Proc. BCPC Symposium : Persistence of Insecticides and Herbicides (1976

PHYSICAL PROCESSES INVOLVED IN THE ADSORPTION OF PESTICIDES AT SOIL SURFACES

M. H. B. Hayes

Chemistry Department. P. O. Box 363, University of Birmingham, Edgbaston,
Birmingham B15 2TT

Summary Adsorption is one of the important processes which influences the fates of soil applied pesticides. Its extent is governed by the physico-chemical properties of the chemical and by the composition of the soil colloids. In order to understand the adsorption mechanisms which operate in any soil system it is necessary to understand the structures of sites available for adsorption and to be able to accurately measure the uptake of pesticide by the adsorbent. This review summarises some of the information which is available on structures of soil colloids, outlines procedures for measuring adsorption in soil systems and for interpreting the data. Some uses of spectroscopy, X-ray diffraction, calorimetry and thermal analysis procedures for the study of adsorption mechanisms are presented and selections of mechanisms which have been suggested for the adsorption by soil constituents of s-triazines, substituted ureas, organophosphorus compounds and pyridinium and bipyridylium salts are briefly reviewed.

INTRODUCTION

In excellent reviews Bailey and White (1964 and 1970) have outlined how factors such as soil or colloid type, the physico-chemical nature of the pesticide, soil reaction, temperature, the nature of the saturating cation on the colloid exchange sites, and the nature of the formulation influence the adsorption-desorption of pesticides by soils. They regarded adsorption by the soil colloids as one of the most important factors which influence the performance of a soil applied biocide.

The heterogeneity of soils complicates their study as adsorbents. Because under normal circumstances they contain solid, liquid and gaseous phases, all of the recognised interfaces (i.e. solid-liquid (S-L), solid-gas (S-G), liquid-liquid (L-L) and liquid-vapour (L-V)) can occur in soil systems. Adsorption (or the enrichment or concentration of one or more components of a given system in an interface (IUPAC, 1972)) at the soil colloid-soil solution interface is generally of greatest interest to soil scientists. However, wetting and drying phenomena in soils necessarily involve the S-G and L-V interfaces, and because chemicals may be added to soils in solid, liquid (solutions and emulsions) and gaseous forms it can readily be seen how all four interfaces can be important, depending on the formulations of extraneous additions and the climatic conditions (or the wetness or dryness of a particular soil).

Most progress on the theory of adsorption has been made from studies on the S-G interface (see reviews by Young and Crowell, 1962 and Thomas and Pierotti, 1972) but without particular reference to systems involving soil colloids. This circumstance has led to an accumulation of data for adsorption from dilute solution on solid soil components which have been analysed by methods more appropriate for the adsorption of gases. Recently, however, progress has been made towards a coherent theoretical treatment of adsorption from dilute solution at the S-L, L-L and L-V interfaces (Kipling, 1965; Everett, 1973).

This review will briefly consider the nature of adsorbing soil surfaces, will present some appropriate procedures for measuring and interpreting data for adsorption at such surfaces, and it will outline some mechanisms which are thought to be involved in the binding of selected organic chemicals by soils.

SOIL ADSORBENTS

It is well recognised that the materials of colloidal dimensions are the most active of the soil constituents in adsorption processes. Correlations between the amounts of chemical adsorbed and the compositions of soils established about twenty years ago that soil organic matter is especially active for the binding of neutral aromatic and aromatic ionizable biocides (such as some substituted ureas and the triazines). The advent of the bipyridylium herbicides focused attention on the binding capacity of soil clays for quarternised pyridinium derivatives. More recently the significance of various oxides and of hydrous oxides in soil adsorption processes is being increasingly recognised, as is the necessity to carry out adsorption studies on the total colloidal isolates from soils. There follows a brief outline of possible structures contained in these colloidal constituents.

1. Clay structures

Clays belong to the phyllosilicate class of silicate structures. This class contains sheets with six-membered rings of SiO_4 tetrahedra condensed with octahedral alumina (as in gibbsite) or magnesia (as in brucite) sheets. One oxygen atom (the 'tip' oxygen) of the tetrahedral layer is co-ordinated with two alluminium or with three magnesium atoms in the octahedral structures. Diphormic (or 1:1) structures are obtained when one tetrahedral and one octahedral sheet are condensed. In triphormic two tetrahedral and one octahedral (2:1) and in tetraphormic (2:2 or 2:1:1) two tetrahedral and two octahedral sheets are condensed in the repetitive layers. In dioctahedral structures only two out of three of the octahedral positions are occupied. Kaolinite, a widely distributed soil clay, is a diphormic dioctahedral structure in which each aluminium in the octahedral sheet is co-ordinated with two 'tip' oxygens from the tetrahedral sheet and with four hydroxyl groups. It has an idealised formula

$$Al_4Si_4,\ O_{10}(OH)_8$$

Isomorphous substitution in which, for example, dioctahedral Al^{3+} is replaced by Mg^{2+}, or Si^{4+} is replaced by Al^{3+}, gives rise to negative charges in clay lattices. These charges are satisfied by cations external to the layer and these cations may or may not be displaced by cations in solution. Montmorillonite, a triphormic (2:1) dioctahedral structure in which the lattice is composed of one octahedral sheet sandwiched by two tetrahedral sheets, has a net negative charge equivalent to a cation-exchange capacity (CEC) of *ca*. 100 milliequivalents (m.eq.) 100 g^{-1} arising from replacement of Al^{3+} in the octahedral sheet by Mg^{2+}. It has an idealised formula

$$0.67\ M^+(Al_{3.33}Mg_{0.67})Si_8O_{20}(OH)_4$$

Dioctahedral and trioctahedral triphormic vermiculites occur in soils, although the dioctahedral species is rare. These clays are characterised by isomorphous substitution in the tetrahedral layer and they have a relatively high charge density (with a CEC often greater than 150 m.eq. 100 g^{-1}). Trioctahedral vermiculite may be represented by the formula

$$1.73\ M^{+}(Mg,\ Fe,\ etc.)_6(Si,Al)_8O_{20}(OH)_4$$

Potassium ions when present in the medium, become trapped in the hexagonal holes (bounded by oxygens of the surface layer structure) and can then cement adjacent lattices together to confer a biotite type mica structure on vermiculite.

Dioctahedral illite (triphormic) is analogous to dioctahedral vermiculite where most adjacent lattices are cemented by K^{+} ions (imagine a largely fused stack of platelets). This clay is widely distributed in British soils.

In recent times it has been recognised that interstratified clay structures are often predominant in soils (MacEwen and Ruiz-Amil, 1975). This phenomenon arises because the structural similarities of clay minerals allow two or more types of structures to combine and form 'hybrid' species.

The reader is referred to the excellent contributions on clay structures in the recently published book edited by Gieseking (1975).

