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BIOACCUMULATION IN THE SOIL TO EARTHWORM SYSTEM

Des W. CONNELL and Ross D. MARKWELL\*

Centre for Catchment and Instream Research  
Division of Australian Environmental Studies,  
Griffith University, Nathan, Qld. 4111.  
Australia.

Abstract

A three phase model involving soil to soil water and soil water to earthworm partitioning has been developed for bioaccumulation of stable lipophilic compounds from soil by earthworms. Data on bioaccumulation has been collated from the literature to test the model. The soil water to earthworm bioconcentration factor (log form) was linearly related to the octan-1-ol to water partition coefficient (log form) as expected from the model and similar to bioconcentration with oligochaetes and aquatic organisms. The model predicted that the bioaccumulation factor (soil based) would be weakly dependent on the octanol to water partition coefficient but strongly influenced by the lipid content of the soil. The experimental data was in support of these predictions.

INTRODUCTION

Lipophilic agricultural chemicals, due to their low aqueous solubility and affinity for soil associated organic matter, become sorbed preferentially to the organic matter in soil and stream sediments. As a result, biota associated with the soil or sediment are exposed to relative high concentrations of pesticides and may bioaccumulate such materials. }

A number of investigations have been completed on the bioaccumulation of contaminants from sediments by both marine (Shaw and Connell, 1987) and freshwater (Oliver 1984, 1987) worms. It has been shown (Connell et. al., 1988; Markwell et. al., 1989) that these species accumulate lipophilic compounds from the sediment by effectively passive partition processes, firstly between the sediment and the interstitial water and, subsequently, between the interstitial water and the organism. This is consistent with the



## EXPERIMENTAL DATA

Table I Literature and derived data on Bioaccumulation by Earthworms.

Compound	Log $K_{ow}$	$C_w$ ppm $\times 10^5$	Log $K_b$	BF	Ref	Compound	Log $K_{ow}$	$C_w$ ppm $\times 10^5$	Log $K_b$	BF	Ref
Fenuron	1.0		1.34		1	Dieldrin	4.32		3.62*		1
Methylpenta fluorophenyl sulphone	1.11		1.65		1			57.39	4.05	10.00	3
Carbendazim	1.4		1.57*		1			57.39	4.18	13.60	3
Aldicarb	1.57		1.64		1			57.39	4.42	23.60	3
Simazine	2.18		2.16		1			57.39	4.51	28.80	3
Carbaryl	2.36		1.64		1			57.39	4.43	24.40	3
3-ClPhenol	2.50		1.00	1.1	2			0.27	4.46	25.60	3
			1.32	1.4	2			44.84	4.69	44.00	3
			2.17	16.3	2			76.22	3.80	5.60	3
			2.18	10.1	2			98.64	3.73	4.80	3
Captafol	2.51		3.35*		1			107.61	3.73	4.80	3
Captan	2.54		2.67		1			0.27	3.65	4.00	3
3,4-Cl <sub>2</sub> phenyl urea	2.66		1.80		1			44.84	4.62	37.20	3
								76.22	4.21	14.40	3
Fenamiphos	3.18		2.09		1			98.64	4.03	9.60	3
3,4-Cl <sub>2</sub> Phenol	3.20		1.94	1.8	2			98.64	4.06	10.40	3
			1.80	0.8	2			107.91	3.90	7.20	3
			1.79	1.3	2			134.60	4.23	25.56	4
			2.04	1.4	2			116.80	4.35	38.53	4
Chlorfenvin- phos	3.23		2.30*		1			120.80	4.52	45.86	4
								52.58	4.98	135.4	4
Dowco 275	3.51		1.96		1	2,3,4,5-Cl <sub>4</sub> - Phenol	4.50		2.61	0.5	2
Folpet	3.63		3.32		1			2.73	0.4		2
2,4,5-Cl <sub>3</sub> - Phenol	3.72		2.39	1.5	2			3.53	4.1		2
			2.04	0.4	2	Heptachlor	4.61	40.63	3.56	2.7	4
			2.61	2.5	2			26.79	3.16	1.26	4
			3.36	8.4	2			13.27	3.28	1.32	4
BHC	3.80	1.78	3.16	6.4	3			8.58	3.11	0.92	4
		1.78	3.13	6.0	3	1,2,3,5-Cl <sub>4</sub> - Benzene	4.92		3.45		1
		1.78	3.39	10.8	3						
		1.78	3.47	13.2	3	Cl <sub>3</sub> Phenol	5.24		4.50	5.3	2
		1.78	3.58	16.8	3				4.53	3.4	2
		1.78	3.23	7.6	3				4.38	4.0	2
Diazinon	3.81		2.75*		1				4.90	8.0	2
Parathion	3.93		3.14		1	Cl <sub>6</sub> Benzene	5.31		4.29		1
Phorate	4.26		3.34*		1	Aldrin	5.52	0.68	4.00		1

