

Predicting the Behaviour of Pesticides in Soil from their Physical and Chemical Properties [and Discussion]

Geoffrey G. Briggs, P. B. Tinker and I. J. Graham-Bryce

Phil. Trans. R. Soc. Lond. B 1990 **329**, 375-382

doi: 10.1098/rstb.1990.0179

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. B* go to: <http://rstb.royalsocietypublishing.org/subscriptions>

Predicting the behaviour of pesticides in soil from their physical and chemical properties

GEOFFREY G. BRIGGS

Schering Agrochemicals Limited, Chesterford Park Research Station, Saffron Walden, Essex, CB10 1XL, U.K.

SUMMARY

Increasingly stringent environmental requirements for pesticides mean that both biological activity and favourable environmental behaviour must be assessed at an early stage in pesticide discovery. Soil behaviour is governed by the physical properties of the molecule: partition coefficient, dissociation constant, vapour pressure and melting point, which control potential movement under particular soil and environmental conditions and the soil persistence. Established chemical structure–physical property correlations generally allow physical properties to be estimated for the large number of compounds in a synthesis programme with adequate precision. Stability to chemical or biological transformations in soil is more difficult to estimate but a combination of measurement for a few compounds and analogy with known chemical and biological transformation rates for various functional groups can give useful structure–stability correlations.

1. INTRODUCTION

As the environmental requirements for pesticides became increasingly stringent then the consideration of environmental behaviour must come earlier in the development process. At least 20000 new compounds are tested for each new product and it is clearly advantageous to try to direct synthesis to those compounds with both environmentally and biologically favourable properties. This implies using estimated values of environmentally important parameters obtained from the chemical structure.

A number of complex models exist that describe the movement of chemicals after application to soil. The primary inputs are rainfall, temperature and evaporation with soil texture as a secondary input to allow the water movement to be described. All the complexity lies in describing the air and water flows, the chemical being described relatively simply in terms of an adsorption coefficient, vapour pressure, solubility and soil persistence. The chemical descriptions, largely as discussed by Goring & Hamaker (1972), may appear too simple, but even a complex process such as the turnover of organic matter in soils over very long periods can be modelled by a small number of rate constants modified for soil temperature and moisture content in diverse climates (Jenkinson *et al.* 1987). The potential for various processes to occur is defined in the chemical structure and this paper shows structure–property relations which can be used to manipulate structures to obtain molecules whose potential behaviour is approximately known.

2. KEY PROPERTIES

Chemicals are sprayed onto plants and soil or incorporated into the soil. During spraying there is potential for evaporation from the spray droplet and subsequently from the soil or plant surface. Chemicals at the surface may be leached below the surface and thus no longer have the potential to volatilize, but under drying conditions may return to the surface in the water (Spencer *et al.* 1988). Degradation is occurring and reduces the mass either leached or volatilized. Plant uptake can occur by root uptake to the transpiration stream, by vapour uptake by roots or leaves and from direct application to the leaf. These potential redistributions depend on the following properties which in turn can be regarded as dependent on other more simply conceived properties:

vapour pressure	boiling point (T_b) and melting point (T_m)
water solubility	octanol–water partition coefficient (K_{ow}) and T_b
air and water distribution	T_b and K_{ow}
soil adsorption	K_{ow}
air and soil distribution	T_b and K_{ow}
plant systemicity	K_{ow}

These apply for unionized molecules. For ionizable compounds the ion and uncharged species will have different behaviour and the observed behaviour depends on the charge, the partition coefficient pK of the compound and the pH of the system.

3. VAPOUR PRESSURE AND VOLATILIZATION

There are sophisticated ways of estimating vapour pressure from chemical structure reviewed in Lyman

et al. (1982), but they are not readily converted to easily manipulated functional group contributions that can be used to design molecules with specific vapour pressures. A relatively crude method described in outline by Briggs (1981*b*) is amenable to simple use and can give very rapid and reasonably close estimates of vapour pressure.

For solids or liquids the vapour pressure (v.p.) in Pascals at 25 °C is given approximately by:

$$\log \text{v.p. (Pa)} = 2.13 - 0.0172 (T_b - 193) - 0.01 (T_m - 25), \quad (1)$$

where T_b and T_m are the boiling point at atmospheric pressure and the melting point, respectively, both in degrees Centigrade. The term involving T_m is an approximation from Yalkowsky (1977) for the work required to convert a solid to an oil and disappears for liquids when T_m is set to 25 °C. This approximation assumes that the heat of fusion is constant and the T_b term makes the same assumption for the heat of vaporization. Making the useful (but incorrect) assumption that boiling point is an additive function, boiling point increments for functional groups can be derived simply by subtraction. Adding these increments to parent structures allows boiling point and hence vapour pressure to be estimated. The calculated boiling point is higher than the true boiling point, but this compensates for the assumption that the heat of vaporization does not decrease with temperature and gives vapour pressures within an order of magnitude for compounds boiling above about 60 °C. A list of boiling point increments is shown in table 1.