2. Oxide and hydrous oxide structures

Structural iron-, aluminium- and manganese oxides and hydroxides are abundant in soils and also some amorphous (or more accurately non-crystalline) iron and aluminium silicates and hydrated oxides of aluminium, iron, manganese and silicon occur (Fieldes and Claridge, 1975; Mitchell, 1975). The term allophane refers to mutual solid solutions of silica, alumina, water and minor amounts of bases. Soil allophane is widely distributed in soils derived from volcanic ash and from weakly developed soils derived from basalt or from other basic rocks. It is amorphous to X-rays, and different samples may have different compositions (Fieldes and Claridge, 1975).

Amorphous silica gel and secondary quartz are also widely distributed in certain soils. Because of its high surface area and porosity silica gel is an active absorbent and thus mixed gels incorporating hydrated silica with aluminium and iron hydroxides are more common in soils than is free amorphous silica (see Mitchell, 1975, p. 405). Such mixed gels can readily be formed in the laboratory.

Oxides and hydroxides of iron and aluminium are especially important because the sign and extents of their charges are pH dependent. Hence their adsorption characteristics are governed by the acidity or alkalinity of the soil medium.

3. Soil organic matter

Soil organic matter is composed of a gradation from undecomposed and partially decomposed plant and animal remains to amorphous organic colloidal constituents which bear little resemblance to the substrates from which they were derived. These colloidal constituents contain dark brown humic substances and polysaccharide, peptide and even traces of nucleic acid components. Humic acids are defined as the components of humic substances which are soluble in aqueous base but precipitated from solution with acid, whereas fulvic acids remain in solution when the alkaline extract is adjusted to pH 1-2

Although humic acids are the most abundant and widely distributed of the naturally occurring polymers their structures are still very imperfectly understood. For the most part their presence in soils in considerable abundance is desirable. They retain moisture and nutrients in sandy soils and also help to promote aggregate structures in clay soils. However, soils which contain appreciable amounts of organic matter (greater than ca. five per cent) generally require significantly increased applications of soil applied pesticides in order to achieve the desired plant protection effects. Some pesticides are inactivated at realistic application rates by the presence of even moderate organic matter contents.

Appreciation of the primary structures of humic acids has been hampered because of the need to use highly energetic procedures to degrade the polymer to meaningful structures. Although vast numbers of degradation products have been identified it has not been possible to assign these unambiguously to structures within the polymers. This fact can be primarily attributed to the lack of model studies which would provide realistic appraisals of the possible origins of the identified structures. Details of humic acid structural studies are outlined in contributions by Flaig et al (1975) and by Schnitzer and Khan (1972).

The available evidence indicates that aromatic phenolic compounds (possibly containing carboxyl groups attached to the aromatic structures), quinones and aliphatic hydroxyl and carboxyl containing functional groups are contained in humic and fulvic acid structures Accurate detailed studies of the secondary structures may never be attempted, and indeed might be irrelevant because humic acids probably depend more for their synthesis on random chemical condensation processes rather than on biological or enzymatic synthesis.

Cameron et al (1972) indirectly contributed very significantly to our understanding of the mechanisms of adsorption by humic acids when they reported their work on humic acid tertiary structures. By exhaustive pressure and gel filtration (through discrete pore size membranes) techniques they were able to isolate humic acid fractions having relatively small polydispersities, and to determine molecular weight values for these fractions by the equilibrium ultracentrifugation technique. They isolated humic acid materials which had molecular weight values ranging from ca. 2.6×10^3 to 1.4×10^6 and recognised that some higher molecular weight materials were not extracted in the sodium hydroxide solution extractant. From their frictional ratio and molecular weight data they deduced that highly hydrated soluble humate salts are randomly structured and highly expanded because of intramolecular repulsion. These strands can coil randomly with respect to time and space.

Imagine then a spherical structure, rather like a ball of wool, in which the distribution of molecular mass is Gaussian, i.e. with mass density greatest at the centre and decreasing towards the outer limits of the sphere. In this model the shape of the Gaussian mass distribution will vary according to whether or not the molecule is tightly or loosely coiled. This in turn will depend on factors such as the extent of solvent penetration, charge density, degree of dissociation, the nature of the counterions, etc. Use will later be made of this type of model when discussing adsorption processes by humic acid.

4. The nature of soil colloid surfaces

Surfaces involved in adsorption processes by soil colloids are inevitably heterogeneous. Soil clays, for instance, can rarely be expected to present clean surfaces. Instead the exposed sheets are likely to be associated with poorly defined combinations of silica with sesquioxides (Follett et al, 1965). Humic substances strongly associate with these. Allophane in particular adsorbs humates strongly, presumably through interaction with the anion-exchange sites (Inoue and Wada, 1968). Almost invariably the organic matter contents of the clay-sized fractions of soils are greater than those of the whole soils.

It is obvious from this brief description that soil colloid surfaces must be almost invariably energetically heterogeneous. Even in cases of pure clay preparations, or of oxides and silicates, some non-uniformity can be expected because of edges, corners, cracks, dislocations and other imperfections.

ADSORPTION PROCESSES

Molecules at a surface or interface usually have different physical properties and energy characteristics from those in the bulk. In the bulk phase, above an interface, the molecules of a gas or liquid move in all directions and continually collide with one another and with the surface. Molecules which move into the interface may be reflected immediately or may remain there temporarily, in which case they are said to be sorbed. The process is termed "adsorption" when the sorbed molecules cannot penetrate the adjoining bulk phase and can only return to their original phase.

Sorption can be regarded as a dynamic process in which the sorbed molecules are continually transferred between bulk and surface phases. When removed from the bulk it is likely that these molecules will continue their motions in a lateral direction along the surface (de Boer, 1968). It follows that any full treatment of sorption must consider: (i) the number of molecules which impinge on the surface and the length of time that they remain there (this is one aspect of the kinetic approach); (ii) the state of sorbed molecules at equilibrium (the thermodynamic approach); (iii) the intermolecular forces which influence factors i and ii, and which attract molecules to an interface in the first place.

Any detailed treatment of the dynamics of adsorption is outside of the scope of this communication and only brief mention will be made of the derivations which lead to the more general equations used to describe adsorption processes. For treatments of the general subject of adsorption the reader is referred to works by Hayward and Trapnell (1964), Ross and Olivier (1964), Gregg and Sing (1967), Aveyard and Haydon (1973). Applications to pesticide-soil systems are given by Hartley (1961), Bailey and White (1970), Hamaker and Thompson (1972), and Burchill et al (1977).