Table I (cont) Literature and derived data on Bioaccumulation by Earthworms.

Compound	Log $K_{ow}$	$C_w$ ppm $\times 10^5$	Log $K_B$	BF	Ref	Compound	Log $K_{ow}$	$C_w$ ppm $\times 10^5$	Log $K_B$	BF	Ref
Aldrin	5.52	5.69	3.56	0.29	3	DDT	6.36	0.68	5.77	6.40	3
		5.69	4.30	1.60	3			0.61	5.41	3.04	4
		5.69	4.56	2.84	3			0.67	5.89	10.67	4
		5.69	4.82	5.20	3			0.64	5.54	3.79	4
		5.69	4.65	3.56	3			0.57	5.31	2.30	4
		5.69	4.88	6.00	3			DDE	6.51	0.13	6.19
Chlordane	5.54	1.16	5.53	28.21	4			0.13	6.08	9.20	3
		1.43	5.04	10.53	4			0.13	6.31	15.60	3
		0.85	5.49	24.00	4			0.13	6.52	25.20	3
		0.87	5.88	59.55	4			0.13	6.35	16.80	3
DDT	6.36	0.68	5.50	3.40	3			0.13	6.12	10.00	3
		0.68	5.65	4.80	3			0.01	7.64	367.0	4
		0.68	5.95	9.60 <sup>a</sup>	3			0.03	6.65	43.13	4
		0.68	6.23	18.40	3			0.06	7.13	105.2	4
		0.68	5.97	10.00	3			0.06	6.60	31.32	4

References 1 Lord et. al.(1980), 2 Van Gestel and Ma (1988), 3 Wheatley and Hardman (1968), 4 Gish and Hughes (1982).

<sup>a</sup> whole worms adsorbing. Other values from this reference are macerated worm solids adsorbing.

Data on the bioaccumulation of lipophilic compounds was obtained from the literature. Pesticide residues found in earthworms in four independent studies from different soils and using different species of earthworm were obtained. Values of BF from the work of Wheatley and Hardman (1968) are presented in table 1 along with those calculated from the soil and biotic concentrations presented by Gish and Hughes (1982). Calculated values of the soil water concentrations determined using the relationship of Rao and Davidson (1980) are also presented and the values of  $K_B$  calculated therefrom included for the data of Wheatley and Hardman (1968) and Gish and Hughes (1982). Values of  $K_B$  from the work of Van Gestel and Ma (1988) were determined by multiplying the BCF by the calculated soil/water partitioning coefficient. Values from the data of Lord et. al. (1980) are presented as reported. Values of  $K_{ow}$ , extracted from the Thor (1989) database where possible, are included in table 1 for comparison. For the data of Gish and Hughes (1982), the first data set was ignored to ensure that equilibrium had been attained and only the first four months of data were considered as it has been observed (Chessels et. al., 1988) that, over long periods of time, concentration gradients of chemicals are established in the soil. Data from Wheatley and Hardman (1968) were corrected to dry weights using an average dry matter percentage (25% from Gish and Hughes (1982) and Lord et. al. (1980).