For example, using this table, T_b of 2,4,8-trichlorobenzofuran can be calculated by adding the values for two (CH)₄ fragments (140 × 2) and three Cl atoms (40 × 3) to the boiling point of furan (32 °C) giving a calculated value of 432 °C. Substituting this value and the melting point (154 °C) into equation (1)

gives a calculated vapour pressure of 5×10^{-4} Pa for the solid, within an order of magnitude of the experimental value of 9×10^{-5} Pa (Rordorf 1989).

Changes in vapour pressures for changing substituents can readily be calculated. Gubler *et al.* (1987) quote a 280-fold difference in the vapour pressures of the fungicide propiconazole and an analogue in which a chlorine atom had been replaced by a chlorophenoxy group and one CH₂ group removed. The increments in table 1 show that T_b should increase by 140 °C (+160 for OC₆H₅–20 for loss of CH₂), which equation (1) shows should give a 250-fold difference in vapour pressure.

Vapour pressure and volatilization rates are inextricably linked and either can be used to estimate the other (Dobbs *et al.* 1984). Table 2 gives estimated half-lives for a 1 kg ha⁻¹ deposit on an inert surface calculated by using equation (2), which can be derived from the experimental data of Guckel *et al.* (1973) on the relation between vapour pressure and evaporation rate (E) (in moles per square centimetre per hour),

$$\begin{aligned} \log E &= \log \text{vapour pressure (Pa)} - 6.62 \\ &= \log \text{vapour pressure (mmHg)} - 4.5. \end{aligned} \quad (2)$$

The boiling point in table 2 assumes a liquid state. Equation (1) shows that a 58 °C change in T_b or a 100 °C change in T_m changes vapour pressure tenfold so adding $T_m/2$ to the boiling point gives a quick estimate for solids. These evaporation rates give an indication of the potential for vapour loss in the initial screen as well as in the field. The fungicide chlobenthiazole has a calculated T_b of 360 °C and reported T_m 133 °C and Table 2 shows substantial vapour losses over a few days, confirmed by the change in spray concentration required for disease control which increases from 6 mg l⁻¹ to 200 mg l⁻¹ as the time from spraying to inoculation increases from 4 h to 4 days (Inoue *et al.* 1981).

4. WATER SOLUBILITY

A knowledge of the water solubility of a compound is important as an indication of how a chemical may behave in aqueous systems. Equation (3), from Yalkowsky (1977) gives a good estimate of the water solubility (WS) of many compounds from their octanol–water partition coefficients and melting points (T_m in degrees Centigrade),

$$\log \text{ws (moles per litre)} = 0.5 - \log K_{ow} - 0.01 T_m. \quad (3)$$

As the octanol–water partition coefficient can be calculated from the structure (Hansch & Leo 1979) then the water solubility can be calculated if T_m is known. There are no calculation methods for T_m but various compound types have characteristic ranges that can be used. The T_m term in equation (3) shows that the relation between lipophilicity, given by K_{ow} , and water solubility can be distorted by those compounds that have high melting points and are therefore relatively insoluble although not necessarily very lipophilic. An oil and a solid of T_m 300 °C which

Table 1. *Changes in boiling point and partition coefficient*

	aromatic		aliphatic	
	ΔT_b	$\Delta \log K_{ow}$	ΔT_b	$\Delta \log K_{ow}$
CH ₃	20	0.5	20	0.5
CF ₃	20	0.8	20	0
C≡CH	65	0.4	50	-0.3
F	0	0.1	0	-0.6
Cl	40	0.7	40	-0.1
Br	70	0.8	70	0
I	100	1.1	100	0.3
NO ₂	130	-0.2	100	-1.4
SMe	110	0.6	90	-0.2
SO ₂ Me	230	-1.7	230	-2.4
NH ₂	100	-1.2	55	-1.8
NMe ₂	115	0.2	70	-0.8
NHAc	230	-1.0	200	-2.1
OH	100	-0.7	80	-1.8
OMe	70	0	50	-1.7
COOMe	120	0	100	-0.9
C ₆ H ₅	160	1.8	160	1.7
OC ₆ H ₅	160	1.9	160	1.0
(CH) ₄	140	1.3		

Table 2. Boiling point, vapour pressure and vapour loss

$T_b/^\circ\text{C}$	Vapour pressure ^a		time taken for loss of half of a 1 kgha ⁻¹ deposit from an inert surface/days ^b		
	Pascal	mmHg	U.K. spring	U.K. summer	U.S. summer
200	90	7×10^{-1}	< 1 min	< 1 min	< 1 min
300	1	1×10^{-2}	2 min	< 1 min	< 1 min
350	2×10^{-1}	2×10^{-3}	20 min	10 min	4 min
400	4×10^{-2}	3×10^{-4}	3 h	90 min	40 min
450	5×10^{-3}	4×10^{-5}	30 h	15 h	6 h
500	7×10^{-4}	5×10^{-6}	12 days	6 days	2 days
550	9×10^{-5}	7×10^{-7}	120 days	60 days	25 days
600	1×10^{-5}	1×10^{-7}	1200 days	600 days	250 days

^a For liquid state. Add $0.5 T_m$ to T_b to give value for solids.

