearly with the surface coverage due to adsorbent-adsorbate interactions. It describes behaviour of adsorption systems on heterogeneous surfaces and is given as:

$$Q_e = RT/b \ln(AC_e)$$

Where: R – gas constant (8.314 J/mol K); T – temperature (K); b – Temkin constant related to the heat of sorption; A – Temkin isotherm constant (L/mg).

As per the R^2 value (Table 2), the data was fitted better to Freundlich model as compared to Temkin model indicating that adsorption mechanism was related to non-ideal, reversible and multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Bajeer et al. 2012). Adsorption isotherms along with trend lines (Freundlich isotherm equation) for one soil (soil B) are shown in Figure 1. Although isotherm does not give confirmations about adsorbate-adsorbent interaction (Giles et al. 1960), but its shape helps in understanding the adsorption mechanism. At higher temperature of 40°C, the trend line is almost linear (also indicated by near unity value of *1/n*, Table 2), suggesting that competition for pesticide between soil and aqueous phase was the same or increasing at the same rate. Here the K_f can also be named as partition coefficient K_d. However, as the temperature decreased to 20°C or 10°C, the *1/n* value deviated from unity indicating the non linear relationship between Q_e and C_e with relatively strong adsorption of pesticide on soil as compared to that of water. This is a common feature for adsorption of organic chemicals in soils with low organic matter

Table 2. Adsorption isotherm model constants, coefficient of determination (R^2) and organic matter normalized coefficient (K_{OM}) for triazophos adsorption

Soil	Temperature (°C)	Freundlich isotherm			Temkin isotherm			K_{OM} (kg/L)
		K_f	*1/n*	R^{2*}	RT/b	A	R^{2*}	
A	10	9.76	1.55	0.962	36.29	1.66	0.951	1711.58
	20	4.98	1.72	0.985	32.05	1.34	0.960	874.39
	40	2.59	0.91	0.980	8.75	1.27	0.876	454.79
B	10	8.88	1.63	0.942	35.14	1.67	0.888	1325.33
	20	4.79	1.68	0.958	30.73	1.33	0.902	715.42
	40	3.24	0.89	0.991	9.096	1.51	0.942	483.60
C	10	8.76	1.36	0.995	27.91	1.84	0.762	1683.90
	20	4.69	1.54	0.960	27.30	1.35	0.888	901.62
	40	2.57	0.99	0.981	10.15	1.23	0.784	494.98

*$P \leq 0.05$. K_f – Freundlich adsorption coefficient; *1/n* – adsorption constant; R – gas constant (8.314 J/mol K); T – temperature (°C); b – Temkin constant; A – Temkin isotherm constant (L/mg)

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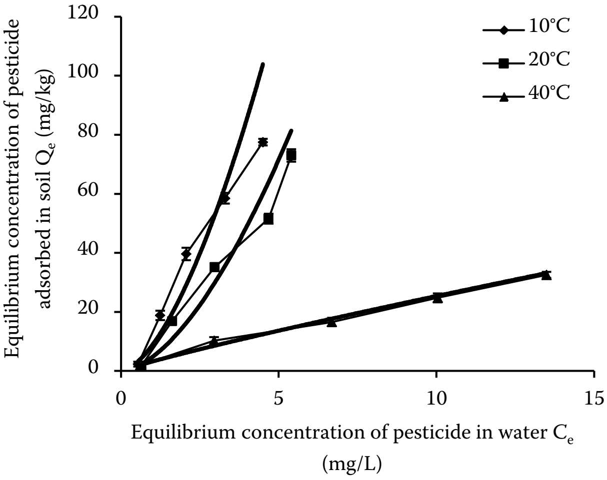

Figure 1. Adsorption isotherms of triazophos pesticide at different temperatures in soil B. Error bars show standard deviation

or low clay content (the soils under study have clay content < 11% and organic matter (OM) < 0.67%, Table 1) (Vagi et al. 2010). Moreover, the slope of the trend line at 40°C was significantly less as compared to those at 20°C or 10°C (also indicated by the low K_f value at 40°C, Table 2). Irrespective of the soil type, almost three-fold decrease in value of K_f as temperature increased from 10°C to 40°C signifies the importance of temperature in adsorption process (Table 2, Figure 2). The available literature also suggests that higher temperature causes more adsorption of organophosphorus pesticides in soil (Ten Hulscher and Cornelissen 1996, ElShafei 2009). The K_f values obtained in the study (2.57–9.76) agree with those reported in the literature (Zhu et al. 2010, Liang et al. 2011).

