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Adsorption of Organic Chemicals in Soils

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This paper presents a review on adsorption of organic chemicals on soils sediments and their constituents. The first part of this review deals with adsorption from gas and liquid phases and gives a discussion on the physical meaning of the shape of adsorption isotherms. Results show that no general rules can be proposed to describe univocally the relation between the shape of isotherms and the nature of adsorbate-adsorbent system. Kinetics of adsorption is discussed through the description of various models.

Theoretical developments exist both for the thermodynamics and the kinetics of adsorption, but there is a strong need for experimental results. Possible adsorption mechanisms are ion exchange, interaction with metallic cations, hydrogen bonds, charge transfers, and London-van der Waals dispersion forces/hydrophobic effect. However, direct proofs of a given mechanism are rare. Several factors influence adsorption behavior. Electronic structure of adsorbed molecules, properties of adsorbents, and characteristics of the liquid phase are discussed in relation to adsorption. Such properties as water solubility, organic carbon content of adsorbing materials, and the composition of the liquid phase are particularly important. Evaluation of adsorption can be obtained through either laboratory measurements or use of several correlations. Adsorption measurements must be interpreted, taking into account treatment of adsorbent materials, experimental conditions, and secondary phenomena such as degradations. Correlations between adsorption coefficients and water-octanol partition coefficient or water solubility are numerous. They may be useful tools for prediction purposes. Relations with transport, bioavailability, and degradation are described.

Introduction

Development of agricultural practices in plant protection, of industrial activities, and of urban areas producing waste waters and leading to various land disposals are accompanied by the introduction in the natural environment of an increased number of organic chemicals. This is the result of either normal activities or of several accidents responsible for spills and leaks. Some of these chemicals are dangerous for plants, animals, and human life; they are called pollutants. Although the corresponding risk may be variable, it is necessary to know and to predict the behavior of these organic chemicals in the environment as they are sometimes dispersed in soils, groundwaters, and surface waters.

Transport, transformations, and biological effects of organic chemicals in soils and aquatic systems depend strongly on their retention by the solid organo-mineral phase. Retention has two possible causes. The first is an association with organic soil constituents, probably mainly due to reactions leading to covalent bonds between solute compounds and the solid phase. This is usually called "chemical fixation." The second, with which this paper is concerned, is adsorption of solutes from an aqueous medium on a solid surface.

According to IUPAC terminology (*1*), adsorption is the enrichment (positive adsorption) or the depletion (negative adsorption) of one or more chemical species at an interface. Adsorption of chemicals on soils and sediments and on their constituents has been extensively studied and has given rise to many publications. Several reviews have given much information and many discussions on this subject (*2–6*). However, because of the great variety of chemicals, soil and sediment components, and experimental situations, there are many results, explanations are not always clear, and valuable conclusions are difficult to draw. It is thus worthwhile reconsidering the literature data in order to try to improve the presentation of our knowledge concerning adsorption. The purpose of this paper is to give a new review on this subject. Though it is impossible to claim that this review is exhaustive, it is hoped that the main results will be taken into account.

Description of Adsorption

For soils, sediments, and their constituents in natural conditions, adsorption is the passage of a solute from an aqueous phase to the surface of a solid adsorbent, desorption being the reverse process. The solute may be a neutral molecule or an ionic specie and the process can take place either in the macropores or in the micropores of the medium. The role of its structure and of molecular diffusion will be discussed later in the paragraphs dealing with kinetics and methodology.

In order to describe an adsorption phenomenon, it is

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necessary to obtain information about *a*) the relationships at equilibrium between the amount adsorbed and the concentration of the bulk solution in contact with the adsorbent; this is given by isotherm curves of adsorption and desorption; *b*) the energies that characterize the equilibrium between the solid surface and the liquid phase; thermodynamic treatments of adsorption data allow their values to be obtained; and *c*) the speed at which equilibrium is attained and the magnitude of energies involved. These data are given by kinetic studies.

Adsorption Isotherms

Adsorption from a Gas Phase. Adsorption of gas has been widely studied (*7,8*) but it rarely concerns organic chemicals in natural systems. The reason is that the solid surfaces have to be directly accessible to allow adsorption from a gas phase. This only occurs in soils sufficiently dry with no adsorbed water molecules on solid constituent surfaces. Furthermore, chemicals must have a high vapor tension (e.g., trifluralin, DDT) or be gaseous (e.g., methyl bromide, ethyl bromide). Three types of isotherms have been observed: Langmuir, Freundlich, and BET isotherms.