## The Soil to Water Process

The transfer of lipophilic chemicals from the soil into the soil water should occur by the same partition process as that observed in the sediment to interstitial water transfer. In most investigations of earthworm bioaccumulation, this equilibrium was not evaluated. However, Lord et. al. (1980) conducted a limited examination of this process and observed a linear relationship between  $\log K_{ow}$  and  $\log K_{om}$ , the soil organic matter to water partition coefficient.

$$\log K_{om} = 0.53 \log K_{ow} + 0.69 \quad (9)$$

Alternatively, for sediment or soil to water equilibria, there are a number of established general relationships between  $K_{oc}$  and  $K_{ow}$  available. Notably, the relationship observed by Rao and Davidson (1980) has been applied successfully to bioaccumulation in oligochaete worms (Markwell et. al., 1989).

$$\log K_{oc} = 1.029 \log K_{ow} - 0.18 \quad (10)$$

The earlier results of Wheatley and Hardman (1968) and of Gish and Hughes (1982) include the soil concentrations but not the soil water concentrations. Hence, soil water concentrations must be obtained by substituting into equation 11 and rearrangement:

$$\begin{aligned} C_w &= C_{oc} / 0.66 K_{ow}^{1.029} \\ &= C_s / f_{oc} 0.66 K_{ow}^{1.029} \end{aligned}$$

Hence, using the values of  $f_{oc}$  reported for each sample time, the concentrations of chemicals in the water may be determined for the results of Gish and Hughes (1982) and those of Van Gestel and Ma (1988) and are reported in table 1. Although water concentrations were determined by a similar method in the work of Van Gestel and Ma (1988), the Rao and Davidson equation was used in order to produce consistent results. Soil concentrations were not reported for the data of van Gestel and Ma (1988) and so water concentrations were not determined. However, this equation may be used to calculate  $K_{sw}$ , which is useful in later calculations.

## The Water to Worm Process

The water to worm bioconcentration process is parameterised by the bioconcentration factor,  $K_b$ , which should be related to the octan-1-ol to water partition coefficient,  $K_{ow}$ , in accordance with the theoretical equation 5. Lord et. al. (1980) found that, when lipophilic compounds were equilibrated between worm body solids and water, the process could be represented by the equation:

$$\log K_{ws} = 0.48 \log K_{ow} + 1.04 \quad (11)$$

where  $K_{ws}$  is the equilibrium partition coefficient between water and worm solids. However, the accord between the constants in this relationship and those predicted theoretically is poor. From equation 5, the first constant should have a value of around unity and the second, a negative value. However, with fish and oligochaete worms good accord is obtained between theory and observation.

$$\text{Fish: } \log K_B = \log K_{ow} - 1.32 \quad (\text{Mackay 1982}) \quad (12)$$

$$\text{Oligochaetes: } \log K_B = 1.11 \log K_{ow} - 1.0 \quad (\text{Markwell et. al., 1989}) \quad (13)$$

The data available for whole worms were limited to six selected compounds and, hence, not of great value independently.

Utilising the soil water concentrations previously calculated (table 1), values of  $K_B$  were calculated from the data of Gish and Hughes (1982) and for those of Van Gestel and Ma (1988) by multiplying BCF by the calculated soil/water partitioning coefficient allowing examination of a data set of 40 observations over a wide range of  $K_{ow}$  values. This data is plotted in fig 2 and the following regression equation obtained:

$$\log K_B = 1.26 \log K_{ow} - 1.9 \quad (14)$$

$n = 40, r = 0.92$

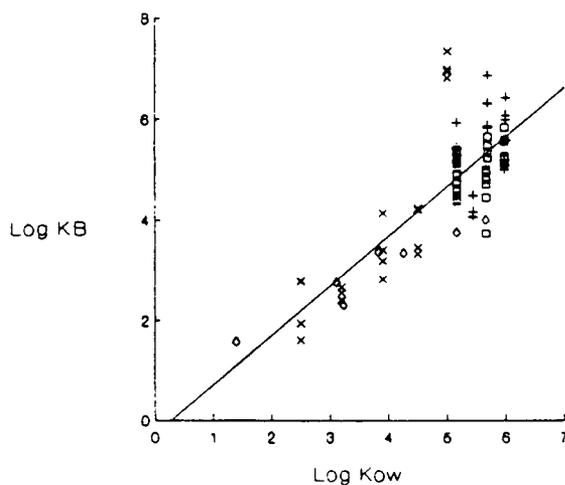


Figure 2 Plot of  $K_B$  data based on soil water concentrations against  $\log K_{ow}$  using results reported by Wheatley et. al. ( $\circ$ ), Gish et. al. (+), Lord et. al. ( $\circ$ ) and van Gestel and Ma ( $\times$ ).