Effect of soil properties on adsorption. The amount of OM greatly affects the adsorption process only if present in large amounts (ElShafei et al. 2009) because the particles of organic matter or clay provide the soil with an increased number of adsorptive sites onto which pesticides molecules can bind. The statistical analysis showed (results not given) that K_f values could not be correlated with OM except at higher temperature of 40°C where it was positively correlated with $R^2 > 0.9$ (Figure 3). This may be due to the fact that all the three soils were having very little OM (0.52–0.67%). The electrical conductivity (EC) also showed positive correlation with K_f only at higher temperature. The K_f correlated positively with clay content at lower temperatures only.

The organic matter partition coefficient, K_{OM} can be used as a tool to assess the mobility of the pesticide in soil. Pesticides with K_{OM} value below 500 are considered mobile with respect to leaching (Swann et al. 1983). The K_{OM} was calculated as:

$$K_{OM} = K_f/f_{OM}$$

Where: f_{OM} – organic matter in the soil (g/g).

As per the criteria, triazophos was found mobile in soil at 40°C only (Table 2).

Thermodynamic analysis. The thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) provide additional information regarding energetic changes involved during the temperature-dependent sorption (Broznic and Milin 2012). The ΔG° was calculated as:

$$\Delta G° = -RT \ln K_d$$

The partitioning coefficient K_d (L/mol) of the pesticide toward a soil is an important parameter for examining the contaminant migration through the soil to the groundwater and is given as:

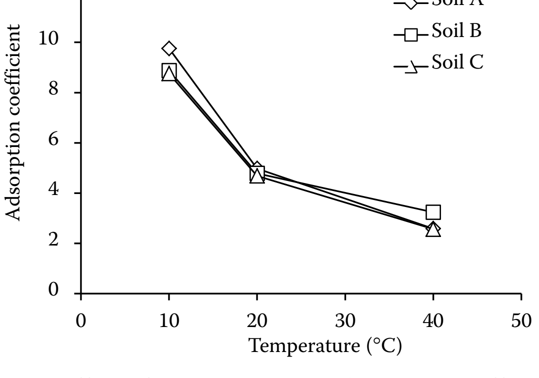

Figure 2. Effect of temperature on adsorption coefficient of triazophos pesticide in different soils

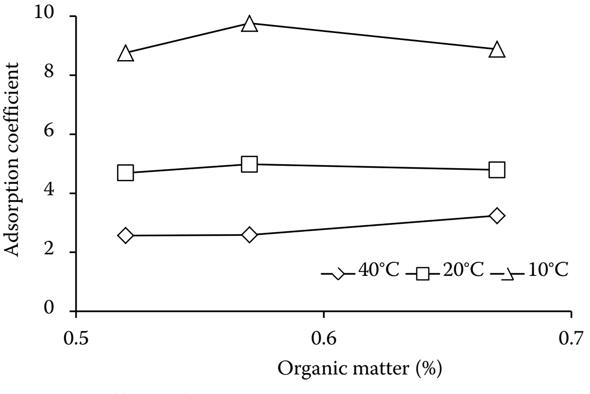

Figure 3. Effect of organic matter content on adsorption coefficient of triazophos pesticide in different soils

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Table 3. Values of thermodynamic parameters of triazophos adsorption on studied soils

Soil	Temperature (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
A	10	–20.267	–50.82	–0.108
	20	–19.396		
	40	–17.078		
B	10	–20.219	–44.672	–0.086
	20	–19.265		
	40	–17.605		
C	10	–19.832	–43.086	–0.082
	20	–19.017		
	40	–17.368		

ΔG° – Gibb's free energy change; ΔH° – enthalpy; ΔS° – entropy

Table 4. Freundlich model constants and R^2 values for triazophos desorption in studied soils

Soil	10°C K_f^{des}	10°C $1/n_{des}$	10°C R^{2*}	20°C K_f^{des}	20°C $1/n_{des}$	20°C R^{2*}	40°C K_f^{des}	40°C $1/n_{des}$	40°C R^{2*}
A	72.91	2.25	0.933	56.97	1.88	0.929	12.68	1.11	0.981
B	51.21	1.62	0.979	46.21	1.85	0.979	11.74	0.93	0.996
C	56.32	1.99	0.902	41.08	1.77	0.927	12.39	1.23	0.998

$^*P \leq 0.05$. K_f^{des} and n_{des} – Freundlich desorption constants

$$K_d = MQ_e/C_e$$

Where: M – molecular weight of pesticide (313.34).

The other thermodynamic parameters were calculated using the following equation:

$$\Delta G° = \Delta H° – T\Delta S°$$

ΔG° values ranged from –17.08 to –20.27 kJ/mol (Table 3). The absolute values decreased with increase in temperature of adsorption indicating that the adsorption decreased with rise in temperature. This change in ΔG° value may be due to the increase in degree of freedom which might have enhanced desorption rather than adsorption at higher temperatures. The ΔH° values were negative and varied from –43.09 to –50.82 kJ/mol. It shows that the adsorption process was spontaneous and exothermic in nature and occurred through chemisorptions mechanism. Derived enthalpies indicate that hydrogen bonding, charge transfer and ligand-exchange interactions may have a role to play in adsorption mechanism (Calvet 1989, Broznic and Milin 2012). The small negative values of ΔS° (–0.082 to –0.108 kJ/mol K) suggested the decreased randomness on solid/solute interface during the adsorption.