Langmuir Isotherm. The Langmuir isotherm describes adsorption on a homogeneous surface, with a maximum adsorbed amount corresponding to a monolayer and without lateral molecular interactions. Its expressions is

$$\theta = \frac{b\,P}{a + bP} \tag{1}$$

where:

θ	fractional coverage
P	pressure of gaseous compound
a, b	constants

At low pressure the isotherm becomes linear and corresponds to Henry's law.

Freundlich Isotherm. Freundlich isotherms are observed when adsorption takes place on heterogeneous surfaces; it is described by the following formula:

$$q = K_f\, P^{nf} \tag{2}$$

where:

q	amount adsorbed
P	pressure of the gaseous compound
K_f, nf	Freundlich constants

These isotherms may be derived by considering a heterogeneous surface as a juxtaposition of small areas to which Langmuir's isotherm is applied (*8*).

BET (Brunauer, Emmett, Teller) Isotherm. Adsorption of gas on solid surfaces often gives rise to the formation of multimolecular layers, and the BET theory provides a tool for description of isotherms. Several shapes have been observed, some of which show a capillary condensation (*7*). The general expression of the isotherms is:

$$W = \frac{W_m X C}{1 - X}\left[\frac{1 - (n+1)X^n + nX^{n+1}}{1 + (C-1)X - CX^{n+1}}\right] \tag{3}$$

where:

W	amount of vapor adsorbed at pressure P
W_m	weight adsorbed corresponding to a monolayer
X	P/P_o; P_o = saturation pressure
C	parameter related to the heat of adsorption and to the heat of liquefaction of the vapor
n	number of adsorbed layers

When adsorption is limited to a monolayer, Eq. (3) reduces to a Langmuir-type equation.

Jurinak and Volman (*9*) have used the following transformation of Eq. (3):

$$\frac{\phi(nX)}{W} = \frac{1}{W_m C} + \frac{\Theta(nX)}{W_m}$$

$$\phi(nX) = \frac{X[(1-X^n) - nX^n(1-X)]}{(1-X)^2}$$

$$\Theta(nX) = \frac{X(1-X^n)}{1-X} \tag{4}$$

Adsorption of ethylene dibromide on several soils containing various types of clays follows this kind of isotherm (*9*) as illustrated in Figure 1 for montmorillonitic soils.

Adsorption from a Liquid Phase

The most frequent situation is that the liquid phase is aqueous in soils and sediments. However, adsorption studies from pure organic solvents or from organic solvent-water mixtures are useful from a methodological point of view to obtain information about solute-surface interaction mechanisms. This point will be discussed later.

A detailed theoretical treatment and a well-documented experimental description was given by Kipling (*10*). The more general situation corresponds to systems with two miscible compounds where the adsorption from the solution takes place over the full range of molar fractions. However, systems consisting of an aqueous phase and dissolved organic chemicals are quite different. This is due to the low water solubility of chemicals, which is often less than 100 mg/L. It is especially the case of hydrophobic compounds whose solubility can be as low as 0.00095 mg/L (2,4,5,2′,4′,5′-PCB). As a con-