^b Equation (2) was derived under still-air conditions at 20°C . Rate adjusted to allow for temperature and wind differences.

Table 3. Half-life (days) for chemical volatilization from a 10 cm water column at 20°C

$T_b/^\circ\text{C}$	$\log K_{ow}$								
	-1	0	1	2	3	4	5	6	
100	4	0.4	0.04	0.02	0.02	0.01	0.01	0.01	0.01
200	200	20	2	0.2	0.04	0.02	0.01	0.01	0.01
300	> 1000	1000	100	10	1	0.08	0.03	0.02	
400	> 1000	> 1000	> 1000	500	50	5	0.04	0.06	
500	> 1000	> 1000	> 1000	> 1000	> 1000	200	20	2	
600	> 1000	> 1000	> 1000	> 1000	> 1000	> 1000	1000	100	

have the same solubility differ in $\log K_{ow}$ by 3, or if they have the same K_{ow} differ 1000-fold in water solubility.

Equation (3) gives water solubilities within a factor of 4 for the series of chlorinated dibenzofurans determined by Friesen *et al.* (1990). For example, the $\log K_{ow}$ for 2,3,7,8-tetrachlorodibenzofuran (T_m 227 $^\circ\text{C}$ from Rordorf (1989) calculated by using the $\Delta \log K_{ow}$ values in table 1 is 6.7 ($\log K_{ow}$ furan = $1.3 + 2$ (CH)₄ substituents + 4Cl substituents). Equation (3) gives a calculated water solubility of 3.4×10^{-9} M, the experimental value being 1.4×10^{-9} M (Friesen *et al.* 1990).

5. VOLATILIZATION FROM WATER

The air-water distribution, K_{aw} , or Henry's Law constant is given by the ratio of the saturated vapour concentrations and the saturated water concentration. In this ratio the melting point term disappears on combining equation (1), converted to concentration, and equation (3) to give the dimensionless Henry's Law constant from equation (4), which can be obtained directly from the structure,

$$K_{aw} = \frac{10^{-0.0172(T_b-193)} \times K_{ow}}{51000}. \quad (4)$$

The ΔT_b and $\Delta \log K_{ow}$ values for various substituents listed in table 1 allow rapid assessment of changes in K_{aw} if structural modifications are made. For example, introducing a chlorine into an aromatic ring decreases vapour pressure *ca.* 4.8-fold, but also

decreases water solubility by a comparable factor so that all the polychlorinated biphenyls should have similar K_{aw} . Equation (4) gives good agreement with many published values of K_{aw} , including those recently measured by Fendinger *et al.* (1989).

Volatilization from water is controlled by K_{aw} and the liquid and gas phase exchange coefficients K_l and K_g (Mackay & Leinonen 1975; Lyman *et al.* 1982). Half-life ($t_{1/2}$ for volatilization from a water column depth Z cm is given by Mackay & Leinonen (1975) as:

$$t_{1/2} \text{ (hours)} = 0.69 Z(1/K_l + 1/K_g \cdot K_{aw}). \quad (5)$$

The values of the exchange coefficients depend on wind speed and other environmental variables but values for relatively still conditions of 18 and 1100 cm h⁻¹ for K_l and K_g inserted in equation (4) with K_{aw} calculated from equation (4) give the half-lives (days) shown in table 3. For a 1 m depth the times would be 10 times longer and for thin water films correspondingly shorter. The calculated half-lives give good agreement with the values quoted by Lyman *et al.* (1982) for a range of chemical types. The rice herbicide molinate has a boiling point *ca.* 340 $^\circ\text{C}$ and $\log K_{ow}$ *ca.* 3 so that considerable vapour losses from flooded rice fields would be expected, as found by Sieber *et al.* (1986).

6. SOIL ADSORPTION

Given the spatial variability of soil in terms of texture, mineralogy and organic content any attempt to make precise predictions of soil interaction is bound

to fail, but broadly useful generalizations have been made.

The soil–water distribution, K_d , is generally proportional to the soil organic matter content for non-ionic compounds. Expressing K_d in terms of organic matter, K_{om} , or organic carbon, $K_{oc} = 1.724 K_{om}$, gives a relatively constant value (range generally one half to twice the mean) for one compound in many soils while the range of K_{om} for different compounds is at least 500 000-fold.