The data of Lord et. al. (1980) from laboratory experiments include values for  $K_B$  for whole worms and macerated worm solids adsorbing chemicals from aqueous solutions in the absence of soil. Inclusion of this data gives equations 15 and 16 respectively. The differences between whole worms and worm solids adsorbing are small.

$$\begin{aligned} \log K_B &= 1.14 \log K_{ow} - 1.3 & (15) \\ n &= 46, r = 0.90 \end{aligned}$$

$$\begin{aligned} \log K_B &= \log K_{ow} - 0.6 & (16) \\ n &= 60, r = 0.91 \end{aligned}$$

Concentrations of pesticides in soil water cannot be calculated from the data of Wheatley and Hardman (1968) because the organic carbon content of the soil was not reported. In order to compare this data with those examined above, a value of 4% was assumed, since this is a commonly reported organic carbon content. If this value is used in equation 10 to obtain the soil water concentration (reported in table 1) and, consequently, the  $\log K_B$  values, the relationship between  $\log K_B$  and  $\log K_{ow}$  becomes:

$$\begin{aligned} \log K_B &= \log K_{ow} - 0.6 & (17) \\ n &= 100, r = 0.91 \end{aligned}$$

While this equation cannot be considered accurate, its consistency with equation 14 is supportive evidence for the three phase partition mechanism.

Further, both these equations are in accord with the theoretical relationship (equation 5), which predicts a slope of unity and an intercept equal to  $\log y_L$ , the lipid content of the worms. From Gish and Hughes (1982), the average  $y_L$  is 0.84% yielding this theoretical relationship:

$$\log K_B = \log K_{ow} - 2.1 \quad (18)$$

This is in remarkable agreement with equations 14 and 15.

#### The Soil to Worm Bioaccumulation

The overall bioaccumulation factor, BF, from soil to earthworm has been shown earlier to be expressed by Equation 8.

$$BF = (y_L/x f_{oc}) K_{ow}^{b-a}$$

Since  $b$  and  $a$  are both often close to unity, the dependence of  $BF$  on  $K_{ow}$  is generally limited or zero. From the data of Lord et. al. (1980), the value of  $b-a$  is 0.05 and, using the data from oligochaete worms (Markwell et. al., 1989) or earthworms as used here, the values are 0.08 and 0.07 respectively. Hence,  $BF$  should be most strongly dependent on  $y_L$  and  $f_{oc}$  and, since  $y_L$ ,  $f_{oc}$ , and  $x$  are all constants, should be invariable for all compounds in a specific soil and worm system. Also, as a consequence of this, the concentrations in the earthworms should be directly proportional to those in the soil for all compounds.

No relationship between  $BF$  and  $K_{ow}$  has been reported to date and this is also the case with the present data. The average  $BF$ , which should equal  $y_L/x f_{oc}$ , is 19. If  $y_L$  is 0.84%,  $x$  is 0.66 from Rao and Davidson (1980) and  $f_{oc}$  is 4%, then  $BF$  should be equal to 0.32, somewhat lower than that observed.

Equation 8 suggests that there should be a linear relationship between  $\log C_{wo}$  and  $\log C_{sed}$ . Markwell et. al. (1989) have found such a relationship with oligochaetes. Also, Wheatley and Hardman (1968) have reported a linear relationship between  $\log C_{wo}$  and  $\log C_{sed}$  for earthworms:

$$\log C_{wo} = 0.80 \log C_{sed} + 0.268 \quad (19)$$

However, the combined data from all four data sets shows no discernable relationship between  $C_{wo}$  and  $C_{sed}$  or  $\log C_{wo}$  and  $\log C_{sed}$ .