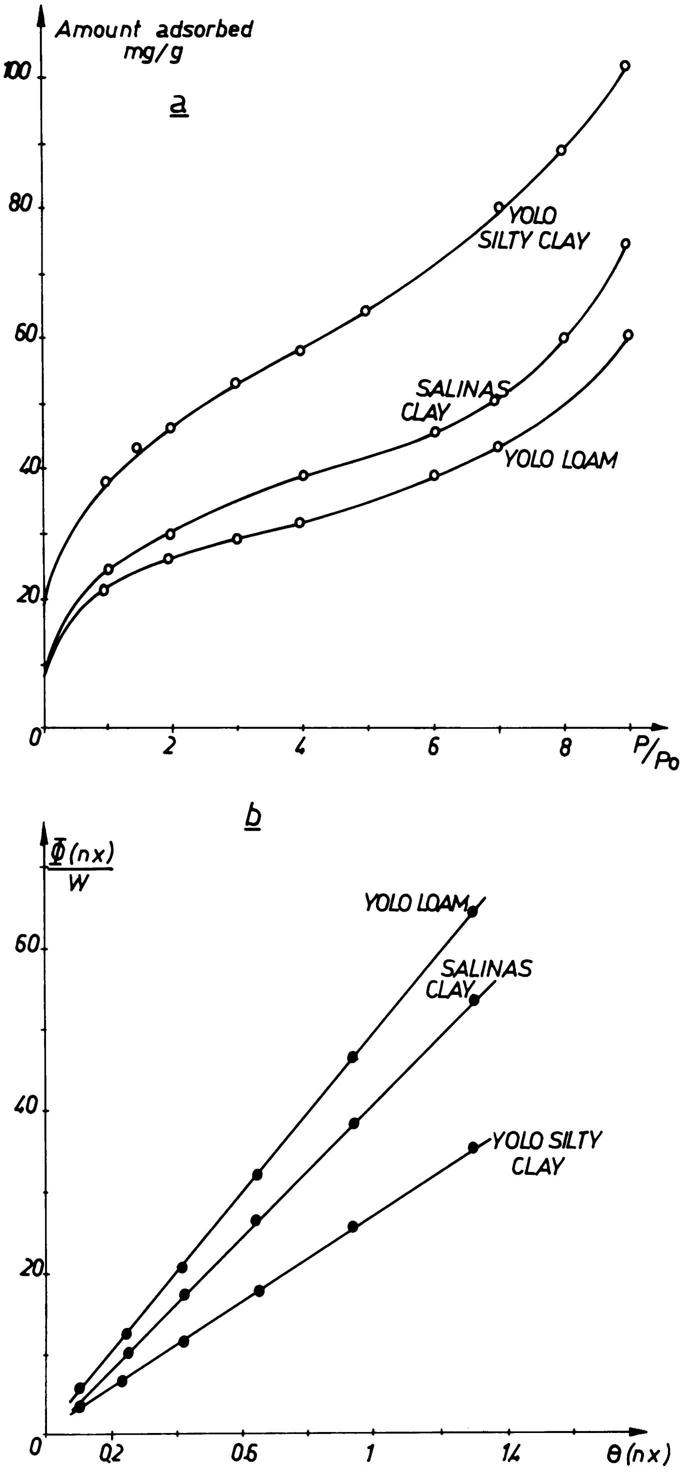


FIGURE 1. (a) Adsorption of ethylene dibromide (EDB) on montmorillonitic soils; (b) adsorption data plotted according to Eq. (3). Redrawn from Jurinak and Volman (*9*).

sequence, adsorption of organic chemicals occurs from dilute solutions with low molar fractions, generally less than 10^{-4}. This probably explains, at least partly, the experimental and theoretical difficulties encountered in adsorption studies.

Adsorption isotherms have first been described on an empirical basis and later some theoretical treatments have been proposed. Here again, homogeneous surfaces have to be distinguished from heterogeneous ones.

Adsorption on Homogeneous Surfaces: Langmuir Formulation. The Langmuir isotherm may be obtained by analogy with Langmuir adsorption of gas. It can also be derived from classical and statistical thermodynamics. For a given solute the adsorbed amount, q, and the equilibrium concentration, C_e, of the bulk solution are related by:

$$q = \frac{kK_LC_e}{1+kC_e} \tag{5}$$

where k and K_L are two constants

Eq. (5) can be rewritten as

$$\frac{1}{q} = \frac{1}{kK_LC_e} + \frac{1}{K_L} \tag{6}$$

Therefore, the graph representing $1/q = f(1/C_e)$ should be a straight line if the Langmuir relation is obeyed.

The above formulation was used by Weber and Gould (*11*) for the adsorption of several pesticides on active charcoal, by Moreale and van Bladel (*12*) for the adsorption of herbicide-derived aniline residues on soils, and more recently by Brown and Combs (*13*) for the adsorption of methylacridinium ions on marine sediments. Figure 2 gives an example of the application of the Langmuir formulation.

It is worth noting that this formulation has a physical meaning only if the assumptions underlying its theoretical derivation are verified. All adsorption sites must have the same adsorption energy (homogeneous surface), lateral molecular attractions have to be negligible, and the monolayer coverage must represent the maximum amount adsorbed. These conditions are sometimes fulfilled for ionic compounds. For nonionic compounds, however, the difficulty arises mainly from the heterogeneous character of adsorbent surfaces that certainly possess sites with various adsorption energies owing to the complex nature of soil and sediment constituents. For these nonionic compounds the monolayer coverage is not a constraint since it is not likely to occur due to low solute water solubilities.