Since K_{oc} or K_{om} are partition coefficients, they can be related to other organic phase–water partition coefficients such as water solubility or the octanol–water partition coefficient. A number of log–log relations have been found with slopes and intercepts varying with the chemicals involved, the use of soils or sediments and the experimental methodology.

$$\begin{aligned} \log K_{oc} &= 1.0 \log K_{ow} - 0.2 \text{ Karickhoff } et al. (1979) \\ &= 0.7 \log K_{ow} + 0.5 \text{ Schwarzenbach \& Westall} \\ &\quad (1981) \\ &= 0.5 \log K_{ow} + 1.4 \text{ Kenaga \& Goring (1980)} \\ &= 0.5 \log K_{ow} + 0.9 \text{ Briggs (1973, 1981a)} \\ &= 0.4 \log K_{ow} + 1.1 \text{ Kanazawa (1989)}. \end{aligned}$$

The various relations give similar answers for their real purpose, which is to estimate K_d from the chemical structure and organic matter content. For soils with organic carbon in the 1–5% range compounds with $\log K_{ow} > 4$ will be strongly adsorbed with $K_d > 10$. Compounds with $\log K_{ow}$ in the range 2–4 will be moderately adsorbed with K_d in the range 1–10 and more polar compounds will be weakly adsorbed by the organic matter through the partition mechanism. However, other adsorption mechanisms occur, particularly adsorption of monocations with K_d ca. 100 and the adsorption of organic phosphates to phosphate adsorption sites (Hance 1976). The relation between mobility on soil thick-layer plates, K_d , K_{oc} and K_{ow} is shown in table 4 for non-ionized compounds.

The simplest way to anticipate the adsorption of organic anions is to use $\log K_{ow}$ for the un-ionized form and subtract 3.5 (Hansch & Leo 1979) for the anion; soil adsorption then depends on the pK_a of the acid and the soil pH, with adsorption decreasing rapidly and soil mobility increasing at a soil pH about two units above the pK_a (Nicholls & Evans 1985). The pK_a values of many acids and bases can be calculated from the chemical structure (Perrin *et al.* 1981) and combined with calculated partition coefficients to give estimated adsorption.

Table 4. *Mobility, adsorption and the octanol–water partition coefficient*^a

Rf soil tlc	K_d	K_{oc}	$\log K_{ow}$
0.02	45	3000	5
0.06	14	950	4
0.19	4	290	3
0.44	1	80	2
0.72	0.4	26	1
0.90	0.1	8	0

^a Soil with 1.5% organic carbon.

Table 5. *Mobility*^a as a function of pK_a and $\log K_{ow}$

pK_a	$\log K_{ow}$			
	1	2	3	4
4	115	85	40	—
5	100	70	50	30
6	95	60	30	20
7	70	40	—	—

^a Relative to atrazine = 100.

Table 5 shows the calculated pK_a and $\log K_{ow}$ of some experimental compounds and their movement, detected by bioassay, on soil thick-layer plates (pH 6). The rules for plant systemicity outlined by Bromilow & Chamberlain (1989) show that plant movement and soil movement are highly associated.

7. VOLATILIZATION FROM SOIL

The air–wet soil distribution K_{as} is obtained by dividing the air–water distribution by the soil–water distribution. Swann *et al.* (see Lyman 1982) found the following inverse relation between K_{as} and the half-life for volatilization from a moist soil surface where water solubility (mg l^{-1}) and vapour pressure (mmHg) is:

$$t_{\frac{1}{2}} \text{ days} = \frac{1.58 \times 10^{-8} (K_{oc} \times \text{water solubility})}{\text{vapour pressure}}. \quad (6)$$

Glotfelty *et al.* (1989) have provided further experimental support for this relation. When both K_{oc} and water solubility in equation (6) are substituted by the appropriate relation to K_{ow} , values calculated by the resulting form of equation (6) are very sensitive to the slope of for the K_{oc}/K_{ow} relation. I find that a good fit to the data of Swann *et al.* is given by equation (7) with values shown in table 6.

$$t_{\frac{1}{2}} \text{ (days)} = \frac{0.02}{10^{-0.0172(T_b-193)} \times K_{ow}^{0.35}}. \quad (7)$$

The half-lives look very short for the more lipophilic compounds, but agree with experimental results. Woodrow *et al.* (1986) found that high rates of herbicidal oils evaporated with $t_{\frac{1}{2}}$ less than an hour and Hance *et al.* (1973) found 50% loss of tri-allate ($T_b \approx 400^\circ\text{C}$ and $\log K_{ow} \approx 4$) in 3 days from wet soil at 20°C .

8. SOIL HALF-LIFE

The degradation rates of chemicals in soils in the field can be thought of in terms of an intrinsic stability of the molecule to microbial and chemical decay, which is modified by soil factors such as organic matter, pH and the climate.