#### CONCLUSIONS

The sources of variation in this study are substantial. Several sources of data from experiments conducted under different conditions are included. Also, it has been demonstrated (Chessels et. al., 1988) that pesticides in soils establish concentration patterns and gradients due to varying environmental conditions, leading to irregular exposure.

Despite these limitations, the data are broadly consistent with the transfer of lipophilic compounds through a three phase system involving soil to soil water to organism partitioning, analogous to that observed in oligochaete worms. This is a passive process and is principally dependent on the lipid content of the worms and the organic carbon content of the soil. Transfer from soil to soil water can be described by the same relationships established for sediment to water equilibria. The transfer from soil water to earthworm is described by:

$$\log K_b = \log K_{ow} + 0.6$$

This relationship is consistent with the theoretically derived equation for bioconcentration, which has been found to apply to bioconcentration by aquatic organisms. The bioaccumulation

factor derived from the three phase partition theory is in accord with the observed bioaccumulation factor. It demonstrates a weak dependence on the log  $K_{ow}$  value and strong dependence on the lipid content of the organism and the organic matter content of the soil.

#### REFERENCES

- Chessels M. J., Hawker D. W., Connell D. W. and Papajcsik I. A. (1988) Factors influencing the distribution of lindane and isomers in soil of an agricultural environment, *Chemosphere* 17, 1741-1749.
- Connell D. W. (1988) Bioaccumulation behaviour of persistent organic chemicals with aquatic organisms, *Rev. envir. contam. Toxic.* 101, 117-154.
- Connell D. W., Bowman M. and Hawker D. W. (1988) Bioconcentration of chlorinated hydrocarbons from sediment by oligochaetes, *Ecotoxicol. Envir. Saf.* 16, 293-302.
- Davis B. N. K. and French M. C. (1969) The accumulation and loss of organochlorine insecticide residues by beetles, worms and slugs in sprayed fields, *Soil Biol. Biochem.* 1, 45-55.
- van Gestel C. A. M. and Ma W. (1988) Toxicity and bioaccumulation of Chlorophenols in earthworms in relation to bioavailability in soil, *Ecotoxicol. Envir. Saf.* 16, 289-297.
- Gish C. D. and Hughes D. L. (1982) Residues of DDT, dieldrin and heptachlor in earthworms during two years following application, *U.S. Fish Wildl. Serv., Spec. Sci. Rep.:Wildl.* 241.
- Lord K. A., Briggs G. C., Neale M. C. and Manlove R. (1980) Uptake of pesticides from water and soil by earthworms, *Pestic. Sci.* 11, 401-408.
- Mackay D. (1982) Correlation of bioconcentration factors, *Envir. Sci. Technol.* 16, 274-278.
- Markwell R. D., Connell D. W. and Gabric A. J. (1989) Bioaccumulation of lipophilic compounds from sediments by oligochaetes, *Wat. Res.* 23, 1443-1450.
- Oliver B. G. (1984) Uptake of chlorinated organics from anthropogenically contaminated sediments by oligochaete worms, *Can. J. Fish Aquat. Sci.* 41, 878-883.
- Oliver B. G. (1987) Biouptake of chlorinated hydrocarbons from laboratory-spiked and field sediments by oligochaete worms, *Envir. Sci. Technol.* 21, 785-790.
- Shaw G. R. and Connell D. W. (1987) Comparative kinetics for bioaccumulation of polychlorinated biphenyls by the polychaete (*Capitella capitata*) and fish (*Mugil cephalus*), *Ecotoxicol. Envir. Saf.* 13, 84-91.
- Thor (1989) from MedChem Release 3.54, Daylight Chemical Information Systems Inc., Claremont, CA.
- Wheatley G. A. and Hardman J. A. (1968) Organochlorine insecticide residues in earthworms from arable soils, *J. Sci. Fd. Agric.* 19, 219-225.

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