1. The Freundlich and Langmuir equations

If N molecules of a given compound strike a unit area of surface in unit time and remain there for an average time T then

$$N^S = TN \qquad (1)$$

where N^S represents the number of molecules of this compound per unit area which will be found at the interface. As pointed out by Boer (1968) this form of expression leads to a very useful visualization of the adsorption process. The simplest case for evaluation of N and T uses ideal gas adsorption onto a hypothetical planar solid which has an energetically uniform surface. N, for such a gas, is given directly by kinetic theory where

$$N = N_A p/(2\pi MRT)^{\frac{1}{2}} \qquad (2)$$

and N_A is Avogadros number, p is the bulk pressure, M is the molecular weight of the gas, R is the gas constant, and T is the absolute temperature.

A molecule which strikes the surface either rebounds specularly with the same velocity as it approached (i.e. reflection) or it loses kinetic energy and lingers before leaving in a direction and with a velocity independent of its approach. Molecules which linger transfer heat in an exchange of energy with the constituent atoms or molecules of the surface. If T_1 is the temperature of the impinging gas, $T_2{}^1$ that of the gas evaporating, and if T_2 is the temperature of the solid, a thermal coefficient of accommodation α_T can be defined as

$$\alpha_T = (T_2{}^1 - T_1)/(T_2 - T_1) \qquad (3)$$

For specular collisions $\alpha_T = 0$ and no adsorption occurs. If attraction exists between the gas and the solid T is finite and α_T will lie between 0 and 1.

To leave the surface adsorbed molecules must acquire sufficient vibrational energy in the direction of the forces that bind them to the surface. Their mean life in the adsorbed state will depend therefore upon the energy of binding and upon the temperature. A value for T is given by

$$T = T_o \exp(q/RT) \qquad (4)$$

where q is the heat of adsorption. i.e. the amount of heat which is liberated by bringing one mole of gas into the adsorbed state. An explanation of T_o is more complicated. Statistical mechanics treatments by Kruger and de Boer (see de Boer, 1956) have shown that T_o is determined by the entropy lost through adsorption. For the simple model of a two-dimensional perfect gas its value approaches the period of a simple surface atom vibration (written as $1/\nu_o$, where ν_o is the frequency of vibration). At room temperature this suggests a value of *ca.* 10^{-13} seconds.

Combination of equations (1), (2) and (4) yield

$$N^S = N_A p T_o \exp(q/RT)/(2\pi MRT)^{\frac{1}{2}} \qquad (5)$$

which, at constant temperature reduces to

$$N^S = Kp \qquad (6)$$

where K is a constant. This expression relates surface coverage to bulk concentration (pressure) and is, therefore, an adsorption isotherm. It is in fact the simplest expression of an adsorption isotherm which applies only in cases where the adsorbing molecules have no influence upon one another.

Equation (6) is based on the assumption that the flux N gives the number of molecules hitting and sticking to a surface. When adsorption is restricted to a single layer of adsorbate it is assumed that, after coverage is complete, molecules which subsequently approach the surface are either deflected or bound for such a short time that further adsorption may not be detected. If there are N^S molecules adsorbed per unit area, and if $(N^S)_m$ corresponds to a completed surface film, then the number of unoccupied sites will be $N^S/(N^S)_m$. By definition $N^S/(N^S)_m = \theta$, and the fraction of unoccupied sites is $(1-\theta)$. Then equation (1) modifies to

$$(N^S)_m \theta = TN(1-\theta) \qquad (7)$$

Combination of (7) with (2) and (4) gives

$$N_A p T_o \exp(q/RT)/(N^S)_m (2\pi MRT)^{\frac{1}{2}} = \theta/(1-\theta) \qquad (8)$$

Although equations (6) and (8) were derived from the kinetic theory of gases they do have some relevance to adsorption at the solid liquid interface. Here, however the situation is more complex for adsorption from solution. To the complicating adsorbate-adsorbate surface interactions must now be added solvent-adsorbate interactions. The solvent usually has an affinity for the surface and can give rise to competition with the solute for sites in the interface.

The relationship between (6) and the empirical Freundlich equation (9) is obvious

$$a = KC^{1/n} \qquad (9)$$

where a is the amount adsorbed per unit weight of adsorbent, C is the equilibrium concentration in the bulk solution (or the equilibrium gas pressure) and K and n are empirical constants. Here interactions between adsorbed species are ignored and the Freundlich isotherm predicts that adsorption increases without limit as the bulk concentration is increased. When expressed in logarithmic form a linear relationship is obtained in which

$$\log a = \log K + 1/n \log C \qquad (10)$$

and the values of K and n can be obtained from the appropriate plots.

In soil-pesticide interactions the proportion of the chemical adsorbed usually decreases as the amount which is present in the equilibrium solution increases. However, a linear approximation can often be assumed over the very dilute concentration ranges which characterise realistic field application rates and expression (11),related to the Freundlich equation,is often used to characterise the extent of adsorption

$$Kd = \mu g \text{ adsorbed } g^{-1} \text{ soil}/\mu g \text{ cm}^{-3} \text{ of equilibrium solution} \qquad (11)$$

The larger the value of Kd the greater will be the binding capacity of the soil for the pesticide in question. Hamaker and Thompson (1972) have catalogued a number of Kd values for different pesticides for soils with different organic carbon contents. Because adsorption of many neutral and ionizable (particularly aromatic) compounds can be correlated with organic matter they point out that

$$Koc = \frac{Kd\ (\mu g\ g^{-1}\ \text{soil})}{\%\ \text{organic carbon}} \times 100 \qquad (12)$$

(where oc represents organic carbon) gives a better representation than Kd of the extent of adsorption of such chemicals in soils.

Graham Bryce (1972) has drawn attention to the facts that: chemicals with very low Kd values will move freely in soils and are easily leached; compounds such as the bipyridylium herbicides which have immeasurably large Kd values at normal rates of usage are so strongly adsorbed that they do not have residual activity in the soil; where Kd values fall between ca. 2 and 30, selectivity can be obtained by depth protection.

The possibility that the formation of a monolayer might represent the limit of adsorption was recognised by Langmuir (1918) who, in a study of adsorption at the solid-gas interface, gave the first theoretical treatment of an adsorption equilibrium. On the basis of a simple kinetic model, and assuming monomolecularity, he showed that adsorption varied with pressure according to

$$p = K_2\theta/(1-\theta) \qquad (13)$$

where θ represents the fraction of adsorption sites in the surface which are covered. This isotherm equation is conveniently obtained by adopting the kinetic approach (de Boer, 1968) described earlier, and note the similarity between equations (13) and (8). These will be the same provided that the heat of adsorption q and the pre-exporential factor T_o in (8) remain constant.

Implicit in the development of the Langmuir equation for the adsorption of a single component gas are the following assumptions about the model of adsorption (Ross and Olivier, 1964): (i) that the adsorbate behaves as an ideal gas in the bulk phase; (ii) that adsorption is confined to a monolayer; (iii) that the surface is energetically uniform; (iv) that adsorbate-adsorbate interactions may be neglected; (v) that the adsorbed molecules are localized i.e. that the adsorbent surface is subdivided into adsorption sites which allow definite points of attachment to the surface. Also it is evident that Langmuir's condition of dynamic equilibrium (when the rates of adsorption and of re-evaporation of adsorbed molecules are equal) must also be fulfilled.