Heterogeneous Surfaces. To account for the existence of sites with different adsorption energies, Giles et al. (*14*) have suggested writing the parameter k of the Langmuir formulation as a function of either the adsorbed amount, q, or of the solution equilibrium concentration, C_e. The isotherm is then expressed by:

$$q = \frac{K_L\omega C_e^{(\beta+1)}}{1+\omega C_e^{(\beta+1)}} \quad \text{with } k = \omega C_e^{\beta} \tag{7}$$

where

ω, β constants

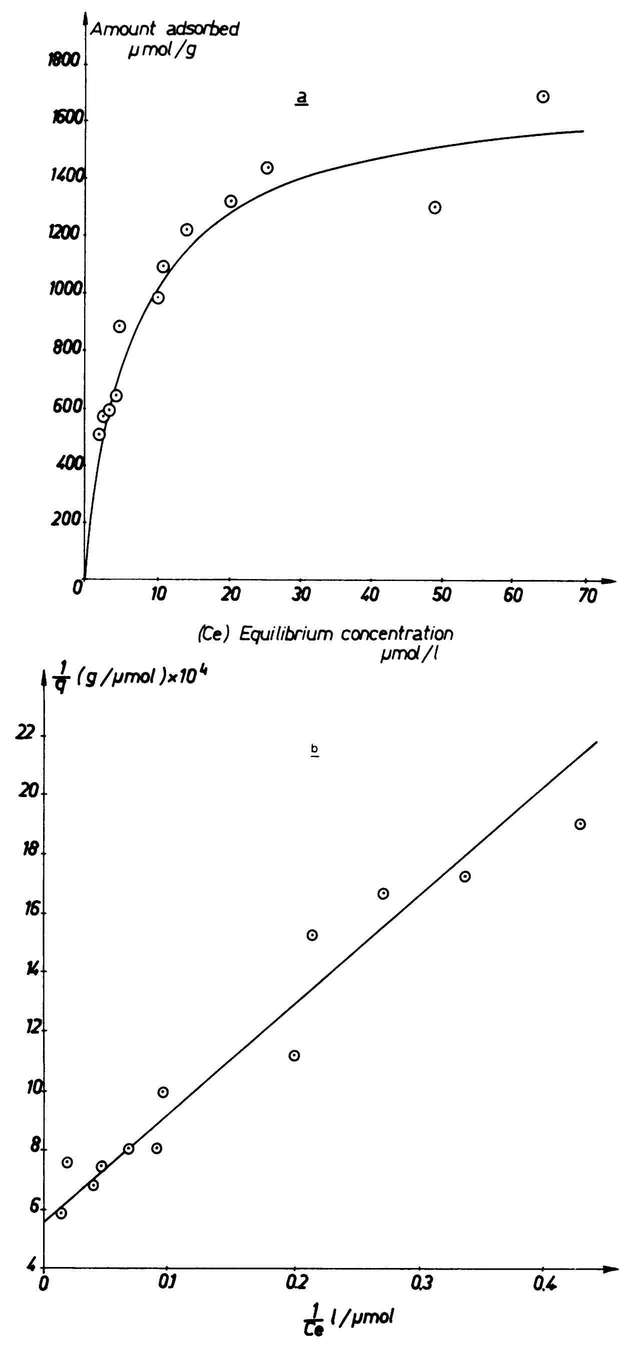


FIGURE 2. (*a*) Adsorption isotherm of 2,4,5-T on active charcoal; (*b*) corresponding Langmuir plot. Redrawn from Weber and Gould (*11*).

This formulation allows all kinds of adsorption isotherms to be described (*4*) and presents two particular cases:

$\beta = 0$ **corresponds to the Langmuir formulation for sufficiently low concentrations**

$$\omega C_e^{(\beta+1)} << 1, \text{ leading to } q = K_L \omega C_e^{(\beta+1)} \qquad (8)$$

which is analoguous to the Freundlich formula given by Eq. (2):

$$q = K_f C_e^{nf}, \text{ with } K_f = \omega K_L \text{ and } nf = \beta + 1 \qquad (9)$$

This formulation is widely used because it gives good descriptions of experimental results. It is worth noting that experimental values of nf are greater or lower than unity, which implies that β can be positive or negative. However, nf is often nearly equal to unity, a simple situation that corresponds to a linear isotherm. In this case, the adsorption coefficient is equivalent to a partition coefficient of the solute between the solution and the solid surface. Several examples of K_f and n_f values are reported in reviews such as those of Hamaker and Thomson (*2*) and Calvet et al. (*4*).

Adsorption isotherms can also be expressed as a polynomial function of the equilibrium concentration as proposed by Lambert (*15*).

Shape of Adsorption Isotherms. The shape of adsorption isotherms is an important characteristic because it provides information about adsorption mechanisms. Giles et al. (*14*) have proposed to classify isotherms into several categories. This classification is based on the initial slope $(dq/dC_e)_{Ce=0}$, which is important because it depends on the rate of change of site availability. Figure 3 shows the four classes of possible isotherms together with the corresponding conditions for the parameter β of Eq. (7).

