Chinese Chemical Letters Vol. 12, No. 3, pp. 261–264, 2001

A New Rapid Determination Method of Soil Organic Carbon Adsorption Coefficients of Pesticides with Soil Column Liquid Chromatography

Wei Min WANG, Xin Miao LIANG*, Qing ZHANG

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116011

Abstract: Soil column liquid chromatography (SCLC) was developed to determine soil organic carbon adsorption coefficients (K_{oc}) for chemicals. The uptake by soil of pesticides from water can be conveniently calculated from the related breakthrough curves (BTC). The nine pesticides chosen for determination in this study are soluble ones, with their water solubility ranging from 62 mg/L to 2 mg/L. In comparing with existing methods of K_{oc}, SCLC possesses rapid, online and accurate characteristics.

Keywords: Soil organic carbon adsorption coefficients (K_{oc}), determination, soil column.

Recent legislation in many countries requires extensive testing of all manufactured chemicals for environmental evaluation and registration. Among the requirements are water solubility, solvent (usually octanol) – water partition coefficient, soil adsorption and bioconcentration factors in aquatic organisms. Soil adsorption influences the extent of vaporization of a compound from the soil surface and its lateral (run-off) or vertical transport including groundwater contamination. Additionally, adsorption processes may influence abiotic or biotic processes, *e.g.* bioavailability, biodegradation and phytolysis on the soil surface[1].

Earlier studies of the uptake by soil of chemicals from water have indicated that soil organic matter is the principal adsorbent. And it has been speculated that the high surface area of this organic matter is an important factor[2]. The soil organic carbon adsorption coefficient (K_{oc}) of a chemical is defined as:

$$K_{oc} = K_d / f_{oc} \qquad (1)$$

where f_{oc} is the organic carbon fraction of the soil (expressed in grams per gram). The distribution coefficient K_d is given by

$$K_d = C_s / C_e^{1/n} \qquad (2)$$

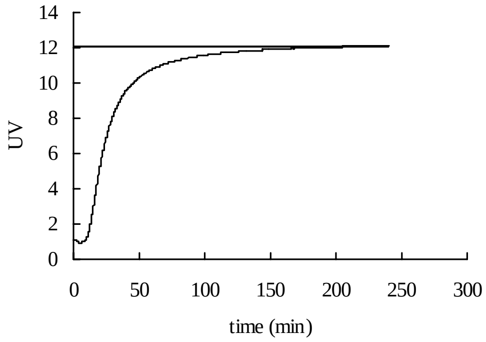
where C_s (micrograms per gram) is the concentration of the chemical adsorbed onto the soil, C_e (milligrams per liter) is the concentration in the soil solution, and n is a dimensionless exponent. In fact, the above equation is known as the nonlinear Freundlich isotherm and n as the Freundlich exponent.

Until now, two methods have been widely applied to directly determine K_{oc}. One is the batch equilibrium method, in which an aqueous solution of the test compound is added to the soil[3]. After adsorption equilibrium reached, the concentrations of the chemical in both the adsorbed state and the soil solution can be obtained. By using Eqn (1) and (2), soil adsorption coefficient is calculated. Both the OECD test guideline[4] and the US-EPA guideline[5] for testing of chemicals describe this method for measuring K_d and K_{oc} using natural soils. The other is soil column method. Movement of the chemical through saturated soil columns was estimated using the displacement technique. A column packed with soil was eluted with the aqueous solution of a chemical at a constant rate. Elution was stopped when the effluent concentration approached a constant, or became identical to the input concentration. Then the adsorbed chemical was displaced by a certain strong solvent and analyzed. Both of the methods are time-consuming and laborious. Therefore they are not suitable for the routine measurement and screening of many substances.

Many attempts have been made to estimate K_{oc}. It is generally accepted that most of environmentally important properties can be characterized by a partition coefficient. It was estimated from water solubility[6], octanol/water partition coefficient[7], molecular topological indices[8] and RP-HPLC capacity factor[9,10]. B. M. Gawlik *et. al* have reviewed these estimation methods[11].

In this study, a new rapid online determination method was developed to directly determine K_{oc} of any hydrophobic compounds. Before being packed into the column, the soil was air dried at ambient temperature and sieved to a particle size from 60 to 80 mesh. Test compounds were insecticides azinphos-methyl, methiocarb, parathion-methyl, fenthion; herbicides atrazine, simazine, diuron; and fungicides triadimenol, tebuconazole. Purities ranged from 99.9% to 98.3% (triadimenol).

Figure 1 The breakthrough curve (BTC) of adsorption of diuron on the soil



Adsorption isotherm of each pesticide involved at least six points (OECD guideline), and all isotherms were duplicated. The aqueous solutions of pesticides (C_e) were used as the eluent at a flow rate of 0.2 mL/min. The solution concentrations ranged approximately from 100 to 5% of the pesticide water solubility. After equilibrium, the effluent had the same concentration as C_e. The BTC for diuron was given in **Figure 1**.