Other useful forms of the Langmuir equation include

$$x/m = K_1K_2C/(1+K_2C) \qquad (14)$$

where x/m represents the amount of compound adsorbed per unit weight of adsorbent, C is the equilibrium solution concentration, and K_1 and K_2 are constants. At low concentrations the product K_2C can be neglected and equation (14) reduces to

$$x/m = K_1C \qquad (15)$$

where the amount adsorbed becomesdirectly proportional to the concentration in solution. Hence the justification for (9) and (11).

However, although forms of the Langmuir isotherm fit data for some adsorptions from solution or from gases, it is well recognised that the model is not generally valid. This is readily realised on considerations of the assumptions described above which are implicit in the treatment.

2. Multilayer adsorption

Although the thickness of adsorbed layers depends largely upon the nature of the system, adsorption at the L-L, L-V, and S-L interfaces often appears to provide films of approximately one molecular layer thickness. However, for the physical adsorption of gases at higher pressures, the amounts adsorbed sometimes indicate the adsorption of films of several molecular layers (or multilayers) even though adsorption might not extend beyond monolayer coverage for physical adsorption, at low pressures, or for chemisorption (when covalent bonds are formed between adsorbate and adsorbent). Brunauer, Emmett, and Teller (1938) modified Langmuir's treatment of monolayer adsorption to include this possibility. Although it does provide useful qualitative descriptions the BET theory is open to severe criticism and several more refined treatments of multilayer adsorption have been proposed (reviewed by Young and Crowell, 1962). The theory, however, provides a simple means of determining surface areas which are fundamental to descriptions of colloidal behaviour.

For the purposes of a statistical derivation the main features of the BET model of adsorption are as follows (Hill, 1952). It is assumed that adsorption is localized and that each molecule adsorbed in the first layer acts as a potential adsorption site for a second layer molecule, which in turn acts as a site for a third layer and so on. Further it is assumed that the stacks of molecules so formed do not interact energetically while the partition function and the energy of molecules in the second and third layers are equated with those of the pure liquid condensate. For a non-porous adsorbent the resultant isotherm equation may be written in linear form as:

$$p/x(p^{o}-p) = 1/x_{m}C+(C-1)p/x_{m}Cp^{o} \qquad (16)$$

where x is the amount of gas adsorbed at bulk pressure p, p^{o} is the saturated vapour pressure, C is a constant which is determined by the difference in free energy of adsorption between the first and all subsequent layers of adsorbate, x_m is often taken to be the monolayer capacity - defined for physical adsorption as the amount of adsorbate needed to cover the surface with a complete layer of molecules in close-packed array.

When adsorption of the first layer is strong relative to that of the higher layers C is large and a type II vapour isotherm (see Gregg and Sing, 1967) is predicted. From this isotherm x_m can be obtained and this corresponds to $(N^{s})_{m}$. Also when the cross-sectional area of the adsorbate molecule is appreciated the surface area corresponding to x_m can be calculated.

According to equation (16) a plot of $p/x(p^{o}-p)$ versus p/p^{o} should be linear and from the slope and intercept values for x_m and C can be obtained.

Localized adsorption in layers other than the first is not consistent with their being liquid. Also, molecules are assumed to interact with two nearest neighbours (above and below them) in their respective stacks. The actual number of equidistant nearest neighbours in a bulk liquid is closer to 12. Despite these limitations de Boer (1970) and others (Young and Crowell, 1962) have drawn attention to the fundamental significance of x_m and they suggest that the BET method retains its usefulness in providing a simple graphical procedure for measuring the extent of monolayer adsorption.

3. The Gibbs adsorption equation

This equation is a thermodynamic expression which relates the surface concentration or the surface excess of an adsorbing species to both the surface tension, γ (or the isothermal reversible work done in extending the interface by unit area at constant volume V and n_i, the number of moles of i in the system) and the bulk activity or fugacity of the adsorbate. An account of surface thermodynamics in terms of the Gibbs surface is given in most comprehensive texts on chemical thermo-dynamics (see e.g. Lewis and Randall, 1961). The reader is referred to the review by Aveyard and Haydon (1973). These authors consider the uses of both the surface phase and the Gibbs dividing surface.

The general form of the Gibb's adsorption equation can be written as

$$-d\gamma = \sum_{i} \Gamma i^{s}\, d\mu_{i} \qquad (17)$$

where $\Gamma_i^{s} = n_i^{s}/A$ and A is the area of the interface and μ refers to the chemical potential. Kipling (1965) has shown how the Freundlich equation can be derived from (17).

MEASUREMENTS OF ADSORPTION

The agronomically most useful pesticide adsorption procedure would rapidly measure the binding of chemical by soil and express the data in terms which could readily and accurately be interpreted in terms of field application recommendations. Other contributors to the Proceedings of this Symposium will discuss the unreliabilities of extrapolations from laboratory and greenhouse measurements to field conditions. However, the behaviour of pesticides in soil adsorption experiments in the laboratory can give a broad indication of the manner in which they will behave towards the field soil and the uses to which they can be put (Graham-Bryce, 1972). The same adsorption forces will be active in both locations, but equilibrium will be more rapidly reached in the idealised conditions under which most laboratory experiments are carried out.

Adsorption by whole soil samples can be expected to give better indications of pesticide field performances than adsorption by soil fractions. However, it is necessary to fractionate soils in order to determine the seats of adsorptive activities.

1. Fractionation of soils

Earlier it was pointed out that the colloidal components are the most active of the soil constituents for adsorbing pesticides. These can be extracted after breaking down the natural soil aggregates (e.g. by ultrasonication, Edwards and Bremner, 1967) by centrifugation techniques (Baver et al., 1972) or by the technique of filtration through graded porosity membranes which is currently being used in our laboratories. Oladimeji (1976) has obtained similar results from centrifugation and from filtration (through the Whatman filter tubes series 12-80, 12-20, 12-10, 12-03 which retain particles of equivalent spherical diameters, 8, 2, 1 and 0.3 μm, respectively; obtained from Whatman Ltd., Springfield Mill, Maidstone, Kent) after the soils had been ultrasonicated and treated with small amounts of sodium hexametaphosphate dispersing agent. The organic matter content of the clay-size fraction was lowered in the filtered samples and this was attributed to the effects of the dispersing agent.

Many attempts have been made to separate clay and organic materials without damaging the chemical and surface properties of both. R.G. Burns (1972, and references therein), who accepts the thesis that humic substances are bound to clays by polyvalent inorganic cation 'bridge' mechanisms, has (in collaboration with the McLaren group in Berkeley and in his laboratories in the University of Kent) been able to extract from soils organic matter which was enzyme active and free from clay. The procedure involved sonication, followed by salt extraction, filtration and dialysis.