The influence of environmental conditions, especially water content and temperature, on degradation rates is reasonably well described in various models (Walker 1987) with functions that are similar to those in plant residue decomposition models (Jenkinson *et al.* 1987) and simulations of field results using laboratory-derived degradation rates (for soils from the field site)

Table 6. Half-life (days) for chemical volatilization from a moist soil surface at 20 °C

T_b , °C	log K_{ow}							
	0	1	2	3	4	5	6	7
300	1.4	0.6	0.3	0.1	0.06	0.02	0.01	0.004
350	10	5	2	0.9	0.4	0.2	0.1	0.03
400	70	35	15	7	3	1	0.6	0.2
450	500	230	100	45	20	9	4	2
500	> 1000	> 1000	700	300	150	65	30	14
550	> 1000	> 1000	> 1000	> 1000	1000	450	200	90

Table 7. Groundwater ubiquity scores (after Gustafson 1989)

log K_{ow}	K_{oc}	K_d	soil half-life/days				
			10	30	50	100	200
1	10	0.2	2.9	4.3	5.0	5.9	6.7
1.5	25	0.5	2.5	3.7	4.3	5.1	5.8
2.6	100	2	1.9	2.9	3.3	3.9	4.4
3.4	250	5	1.5	2.3	2.6	3.1	3.7
3.9	500	10	1.2	1.8	2.1	2.5	2.8
4.5	1000	20	0.9	1.4	1.6	1.9	2.1

Table 8. Soil half-lives, R , X substituted benzenes

R	X	Soil half-life (days) at 25 °C	
		fresh soil	sterile soil
stable	2,6-Cl ₂	> 100	> 100
stable	2-CH ₃ ,6-COOMe	50	—
stable	2,5-(CH ₃) ₂ ,6-COOMe	> 100	—
stable	2,6-(COOMe) ₂	50	—
stable	2,5-(COOMe) ₂	6	—
stable	2-Cl,6-SMe	< 30	—
degradable	2-Cl,6-COOMe	< 30	> 100
hydrolysable	2,6Cl ₂	< 30	50

and weather data are generally quite successful. For most chemicals the relative change in rate for a 10-degree change in temperature is about 2.6-fold and there is about a four fold decline in rate from field capacity to the wilting point. Typically, under laboratory conditions, half-lives in a range of mineral soils lie within ± 0.33 of the mean unless there is a major influence due to pH on either adsorption or stability. The probable range of half-lives in different soils and climates could probably therefore be reasonably estimated if the half-life in a microbially active soil with low moisture tension at 25 °C could be estimated from the structure.

Structure-degradability correlations in soils have seldom been reported and there is much work to be done before stability predictions from chemical structure can be made. Degradability estimates for specific functional groups can sometimes give useful indications of stability (Briggs 1976, 1980, 1981 *a*).

The observed half-life, $t_{\frac{1}{2}}$, is given by

$$t_{\frac{1}{2}} = H_w(1 + 100K_d/\% \text{ moisture}),$$

where H_w is the half-life in the soil-water phase. This relation can be used to calculate the relative stabilities of functional groups in molecules with widely differing adsorption characteristics, adsorption increasing the half-life by decreasing the availability for chemical or microbial transformations.

Values for H_w for thioether groups depend on steric and electronic effects and are in the range from (0.04 for unhindered thioethers) to 0.2 (for more hindered ones such as aldcarb).

Two recent experimental compounds with K_d about 7 had half-lives of 7 days for an ArSCH₂-heterocycle and > 40 days for an ArCH₂-heterocycle indicating that H_w for the heterocyclic thioether is > 1, about five times more stable than the phenyl thioether.

Esters are often rapidly hydrolysed in soils, often much faster than the aqueous hydrolysis rate would suggest. Fluoroxypyr-1-methylheptyl ester hydrolysed several thousand times faster in dilute soil suspensions than in pH 7 buffer (Lehmann & Miller 1989). For aromatic esters the soil hydrolysis rate depends dramatically on steric effects as shown by the data in table 8 where isomeric compounds can have widely different decomposition rates because of steric effects. The relatively smaller difference between the sterile and fresh soil for compounds containing chemically hydrolysable groups is an important consideration for leachable compounds where the sub-soil microbial degradation rate may be much slower than in the surface soil.

Oxime carbamates hydrolyse at high soil pH and are therefore more stable in acidic subsoils, while the reverse is true for chlorsulfuron (Duffy *et al.* 1987). The rapid hydrolysis reported for a related sulphonylurea over the whole pH range (Palm *et al.* 1989) is an important advance giving short soil half-life at all pH values, probably because the molecule contains both the acid labile sulphonylurea and an activated pyridine which would be subject to nucleophilic attack at higher pH.

The use of spectroscopic data for predicting metabolism is uncommon, although Steen & Collette (1989) reported a relation between microbial transformation rates of some amides and the stretching frequency of the carbonyl group in the infra-red spectrum. Staab (1962) commented on the relation between the hydrolysis rates of N-acyl-azoles and their carbonyl infra-red frequency. The regression derived from these data gives a good prediction of the hydrolysis rate of a carbamoyl azole described by Brookes & Copping

(1975). Inserting the carbonyl frequencies of the amides investigated by Steen & Collette (1989) indicates the great hydrolytic stability of the compounds and the large acceleration in a microbial hydrolysis. Given the wealth of spectroscopic data available such approaches may be used more widely in future.