From BTC given in **Figure 1**, diuron was completely adsorbed by soil at the beginning. The effluent concentration C approached Ce with more mobile phase eluting. Until $C/C_e = 1$, an equilibrium reached. The amount of pesticide adsorbed by soil was shown by the area (A) above BTC, after subtracted with the dead time of HPLC system which was determined with $NaNO_2$ at 220 nm. That is,

$$C_s = A\ u\ C_e / W \qquad (3)$$

where C_s is the uptake of pesticide by soil (micrograms per gram), u is the flow rate of the mobile phase (millilitres per minute), C_e is the initial concentration of pesticide in the mobile phase (milligrams per litre) and W represents the weight of soil packed into the column (grams). At each point of adsorption isotherms, the experiments were performed in duplicate. And A is the mean value. The maximum error was so small that it can be neglected (**Figure 2**). By using Eqn (2), the distribution coefficient (K_d) of each pesticide was obtained. Normalized K_d to organic carbon fraction, soil organic carbon adsorption coefficient was calculated according to Eqn (1). The results are shown in **Table 1**. In comparing with K_{oc} reported in literature, the results of our method are very accurate.

The results suggested that soil column liquid chromatographic method is very suitable to rapidly and accurately determine K_{oc} of pesticides. This method is easy to operate in laboratories since it simplifies the experimental procedures. The run time of the experiment can be shortened. And degradation of pesticides can be avoided. The results of the measurement is more accurate. In general, a data point can be obtained within several hours. And the soil packed into the column can be repeatedly used.

Figure 2 The adsorption isotherms of the test pesticides

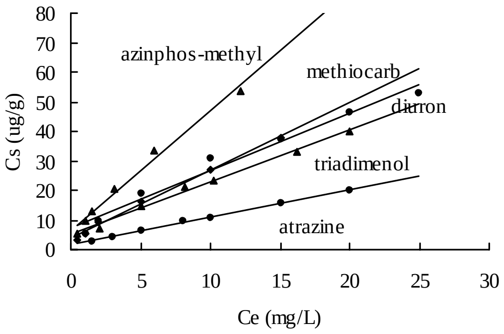


Table 1 The water solubility (Ws), distribution coefficients (K_d), soil organic carbon a dsorption coefficients (K_{oc}) of the pesticides, with K_{oc} reported in literatures

pesticides	Ws (mg/L)	K_d (L/Kg)	n	r	logK_{oc}	logK_{oc}^{1}	logK_{oc}^{7}
simazine	6.2	1.872	1.38	0.9999	2.18	1.78	2.10
atrazine	30	1.934	1.31	0.9981	2.19	1.81	2.24
triadimenol	62	4.119	1.32	0.9979	2.52	2.40	
methiocarb	27	5.484	1.43	0.9993	2.65	2.82	2.32
diuron	42	5.794	1.43	0.9984	2.67		2.40
azinphos-methyl	33	9.200	1.39	0.9990	2.87	2.95	2.28
parathion-methyl	55	9.408	1.37	0.9990	2.88		3.00
fenthion	2	13.90	1.12	0.9991	3.05	3.31	
tebuconazole	32	16.29	1.46	0.9999	3.12	3.01	

Acknowledgment

We sincerely thank Bayer AG and Chinese Academy of Agricultural Sciences for kindly supplying the pesticides.

References

1. W. Kördel, J. Stutte, G. Kotthoff, *Chemosphere*, **1993**, *27*, 2341.
2. C. T. Chiou, L. J. Peters, V. H. Freed, *Science*, **1979**, *206*, 831.
3. S. W. Karickhoff, D. S. Brown, T. A. Scott, *Water Research*, **1979**, *13*, 241.
4. *OECD* Guidelines for testing of chemicals, TG 106 adsorption-desorption in soils, Paris, **1981**.
5. Physical/Chemical properties, measurement and Test. Office of pesticide programs, *EPA*, **1978**.
6. G. G. Briggs, *J. Agric. Food Chem.*, **1981**, *29*, 1050.
7. A. Sabljic, H. Gusten, H. Verharr, J. Hermens, *Chemosphere*, **1995**, *31*, 4489.
8. K. N. Reddy, M. A. Locke, *Chemosphere*, **1994**, *28*, 1929.
9. G. Szabo, J. Guczi, *Chemosphere*, **1995**, *30*, 1717.
10. A. Kaune, R. Bruggemann, M. Sharma, A. Kettrup, *J. Agric. Food Chem.*, **1998**, *46*, 335.
11. B. M. Gawlik, N. Sotiriou, E. A. Feicht, S. Schulte-Hostede, A. Kettrup, *Chemosphere*, **1997**, *34*, 2525.

Received 15 August, 2000