It is generally accepted that the most efficient methods for extraction of soil organic matter involve initial hydrogen ion-saturation of the soil followed by extraction with 0.1 to 0.5N sodium hydroxide. However, the acid treatment is known to cause degradations of the clay lattice structures, and the high pH values of the alkaline medium encourage oxidation of the humic substances. There is need therefore for further development of mild extraction procedures along the lines indicated by Burns.

Two acceptably good techniques are available for destroying the organic matter associated with clays: one involves treatment with H_2O_2, the other with NaOCl. It would appear that interlamellarly adsorbed organic substances have some resistance to such treatments, although humic acids (which constitute the major soil organic matter fraction) do not penetrate into the interlamellar spaces.

The possible contribution of oxides, hydroxides and amorphous aluminosilicates to the soil colloidal constituents has already been referenced. Dithionite procedures are effective for deferration, and alkaline solutions dissolve aluminosilicates. However, it must be emphasized that wholly satisfactory procedures are not available at this time which can be relied upon to isolate the unaltered components of soil colloidal materials. The reader is referred to the various procedures presented in Methods of Soil Analysis (Black, 1965), although he is advised that considerable developments have been made during the past decade in a number of the appropriate areas.

2. Measurement of adsorption by the slurry procedure

For this procedure known weights of soil or of soil separate are equilibrated with predetermined volumes and concentrations of pesticide solutions. After equilibration, adsorbent and the adsorbate solutions are separated by centrifugation or by filtration, and the amount of pesticide adsorbed per unit weight of adsorbent in each case is determined from the change in the solution concentration. Generally a plot is made of the amount adsorbed per gram of adsorbent versus the equilibrium solution concentration. This technique is slow; it involves several weighing and sampling manipulations in order to obtain sufficient data to construct an adsorption isotherm. For measurements of desorption each equilibrium solution must be replaced by water or other desorbing media, new equilibria re-established and measured, and these processes should be repeated for as long as measurable amounts of pesticide are released from the adsorbent. It is not surprising therefore that isotherm data for desorption of pesticides from soil are relatively rare.

3. Measurement of adsorption and of desorption by continuous flow methods

Continuous flow procedures can be expected to remove much of the tedium from adsorption-desorption measurements. In general these involve the passage of a known concentration of adsorbate solution from a reservoir through a cell of known volume containing a known amount of adsorbent and initially water or salt solution (Grice and Hayes, 1972; Grice *et al.*,1973; Burchill *et al.*,1973). For each increment of liquid which enters the cell a corresponding increment must leave and mass balance is maintained. From analysis of the eluate data (which can be obtained automatically) it is possible to construct an adsorption isotherm. Adsorption is complete when the eluate concentration becomes essentially equal to that of the adsorbate in the reservoir. Data for desorption isotherms are obtained after changing the eluent from pesticide solution to water or other appropriate medium.

Smedley (1976) has carried out a detailed analysis of the above methods and, when published, his data will stress: (i), the importance of adsorbate residence time in the cell; (ii), the importance of adequate mixing within the cell in order to achieve equilibrium as rapidly as possible (so that equilibrium solution concentration can be accurately estimated from the adsorbate concentration in the eluate); (iii), the effects, where appropriate, of adsorption or of rejection of adsorbate when membranes are used to hold very fine or soluble adsorbent components in the cell; (iv), the errors which can arise from even minute evaporation losses when eluate samples are collected prior to analysis.

In theory it should be possible to use gradient elution of pesticides through columns of soil or of soil separates. This would be a logical progression of the continuous flow procedure, and it might be expected to provide adsorption-desorption data of greater relevance to field conditions. Failure to reach equilibrium in the high soil:solution ratio used was probably the major reason for the disappointing results in this area by Burchill *et al*, (1973). Graham-Bryce (1972) has referred to the possible slower attainment of equilibrium at the higher soil:solution ratios.

4. Measurement of adsorption by gel chromatography procedures

I.G. Burns *et al.*,(1973) compared the adsorption isotherms obtained by gel filtration and ultrafiltration procedures for studies on the adsorption of paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) by Na^+- humate solutions. Similar studies were carried out at the same time by Khan (1973), and the results from the different experiments establish that gel filtration provides a useful (though slow) method for studying pesticide adsorption on water soluble soil components.

5. Dialysis procedures in measurements of adsorption

Hayes *et al.*,(1968) and Damanakis *et al.*,(1970) enclosed adsorbent suspensions in dialysis sacs in order to eliminate interference from brown humate solutions during the analysis of the equilibrium adsorbate concentrations. This very tedious technique has several disadvantages which can include Donnan effects and the adsorption of adsorbate by the sac. Use of appropriate membranes (with or without a continuous flow assembly) or of gel filtration offer suitable alternative procedures.

MECHANISMS OF BINDING OF PESTICIDES IN SOILS

G.C. Briggs has presented elsewhere in these Proceedings a number of adsorbate structural features which allow some predictions of adsorbability and degradability of pesticides in soils. The remainder of this contribution will consider the manner in which some pesticides are thought to be held in the soil colloid surfaces. Emphasis will be given to binding mechanisms for pyridinium and bipyridylium organocations, to ionizable *s*-triazine compounds, to substituted ureas, and to polar aliphatic organophosphorus compounds because the author is most familiar with systems which involve such materials and because they represent a good cross-section of the major types of pesticide molecules which enter the soil environment.

The reader is referred to Bailey *et al.*,(1968) and to Bailey and White (1970) for a review of some adsorbate chemical and physical properties which are involved in adsorptions by soils, and to Hamaker and Thompson (1972) who list the types of forces which might be involved in such binding processes.

1. The binding of pyridinium and bipyridylium organocations.

It is well recognised that soils which contain clays or/and significant amounts of humified organic matter inactivate the herbicidal effects of bipyridylium herbicides which enter the soil environment. This has led to extensive studies on the extents and mechanisms of binding of the herbicidal bipyridyls paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) and diquat (1,1'-ethylene-2,2'-bipyridylium dibromide) by humic substances (see reviews by: Khan, 1974; I.G. Burns and Hayes, 1974) and by clays (see review by Hayes *et al.*, 1975).

Consider a bipyridylium compound which has entered the environment of soil colloids. Should the clay components contain appreciable contents of associated organic matter it is possible that the organocation will first make contact with it. Earlier in this review the tertiary structure of humic acid was considered to be somewhat analogous to a "ball of wool" structure. Organocations in the environment of this "ball" will approach the outer strands first, displace the neutralizing cations associated with the acidic groups in the humate structure and be retained primarily by cation-exchange mechanisms. Such ion exchanges are three stage processes which involve diffusion of the exchanging counter-ion to the exchange site in the adsorption matrix, then the exchange reaction, and finally the diffusion of the exchanged ion out of the matrix. Kinetic studies show that such diffusion processes are rate controlling in ion-exchange reactions, and Donnan effects are also important at low salt concentrations (discussed by Burns and Hayes, 1974) for regulating the penetration of organocation into the adsorbing matrix.