9. LEACHING IN THE FIELD

Leaching observed in the field is the combination of water flow, adsorption and degradation with current emphasis on leaching below the surface soil layers.

A number of relations, equations (8)–(11), which all contain the ratio of half-life to soil adsorption, have recently been proposed to rapidly assess the potential to leach to groundwater.

$$K_{oc} > at_{\frac{1}{2}} - b \quad (\text{from Jury } et al. 1987). \quad (8)$$

According to this relation leaching to depth will occur unless K_{oc} is greater than the function describing potential flow and soil persistence. Term b depends on bulk density, organic carbon and water content and term a depends on water flow, the change in degradation rate with depth, bulk density, the depth considered and the fraction reaching that depth.

$$\text{percentage percolation loss} = a(t_{\frac{1}{2}}/K_{oc})^b \quad (\text{from Leonard \& Knisel 1988}). \quad (9)$$

Term a is proportional to water solubility and determined by regression of the mean leaching losses over 50 years, calculated from a computer model, against the function $t_{\frac{1}{2}}/K_{oc}$.

$$\text{Leaching index} = \frac{\text{water solubility} \times t_{\frac{1}{2}}}{\text{vapour pressure} \times K_{oc}} \quad (\text{from Laskowski } et al. 1982). \quad (10)$$

Here the water solubility and vapour pressure term takes the potential for vapour loss of surface applied materials into account, the $t_{\frac{1}{2}}/K_{oc}$ ratio being the expression of the necessity to consider both persistence and adsorption in assessing potential leaching.

$$\text{Ground water ubiquity score} = \log t_{\frac{1}{2}} \times (4 - \log/K_{oc}) \quad (\text{from Gustafson 1989}), \quad (11)$$

derived from fitting a hyperbolic function which discriminated between compounds found or not found in Californian groundwater on a log–log plot of $t_{\frac{1}{2}}$ against K_{oc} , scores above 2.8 being associated with groundwater while those below 18 were not. Equation (11) implies that strongly adsorbed materials will never leach significantly while the other equations show that this is possible over a sufficiently long time.

All these relations use K_{oc} as a measure of K_d and tend to overestimate mobility if adsorption on inorganic components is the main mechanism. The groundwater ubiquity scores are given in table 7 for a range of half-lives and adsorption on the K_{oc} , K_d or K_{ow} scales. Inserting values for ammonia ($t_{\frac{1}{2}} = 10$ days, $K_d = 100$), nitrate (long $t_{\frac{1}{2}}$, $K_d < 0.2$), heavy metal ions and phosphate (long $t_{\frac{1}{2}}$, $K_d > 1000$) gives sensible

estimates of the behaviour of some inorganic soil constituents.

Relations such as those described are incorporated in the requirements of regulatory authorities who may demand extensive field monitoring for new compounds with half-lives greater than 20–30 days and K_d less than 5 or K_{oc} less than 300–500.

Since rapid metabolism may lead to significant concentrations of metabolites these too may have to meet the same requirements.

10. CONCLUSION

The relation between chemical structure and physical properties, which can be used to show potential environmental redistribution is relatively well described and the influence of climate on relative degradation rates is reasonably accounted for in current modelling approaches. However, the intrinsic stability of chemicals is very difficult to estimate. Given the crucial importance of short persistence for new pesticides it is not surprising that short persistence is starting to appear in the patent literature as an invention in itself.

REFERENCES

- Briggs, G. G. 1973 A simple relationship between soil adsorption of organic compounds and their octanol/water partition coefficients. *Proceedings 7th British Insecticides and Fungicides Conference* (Vol. 1), pp. 83–86.
- Briggs, G. G. 1976 Degradation in soils. (pp. 41–54.) In *Proceedings of the British crop protection council symposium. Persistence of insecticides and herbicides*.
- Briggs, G. G. 1980 Factors affecting degradation of pesticides in soil. In *Pesticide residues MAFF reference book* (vol. 347), pp. 12–19. London: HMSO.
- Briggs, G. G. 1981a Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors and the parachor. *J. Agric. Food Chem.* **29**, 1050–1059.
- Briggs, G. G. 1981b Relationships between chemical structure and the behaviour and fate of pesticides. *Proceedings 1981 British crop protection conference—pests & diseases*. (vol 3), pp. 701–710.
- Bromilow, R. H. & Chamberlain, K. 1989 Designing molecules for systemicity. *Br. Plant Growth Reg. Group Monogr.* **18**, 113–128.
- Brookes, R. F. & Copping, L. G. 1975 Some chemical and physical properties of epronaz, a new herbicide. *Pestic. Sci.* **6**, 665–673.
- Dobbs, A. J., Hart, G. F. & Parsons, A. H. 1984 The determination of vapour pressures from relative volatilization rates. *Chemosphere* **13**, 687–692.
- Duffy, M. J., Hanafey, M. K., Limn, D. M., Russell, M. H. & Peter, C. J. 1987 Predicting sulfonylurea behaviour under field conditions. In *Proceedings 1987 British crop protection conference—weeds* (vol. 2), pp. 541–547.
- Fendinger, N. J., Glotfelty, D. E. & Freeman, H. P. 1989 Comparison of two experimental techniques for determining air/water Henry's law constants. *Environ. Sci. Technol.* **23**, 1528–1531.
- Friesen, K. J., Vilks, J. & Muir, D. C. G. 1990 Aqueous solubilities of selected 2,3,7,8-substituted polychlorinated dibenzofurans. *Chemosphere* **20**, 27–32.