Desorption studies and mass balance. The desorption data were fitted to the Freundlich isotherm model:

$$Q_e^{des} = K_f^{des}(C_e^{des})^{1/n_{des}}$$

Where: K_f^{des} and n_{des} – Freundlich desorption constants.

The values of model constants and R^2 are presented in Table 4. As compared to K_f, the K_f^{des} values were higher indicating that the release of the adsorbed pesticide into water was very difficult especially at temperature below 20°C. The K_f^{des} va-

Table 5. Mass percent balances for free and desorbed pesticide with water in studied soils

Soil	Initial pesticide concentration (mg/L)	10°C free or not adsorbed	10°C desorbed with water	20°C free or not adsorbed	20°C desorbed with water	40°C free or not adsorbed	40°C desorbed with water
A	5	23.60	10.99	36.97	12.60	72.79	35.54
	10	17.96	7.92	27.52	7.88	72.22	26.35
	20	18.80	8.68	26.89	8.04	67.70	28.09
B	5	24.82	12.77	32.49	12.15	59.05	30.89
	10	20.70	10.21	29.68	9.24	66.84	31.32
	20	22.50	9.03	27.00	9.66	67.47	30.10
C	5	30.00	12.00	35.60	11.32	72.26	34.32
	10	27.60	10.77	31.10	8.94	66.51	28.63
	20	25.50	10.60	33.50	9.95	64.54	25.94

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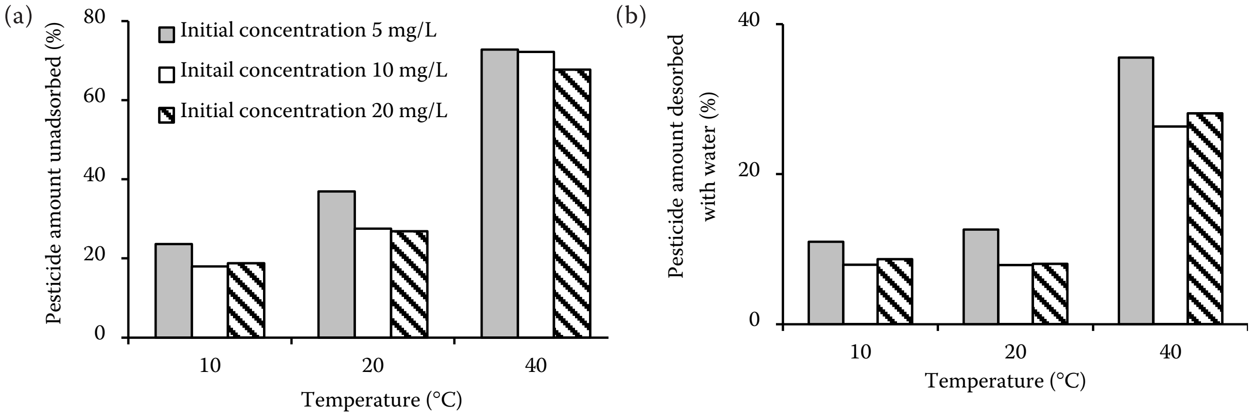

Figure 4. Mass balance during adsorption-desorption of triazophos at different initial concentrations in soil A: (a) amount of pesticide unadsorbed; (b) amount of pesticide desorbed with water

lues increased 4 to 6 times as the temperature of desorption decreased from 10–40°C. The Freundlich isotherm was fitted better to the desorption process than that to the adsorption process as indicated by the R^2 values. Mass balance results (Table 5) indicate that the amount of unadsorbed triazophos varied between 17.2% and 30% when the temperature of the sorption process was 10°C showing that the adsorption on soil was quite strong at lower temperature. The mass balance data for soil A is also presented in Figure 4. As clear from the Figure 4a, an increase amount of pesticide remained unadsorbed with the increase in temperature. At different initial concentration levels, there was a substantial increase in amount of unadsorbed pesticide (96–163%) as the temperature increased from 20–40°C. Similar results were obtained for the other two soils, too. During the desorption process, the desorbed pesticide amount hovered around 10% when the temperature of the process was 10–20°C, but increased with further rise in temperature (Figure 4b). The results indicated that once the pesticide has entered into the soil matrix, there are fewer chances that it will contaminate the ground water due to its leaching from soil especially at lower temperature. However, at higher temperature, more leaching may take place.