Damanakis et al., (1970) and I.G. Burns et al.(see Burns and Hayes, 1974) have used isotherm equations to interpret the adsorption of paraquat by soil organic materials. The Birmingham group tested the adsorption by H^+- humic substances as well as by H^+- resins of well defined cation-exchange properties. Only the Rothmund-Kornfeld equation (18) satisfactorily

$$[\bar{P}^{2+}] \ / \ [\bar{H}^{+}]^{2} = K([P^{2+}] \ / \ [H^{+}]^{2})^{1/n} \qquad (18)$$

fitted the data for the adsorption of the divalent paraquat (P^{2+}) onto the H^+-adsorbents. In (18) the superimposed bars refer to ions in the adsorbent. When n=1 this equation is the law of Mass Action. The test form of (18) is

$$A = \log_e K + (1/n)S \qquad (19)$$

where $A = \log_e [\bar{P}^{2+}] - 2 \log_e [\bar{H}^{+}]$ and $S = \log_e [P^{2+}] -2 \log_e [H^{+}]$

and this can be used to test data fit to the Rothmund-Kornfeld and the Mass Action equations.

Small deviations from the Rothmund-Kornfeld equation were observed at low equilibrium solution concentrations, and these were attributed to non-exchange adsorption mechanisms because of deviations from Donnan behaviour at low concentrations. At higher concentrations the ionic character of the adsorbent was regained and ion exchange predominated as the adsorption mechanism. It was suspected that charge transfer processes contributed to the retention of organocation although no spectroscopic evidence could be quoted. Khan (1974) has indicated that failure of ultraviolet spectroscopy to establish such mechanisms might result from light scattering losses and resultant lack of sensitivity.

The failure of paraquat to saturate all of the exchange sites in Ca^{2+}- and H^+ -saturated humates can be consistent with the "ball of wool" humic structure hypothesis. Introduction of the organocation to the outer strand structures could cause a degree of collapse (and increased density) in these areas and sterically inhibit the penetration of other molecules to the internal exchange sites (or migration out of the matrix). Na^+- humates have more open structures because of repulsion from the charged groups in the polyelectrolyte and thus paraquat was able to adsorb on these polymers almost to the extent of their cation-exchange capacities (I.G. Burns et al., 1973).

Any bipyridyl which reaches the soil clay surface will be energetically adsorbed to an extent which should approach the cation-exchange capacity of the clay. From model studies X-ray diffraction data have shown that diquat and paraquat will penetrate into the interlamellar spaces of montmorillonite causing the lamellae to collapse and to flatten the organocations. Calorimetry has proved that this adsorption process is highly exothermic and spectroscopy data have indicated that charge transfer processes supplement ion-exchange adsorption mechanisms (Hayes et al., 1975).

With vermiculite the situation is different. The extent of diquat and of paraquat adsorption will depend on the resident inorganic cations in the clay. X-ray diffraction data have indicated that the organocations assume configurations edge-on to the lamellar surfaces, and spectroscopy has not indicated contributions from charge transfer to the adsorption mechanisms. These observations can be explained by reference to the water adsorbed on vermiculite surfaces. Such water is energetically held because of the proximity of the charge on the clay to the surface. Considerable energy must be expended in order to displace this water (adsorptions by Na^+-vermiculite are endothermic), and the adsorbate will therefore assume an interlamellar configuration which will require the least displacement of water.

Considerable secondary adsorption was observed (in excess of the cation-exchange capacity) when 1-methyl-4-phenylpyridinium iodide was adsorbed by Na^+-montmorillonite. The enthalpy changes observed were double those for the other monovalent aromatic organocations used and this excess can be attributed to favourable van der Waals attractive forces between the molecules orientated edge-on to the lattice surfaces.

Adsorption of bipyridylium compounds by kaolinite and illite clays (which have non-expanding lattice structures) approached the cation-exchange capacities of the clays, and the adsorption processes were invariably exothermic. Differences in the energetics of the adsorption processes could be attributed to the relative ease of displacement of the resident inorganic cations (Hayes _et al_., 1975).

The extents to which amorphous oxides, hydroxides, and silicates (in isolation or in association with soil clays) will contribute to adsorption of bipyridyls can be expected to be related to the pH of the media.

2. The binding of s-triazines and of substituted ureas

It is generally accepted that the bioactivity in soil of the triazine-and of most urea-derivative pesticides is depleted as the organic matter content of the soil is increased. Hayes (1970) has reviewed triazine-organic matter interactions and Weber (1970) has dealt with their mechanisms of adsorption by clays.

The adsorptivity of the triazines is influenced by the nature of the ring substituents. Replacement of chlorine in the -2-position by methoxy or methylthio groups will provide compounds with higher pK values (_ca_ 4-4.5) which are protonated at pH values approaching field conditioning. Protonated triazine compounds can readily be bound to the soil colloids by ion-exchange mechanisms. Weber's data clearly show that adsorption by clays rapidly falls off as the pH of the medium is raised above the pK value of the chemical.

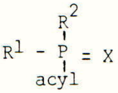
Ion-exchange or hydrogen bonding mechanisms can be involved in the binding of triazines by humic substances and considerably more of these compounds are bound by H^+- than by Ca^{2+}- humate preparations. The possibility that charge transfer processes are also involved must be considered, and other feasible binding mechanisms might involve van der Waals forces and ligand exchange (involving the N atoms of the substituted amino groups attached to the -4 and -6 ring positions: Hayes _et al_., 1968; Hamaker and Thompson, 1972).

Hance (1965) has shown that diuron, or 3-(3,4-dichlorophenyl)-1,1-dimethylurea, was extensively bound to surfaces such as lignin but had only a low affinity for polymers such as cellulose and chitin (composed of highly polar sugar units). In this instance charge transfer processes might explain the adsorptivity differences. Orbital overlaps could take place between the deactivated (as the result of the chlorine ring substituents) aromatic moiety of the herbicide and the lignin aromatic structures activated by -OH and $-OCH_3$ substitutents. Also non-polar attractions could explain the high affinity for lignin. Similar mechanisms could operate for humic substances.

Because most substituted ureas can only be protonated at very low pH values it is unlikely that they would be involved in soil ion-exchange processes. Co-ordination between the carbonyl groups and polyvalent cations adsorbed to the lattices could form a mechanism for binding to clays.