- Glotfelty, D. E., Leech, M. M., Jersey, J. & Taylor, A. W. 1989 Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor and toxaphene. *J. Agric. Food Chem.* **37**, 546–551.
- Goring, C. A. I. & Hamaker, J. W. 1972 *Organic chemicals in the soil environment*. New York: Marcel Dekker.
- Gubler, K., d'Hondt, C. & Steinemann, A. 1987 Synthesis and chemodynamic behaviour of new agrochemicals. Proceedings 31st International Congress of Pure and Applied Chemistry, pp. 126–136.
- Guckel, W., Synnatschke, G. & Rittig, R. 1973 A method for determining the volatility of active ingredients used in plant protection. *Pestic. Sci.* **4**, 137–147.
- Gustafson, D. I. 1989 Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Tox. Chem.* **8**, 339–357.
- Hance, R. J., Holroyd, J. & McKone, C. E. 1973 Some aspects of triallate volatility. *Pestic. Sci.* **4**, 13–17.
- Hance, R. J. 1976 Adsorption of glyphosate by soils. *Pestic. Sci.* **7**, 363–366.
- Hansch, C. & Leo, A. J. 1979 *Substituent constants for correlation analysis in chemistry and biology*. New York: Wiley & Sons.
- Inoue, S., Uemata, T., Noda, C., Osaki, T., Ueda, K. & Kawasa, Y. 1981 Chlobenthiazone, a new systemic fungicide for the control of rice blast. *Proceedings 1981 British crop protection conference—pests & diseases* (vol. 1), pp. 19–27.
- Jenkinson, D. S., Hart, P. B. S., Rayner, J. H. & Parry, L. C. 1987 Modelling the turnover of organic matter in long term experiments at Rothamsted. *Intecol Bull.* **15**, 1–8.
- Jury, W. A., Focht, D. D. & Farmer, W. J. 1987 Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *J. environ. Qual.* **16**, 422–428.
- Kanazawa, J. 1989 Relationship between the soil sorption constants for pesticides and their physicochemical properties. *Environ. Toxicol. Chem.* **8**, 477–484.
- Karickhoff, S. W., Brown, D. S. & Scott, T. A. 1979 Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **13**, 241–248.
- Kenaga, E. E. & Goring, C. A. I. 1980 Relationship between water solubility, soil sorption, octanol–water partitioning and bio-concentration of chemicals in biota. In *Proceedings of the 3rd symposium on aquatic toxicology*. Philadelphia: American Society for Testing and Materials.
- Laskowski, D. A., Goring, C. A. I., McCall, P. J. & Swann, R. L. 1982 Terrestrial environment In *Environmental risk analysis for chemicals* (ed. R. A. Conway), pp. 198–240. New York: Van Nostrand Reinhold.
- Lehmann, R. G. & Miller, J. R. 1989 Soil catalysed hydrolysis of fluroxypyr-methylheptyl ester. *Weed Res.* **29**, 385–389.
- Leonard, R. A. & Knisel, W. G. 1988 Evaluating groundwater contamination potential from herbicide use. *Weed Technol.* **2**, 207–216.
- Lyman, W. J., Reehl, W. F. & Rosenblatt, D. H. 1982 *Handbook of chemical property estimation methods*. New York: McGraw-Hill.
- Mackay, D. & Leinonen, P. J. 1975 Rate of evaporation of low solubility contaminants from water bodies to atmosphere. *Environ. Sci. Technol.* **9**, 1178–1180.
- Nicholls, P. & Evans, A. A. 1985 Adsorption and movement in soil of chlorsulfuron and other weak acids. In *Proceedings British crop protection conference—weeds* (vol. 1), pp. 333–339.
- Palm, H. J., Liang, P. H., Fuesler, T. P., Leek, G. L., Strachan, S. D., Wittenbach, V. A. & Swinchatt, M. L. 1989 New low-rate sulfonylureas for post-emergence weed control in corn. In *Proceedings Brighton crop protection conference—weeds* (vol. 1), pp. 23–28.
- Perrin, D. D., Dempsey, B. & Serjeant, E. P. 1981 *pK_a prediction for organic acids and bases*. London: Chapman & Hall.
- Rordorf, B. F. 1989 Prediction of vapour pressures, boiling points and enthalpies of fusion for 29 dibenzo-*p*-dioxins and 55 dibenzo-furans by a vapour pressure extrapolation method. *Chemosphere* **18**, 783–788.
- Seiber, J. N., McChesney, M. W., Sanders, P. F. & Woodrow, J. E. 1986 Models for assessing the volatilisation of herbicides applied to flooded rice fields. *Chemosphere* **15**, 127–138.
- Schwarzenbach, R. P. & Westall, J. 1981 Transport of non-polar organic compounds from surface water to groundwater. Laboratory studies. *Environ. Sci. Technol.* **15** 1360–1367.
- Spencer, W. F., Cliath, M. M., Jury, W. A. & Zhang, L-Z. 1988 Volatilization of organic chemicals from soil as related to their Henry's Law constants. *J. environ. Qual.* **17**, 504–509.
- Staab, H. A. Syntheses using heterocyclic amides. *Angew. Chem. internat.* **1**, 351–367.
- Steen, W. C. & Collette, T. W. 1989 Microbial degradation of seven amides by suspended bacterial populations. *Appl. environ. Microbiol.* **55**, 2545–2549.
- Swann, R. L., McCall, P. J. & Unger, S. M. 1982 Volatility of pesticides from soil surfaces. (Quoted in Lyman *et al.* (1982).)
- Walker, A. 1987 Evaluation of a simulation model for prediction of herbicide movement and persistence in soil. *Weed Res.* **27**, 143–152.
- Woodrow, J. E., Seiber, J. N. & Kim, Y-H. 1986 Measured and calculated evaporation losses of two petroleum hydrocarbon herbicide mixtures under laboratory and field conditions. *Environ. Sci. Technol.* **20**, 785–789.
- Yalkowsky, S. H. 1977 Solubility and melting point considerations in drug design. In *Design of biopharmaceutical properties through prodrugs and analogs* (ed. E. B. Roche), pp. 392–408. Washington: American Pharmaceutical Association.