In conclusion, the adsorption-desorption behaviour of triazophos was strongly affected by temperature. At higher temperature, pesticide becomes mobile with respect to leaching due to weak adsorption on the studied soils and high desorption rate leading to surface and ground water contamination. However, at lower temperature, pesticide remains in the surface soil or in the upper soil layers and therefore soil remediation may be required. The study results highlight the importance of temperature as a controlling factor for application of triazophos in soil. Due to its greater mobility in soil at higher temperature and under greenhouse conditions, the use of triazophos should be controlled strictly to avoid groundwater contamination.

REFERENCES

Bajeer M.A., Nizamani S.M., Sherazi S.T.H., Bhanger M.I. (2012): Adsorption and leaching potential of imidacloprid pesticide through alluvial soil. American Journal of Analytical Chemistry, 3: 604–611.

Bhandari A., Lesan H.M. (2003): Isotherms for atrazine desorption from two surface soils. Environmental Engineering Science, 20: 257–263.

Bhushan C., Bhardwaj A., Misra S.S. (2013): State of Pesticide Regulations in India. New Delhi, Centre for Science and Environment.

Bouyoucos G.J. (1962): Hydrometer method improved for making particle size analyses of soils. Agronomy Journal, 54: 464–465.

Broznic D., Milin C. (2012): Effects of temperature on sorption-desorption processes of imidacloprid in soils of Croatian coastal regions. Journal of Environmental Science and Health B, 47: 779–794.

Calvet R. (1989): Adsorption of organic chemicals in soils. Environmental Health Perspectives, 83: 145–177.

Carter M.R. (1993): Soil Sampling and Methods of Analysis. Ontario, Canadian Society of Soil Science Publications.

Durovic R., Gajic-Umiljendic J., Dordevic T. (2009): Effects of organic matter and clay content in soil on pesticide adsorption processes. Pesticides and Phytomedicine, 24: 51–57.

doi: 10.17221/704/2014-PSE

ElShafei G.S., Nasr I.N., Hassan A.S., Mohammad S.G. (2009): Kinetics and thermodynamics of adsorption of cadusafos on soils. Journal of Hazardous Materials, 172: 1608–1616.

Giles C.H., MacEwan T.H., Nakhwa S.N., Smith D. (1960): 786. Studies in adsorption. Part XI. A System of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. Journal of the Chemical Society, 1: 3973–3993.

González-Pradas E., Urena-Amate M.D., Flores-Céspedes F., Fernández-Pérez M., Garratt J., Wilkins R. (2002): Leaching of imidacloprid and procymidone in a greenhouse of southeast of Spain. Soil Science Society of America Journal, 66: 1821–1828.

Li W., Qiu S.P., Wu Y.J. (2008): Triazophos residues and dissipation rates in wheat crops and soil. Ecotoxicology and Environmental Safety, 69: 312–316.

Liang B., Yang C., Gong M., Zhao Y., Zhang J., Zhu C., Jiang J., Li S. (2011): Adsorption and degradation of triazophos, chlorpyrifos and their main hydrolytic metabolites in paddy soil from Chaohu Lake, China. Journal of Environmental Management, 92: 2229–2234.

OECD (2000): Guidelines for Testing of Chemicals, Section 1 (106): Adsorption-Desorption Using Batch Equilibrium Method in Soils. Paris, Environmental Health and Safety Division, OECD Environment Directorate.

Rani S., Madan V.K., Kathpal T.S. (2001): Persistence and dissipation behavior of triazophos in canal water under Indian climatic conditions. Ecotoxicology and Environmental Safety, 50: 82–84.

Swann R.L., Laskowski D.A., McCall P.J., Vander Kuy K., Dishburger H.J. (1983): A rapid method for the estimation of the environmental parameters octanol/water partition coefficient, soil sorption constant, water to air ratio, and water solubility. Residue Reviews, 85: 17–28.

Ten Hulscher Th.E.M., Cornelissen G. (1996): Effect of temperature on sorption equilibrium and sorption kinetics of organic micropolutants – A review. Chemosphere, 32: 609–626.

Tomlin C.D.S. (2009): The Pesticide Manual: A World Compendium. Alton, British Crop Production Council.

Vagi M.C., Petsas A.S., Kostopoulou M.N., Lekkas T.D. (2010): Adsorption and desorption processes of the organophosphorus pesticides, dimethoate and fenthion, onto three Greek agricultural soils. International Journal of Environmental and Analytical Chemistry, 90: 369–389.

Vig K., Singh D.K., Agarwal H.C., Dhawan A.K., Dureja P. (2001): Insecticide residues in cotton crop soil. Journal of Environmental Science and Health B, 36: 421–434.

Zhu L.J., Zhang W., Zhang J.C., Zai D.X., Zhao R. (2010): Thermodynamics adsorption and its influencing factors of chlorpyrifos and triazophos on the bentonite and humus. Huan Jing Ke Xue, 31: 2699–2704. (In Chinese)

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