3. The binding of some organophosphorus compounds

This final section will deal with studies referenced under Hayes et al., (1972) which deal with the adsorption by soil and soil constituents of models of organophosphorus insecticides. These have the general formula



$$R^1-\overset{R^2}{\underset{acyl}{P}}=X \qquad (X = O \text{ or } S) \qquad (I)$$

and R^1 and R^2 can be alkyl, aryl, alkoxy, aryloxy, anino, substituted amino or other groups. The acyl group can consist, for example, of fluoride, substituted phenoxy, thioalcohols, aliphatic and heterocyclic enols.

When (I) is highly water soluble, (eg $R^1 = -CH_3$, $R^2 = -OC_2H_5$, $X = O$, acyl = F, i.e. compound (II) or $(C_2H_5O)FP(O)CH_3$, and the acyl group in (II) is replaced by $-OC_2H_5$ to give (III) or $(C_2H_5O)_2\ P(O)CH_3$) adsorption from aqueous solution by soil constituents or by soils is not observed because the excess water competes effectively for the adsorption sites. They are, however, adsorbed from the vapour phase and from solution in non-polar liquids (such as n-hexane).

Compound (III), or O,O-diethyl methylphosphonate, was adsorbed from the vapour phase as a multilayer by a K^+-kaolinite preparation and a T_{max} value of 128° C in the differential thermogravimetric (DTG) thermogram corresponds to an x_m value (for monolayer coverage) of 68 mg g^{-1} of kaolinite indicated on the thermogravimetric analysis (TG) curve. Material desorbed below 128° C had been adsorbed as multilayers TG and DTG curves for desorption from Ca^{2+}-montmorillonite showed that (III) was desorbed over a wide temperature range which indicated sites with different energies of adsorption. A change in slope in the DTG curve indicated x_m, equivalent to adsorption of 45 mg g^{-1} of clay, and X-ray diffraction indicated c-spacing expansions corresponding to adsorption of a bilayer in the interlamellar spaces. From the intermediate peak (200-280°C) in the DTG curve an activation energy (E^*) of 68 k joules $mole^{-1}$ was estimated for desorption from the interlamellar surface. Material desorbed between 300-400° C corresponded to compound co-ordinated with Ca^{2+} ions in the interlamellar spaces (2 moles of III $mole^{-1}$ Ca^{2+}). This strongly endothermic reaction was detected also in differential scanning calorimetry (DSC) experiments, and provided data which showed that the energy required to remove such co-ordinated material was ca 150 k joules $mole^{-1}$ adsorbed. Infrared spectroscopy confirmed the co-ordination to Ca^{2+} mechanism by showing that, after adsorption, absorption of the phosphoryl group shifted from 1245 to 1220 cm^{-1}, indicative of dipole-charge interactions between the phosphoryl group oxygen and the cation. The available evidence from X-ray and molecular dimensions data indicates that the configuration of (III) co-ordinated with Ca^{2+}- in the interlamellar spaces has the P=O plane perpendicular to the surface and associated with the centrally located Ca^{2+} ion. DTG indicated extensive adsorption of (III) on the external surfaces of Ca^{2+}-vermiculite. There was little evidence for co-ordination with Ca^{2+} in the interlamellar spaces because the cation is less electropositive in vermiculite than in montmorillonite.

Replacement of the phosphoryl by a thiophosphoryl group as in (IV), or $(C_2H_5O)_2$ $P(S)CH_3$, and replacement of ethoxy by thioethoxy as in V, or $(C_2H_5O)(C_2H_5S)P(O)CH_3$, and VI, or $(C_2H_5O)(C_2H_5S)P(S)CH_3$, lowered the reactivity of the compounds with clays. Calculations from reaction calorimetry data of integral enthalpies of adsorption values of 34,28,12 and 3 k joules $mole^{-1}$ adsorbed on Ca^{2+} montmorillonite for III, V, IV and VI, respectively.

Acknowledgments

The author thanks several of his colleagues for their research contribution to some aspects of the work referred to here.

References

AVEYARD, R. and HAYDON, D.A. (1973) An Introduction to the Principles of Surface Chemistry. Cambridge Univ. Press. 232pp.

BAILEY, G.W. and WHITE, J.L. (1964) Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. J. Agr. Food Chem. 12, 324-332.

BAILEY, G.W., WHITE, J.L. and ROTHBERG, T. (1968) Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. Soil Sci. Soc. Amer. Proc., 32, 222.

BAILEY, G.W. and WHITE, J.L. (1970) Factors influencing the adsorption, desorption, and movement of pesticides in soil. Residue Reviews, 32, 29-92.

BAVER, L.D., GARDNER, W.H., and GARDNER, W.R. (1972) Soil Physics. Wiley International, London-New York 498 pp.

BLACK, C.A. (1965) Editor-in-Chief. Methods of Soil Analysis, Parts 1 and 2, American Society of Agronomy, Madison, Wisconsin 1572pp.

de BOER, J.H. (1956) Adsorption phenomena. Advances in Catalysis 8, 17-161.

de BOER, J.H. (1968) The Dynamical Character of Adsorption. 2nd ed. Oxford Univ. Press.

de BOER, J.H. (1969) Mobility of molecules along adsorbing surfaces. In Molecular processes on solid surfaces, (E. Drauglis,R.D. Gretz, and R.I. Jaffee, eds.). McGraw-Hill: New York, pp. 3-17.

BRUNAUER, S., EMMETT, P.H., and TELLER, E. (1938) Adsorption of gases in multimolecular layers. J. Amer. Chem. Soc., 60, 309-319

BURCHILL, S., CARDEW, M.H., HAYES, M.H.B., and SMEDLEY, R.J. (1973) Continuous flow methods for studying adsorption of herbicides by soil dispersions and soil columns. Proc. Eur. Weed Res. Coun. Symp. Herbicides-Soil, 70-79

BURCHILL, S., HAYES, M.H.B., and GREENLAND, D.J. (1977) Adsorption. In The Chemistry of Soil Processes (D.J. Greenland and M.H.B. Hayes eds.) Wiley International, for press summer (1976).

BURNS, I.G. (1972) The soil organo-mineral complex in relation to herbicide activity and a possible means of forecasting persistence. Proc. 11th. Br. Weed Control Conf., 3, 1203-1209.

BURNS, I.G., HAYES, M.H.B., and STACEY, M. (1973) Studies of adsorption of paraquat on soluble humic fractions by gel filtration and ultrafiltration techniques. Pestic. Sci., 4, 629-641.

BURNS, I.G. and HAYES, M.H.B. (1974) Some physico-chemical principles involved in the adsorption of the organic cation paraquat by soil humic materials. Residue Reviews, 52, 117-146.

CAMERON, R.S. THORNTON, B.K., SWIFT, R.S., and POSNER, A.M. (1972) Molecular weight and shape of humic acid from sedimentation and diffusion measurements on fractionated extracts. J. Soil Sci., 23, 394-408.