Discussion

P. B. TINKER (*NERC*, Polaris House, North Star Avenue, Swindon, U.K.). Dr Briggs has mentioned the volatility of a number of pesticides. How important is the concentration of any pesticide vapour in the atmosphere? Is the deposition from this source significant?

G. G. BRIGGS. This is, I feel, a political rather than a scientific question which I shall try to answer scientifically. The requirement for incorporation of some soil-applied herbicides to preserve efficacy and incidents of vapour drift damage from volatile hormone esters have been known for many years. The papers in the text by Glotfelty *et al.* (1989), Gubler *et al.* (1987), Hance *et al.* (1976), Seiber *et al.* (1986), and further references within those papers give a clear indication that losses to the atmosphere are possible following normal applications in the warmer seasons of compounds with appropriate properties for evaporation from spray droplets and soil, leaf or water surfaces. Compounds entering the atmosphere are then part of a cycle of decomposition, transport and deposition (Schoeder & Lane 1988), which includes both natural and synthetic chemicals from many sources. The

evidence for the old organochlorine insecticides being widely distributed and having biological effects in some wildlife was sufficient to limit or curtail their use, mainly because of their long stability. There are industrial chemicals with the combination of both stability and physical properties which could lead to redistribution and bioaccumulation, but not I think among the modern pesticides.

Reference

Schoeder, W. H. & Lane, D. A. 1988 *Env. Sci. Technol.* **22**, 240–246.

I. J. GRAHAM-BRYCE (*Shell, The Netherlands*). I would strongly support the concept of including systematic quantitative consideration of physico-chemical properties and environmental behaviour in the earliest stages of pesticide selection and design. This implies combining optimization for pesticide potency and environmental behaviour. For example, degradation at any point in the molecule will limit persistence and there is some room for manoeuvre in the specification of optimum physico-chemical properties. In contrast, the optimum configuration for maximum potency and best fit at a site of action is often very precise and restricted. Please would Dr Briggs comment on this.

G. G. BRIGGS. Different laboratories approach environmental issues in different ways but we try, with varying success, to develop structure–biological activity and structure–behaviour at the same time.

The difficulty varies from one group of chemicals to another. For those described in table 8 intrinsic activity in an enzyme test was eventually well predicted from structure as was the soil half-life. However, high herbicidal activity and high persistence were difficult to separate and when they were the non-persistent active compounds had highly unpredictable and not very useful selectivity.

As far as the restrictions posed by the site of action are concerned this is true for some sites, but I am continually surprised by the range of properties allowed at others. The organophosphate and pyrethroid classes of insecticides both cover at least six (different) orders of magnitude in partition coefficient and vapour pressure while the inhibitors of branched chain amino acid biosynthesis in plants have a huge variety of weak acid structural types allowing for extensive synthesis to vary activity and behaviour. There is only one glyphosate whose environmental properties represent a major stroke of good fortune.