DAMANAKIS, M., DRENNAN, D.S.H., FRYER, J.D. and HOLLY, K. (1970) The adsorption and mobility of paraquat on different soils and soil constituents. Weed Res., 10, 264-277.

EDWARDS, A.P. and BREMNER, J.M. (1967) Micro-aggregates in soil. J. Soil Sci., 18, 64-73.

EVERETT, D.H. (1973) Adsorption at the solid/liquid interface: Non-aqueous systems. In Colloid Science (Specialist Periodical Reports of Chem. Soc., London; D.H. Everett ed.), 1, 49-102.

FIELDES, M. and CLARIDGE, G.G.C. (1975) Allophane. In Soil Components. Vol. 2., Inorganic Components (J.E. Gieseking, ed.) Springer Verlag, Berlin-New York, 351-393.

FLAIG, W., BEUTELSPACHER, H., and RIETZ, E. (1975) Chemical composition and physical properties of humic substances. In *Soil Components*, *Vol. 1*, *Organic* (J.E. Gieseking, ed.). Springer-Verlag, Berlin-New York. pp. 1-211.

FOLLETT, E.A.C., McHARDY, W.J., MITCHELL, B.D., and SMITH, B.F.L. (1965) *Chemical* dissolution techniques in the study of soil clays. II. *Clay Min*. 6, 35-43.

GIESEKING, J.E. ed (1975) *Soil Components*, *Vol. 2*. *Inorganic Components*. Springer Verlag, Berlin-New York. 684 pp.

GRAHAM-BRYCE, I.J. (1972) Herbicide movement and availability in soils. *Proc. 11th. Weed Control Conf.*, *3*, 1193-1202.

GREGG, S.J. and SING, K.S.W. (1967) *Adsorption, Surface Area and Porosity*. Academic Press, London.

GRICE, R.E., and HAYES, M.H.B. (1972) A continuous flow method for studying adsorption and desorption of pesticides in soils and in soil colloid systems. *Proc. 11th. Br. Weed Control Conf.*, *2*, 784-791.

GRICE, R.E., HAYES, M.H.B., LUNDIE, P.R. and CARDEW, M.H. (1973) Continuous flow method for studying adsorption of organic chemicals by a humic acid preparation *Chem. & Ind*. (London), 233-234

HAMAKER, J.W. and THOMPSON, J.M. (1972) Adsorption. In *Organic Chemicals in the Soil Environment* (C.A.I. Goring and J.W. Hamaker, eds.) Marcel Dekker, New York, pp. 49-143.

HANCE, R.J. (1965) Observations on the relationship between the adsorption of diuron and the nature of the adsorbent. *Weed Research*, *5*, 108.

HARTLEY, G.S. (1961) Physico-chemical aspects of the availability of herbicides in soils. In *Herbicides in the Soil*, (K.K. Woodford and G.R. Sagar, eds.) Blackwells.

HAYES, M.H.B., PICK, M.E., and TOMS, B.A. (1975) Interactions between clay minerals and bipyridylium herbicides. *Residue Reviews*, *57*, 1-25.

HAYES, M.H.B. (1970) Adsorption of triazine herbicides on soil organic matter, including a short review of soil organic matter chemistry. *Residue Reviews*, *32*, 131-174.

HAYES, M.H.B., LUNDIE, P.R. and STACEY, M. (1972) Interactions between organophosphorus compounds and soil materials I. Adsorption of ethyl methylphosphonofluoridate by clay and organic matter preparations and by soils. *Pestic. Sci.*, 3, 619-629; (1975) II. Mechanisms of interactions with clay preparations. *Proc. Intern. Clay Conf.*, (Mexico), p. 507; (1976) Mechanisms of clay-organophosphorus reactions. To *Surface Technology*.

HAYES, M.H.B., STACEY, M. and THOMPSON, J.M. (1968) Adsorption of s-triazine herbicides by soil organic matter preparations. In *Isotopes and Radiation in Soil Organic-Matter Studies*. *Internat. Atomic Energy Agency, Vienna*. pp. 75-90.

HAYWARD, D.O. and TRAPNELL, B.M.W. (1964) *Chemisorption*. 2nd ed. Butterworth.

HILL, T.L. (1952) Theory of physical adsorption. *Advances in Catalysis*, *4*, 211-258.

INOUE, T. and WADA, K. (1968) Adsorption of humified clover extracts by various clays. *Trans. 9th. Intern. Congr. Soil Sci.*, (Adelaide), *3*, 289-298.

IUPAC (1972) Manual of symbols and terminology for physicochemical quantities and units. App. II, Definitions, terminology and symbols in colloid and surface chemistry. Part I. *Pure Appl. Chem.*, *31*, 579.

KHAN, S.U. (1973) Interaction of humic substances with bipyridylium herbicides. *Can. J. Soil Sci.*, *53*, 199-204.

KHAN, S.U. (1974) Humic substances reactions involving bipyridylium herbicides in soil and aquatic environments. *Resid. Rev.*, *52*, 1-26.

KIPLING, J.J. (1965) Adsorption from Solutions of Nonelectrolytes. Academic Press (London).

LANGMUIR, I. (1918) The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Amer. Chem. Soc., 40, 1361-1403.

LEWIS, G.N. and RANDALL, M. (1961) Thermodynamics. (revised by K.S. Pitzer and L. Brewer), 2nd edition. McGraw-Hill : New York.

MacEWAN, D.M.C. and RUIZ-AMIL, A. (1975) Interstratified clay minerals. In Soil Components Vol. 2, Inorganic Components (J.E. Gieseking, ed.). Springer Verlag, Berlin-New York. pp. 265-334.

MITCHELL, B.D. (1975) Oxides and hydrous oxides of silicon. In Soil Components Vol. 2, Inorganic Components (J.E. Gieseking, ed.), Springer Verlag, Berlin-New York, 351-393.

OLADIMEJI, O.M. (1976) Chemistry Dept., University of Birmingham; personal communication.

ROSS, S. and OLIVIER,R.J.P. (1964) Physical Adsorption. Wiley, New York.

SCHNITZER, M. and KHAN, S.U. (1972) Humic Substances in the Environment. Marcel Dekker, New York, 327 pp.

SMEDLEY, R.J. (1976) Chemistry Dept., University of Birmingham, personal communication.

THOMAS, H.E. and PIEROTTI, R.A. (1972) Physical adsorption : the interaction of gases with solids. In Surface and Colloid Science (E. Matijevic ed.) Wiley-Interscience, New York, Vol. 4, p. 93.

YOUNG, D.M. and CROWELL, A.D. (1962) Physical adsorption of gases. Butterworth (London).

WEBER, J.B. (1970) Mechanisms of adsorption of s-triazines by clay colloids and factors affecting plant availability. Residue Reviews, 32, 93-130.