S-ISOTHERMS. This type of isotherm implies that adsorption becomes easier as the concentration in the liquid phase increases. According to Giles et al. (*14*), this is observed when the solute molecule is monofunctional; has a moderate intermolecular attraction leading to a vertical packing in the adsorbed layer; and meets

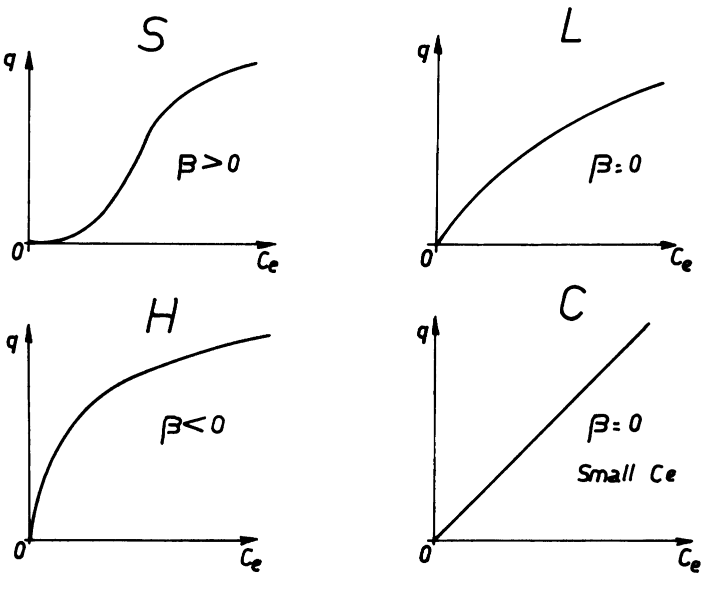


FIGURE 3. Different shapes of adsorption isotherms (*14*). q is the adsorbed amount and C_e the equilibrium concentration.

a strong competition for sites from molecules of solvent or of another species.

For Giles et al. monofunctionality, as far as adsorption is concerned, means that the solute molecule has a fairly large hydrophobic part (> C5) and a marked localization of the force of attraction for the substrate. For a given molecule, this character may depend on both the nature of the adsorbent surface and the nature of the solvent.

Literature shows that S-isotherms are often observed with smectites (essentially montmorillonites) and sometimes also with other clays. Thus, one can suggest that S-curves would be characteristic of organic molecules adsorption on clay surfaces. This is consistent with some other observations. The adsorption isotherm of bromacil is transformed from an L to an S type when the organic matter of a montmorillonitic soil is oxidized (*16*). Weber et al. (*17*) have noted that adsorption of fluridone was described by an S-isotherm in soils having a high montmorillonite content and a low organic matter content. Table 1 gives several examples of systems with S-isotherms. Furthermore, it can be noted that the nature of the solute molecule does not appear to be an important factor except that all mentioned molecules are polar. S-isotherms are illustrated in Figure 4.

L-ISOTHERMS. L-isotherms correspond to a decrease of site availability as the solution concentration increases. This means that molecules are most likely to be adsorbed in a flat position and that they do not suffer a strong competition from solvent molecules (*14*). Examples of systems showing this type of isotherm are systems with high polar solutes and substrates and monofunctional ionic substances presenting very strong intermolecular interactions.

L-isotherms have frequently been observed as shown by results reported in the literature. Yet, no general trend can be described because L-curves may be obtained with extremely different solute/adsorbent systems. Organic cations as well as neutral molecules with low or high water solubility are adsorbed in this way. Likewise, mineral and organic adsorbents as well as various soils and sediments adsorb solutes according to L-isotherms. Table 2 gives some examples of systems and Figure 5 shows an illustration of the corresponding results.

Table 1. Systems with S-isotherms.

Compounds	Adsorbents	Reference
Oxamyl Dimecron	Cu-, Cd-, Zn-, Mn-, Co-, Ni-montmorillonites	(*55*)
Bromacil	Ca-montmorillonite, oxidized soils	(*16*)
Azinphos-methyl	Ca-, Cu-montmorillonites, Ca-hectorite	(*62*)
Organophosphorus compounds	Na-, Ca-, Fe-montmorillonites	(*95*)
Metabenzthiazuron Terbutryne Napropamide	Ca-montmorillonite at pH 3	(*118*)
Bromacil, Isocil	Na-montmorillonite, Na-kaolinite	(*168*)
Fluridone	Soils	(*17*)
Carbaryl	Ca-montmorillonite, soils	(*169*)
Metolachlor	Soils	(*170*)

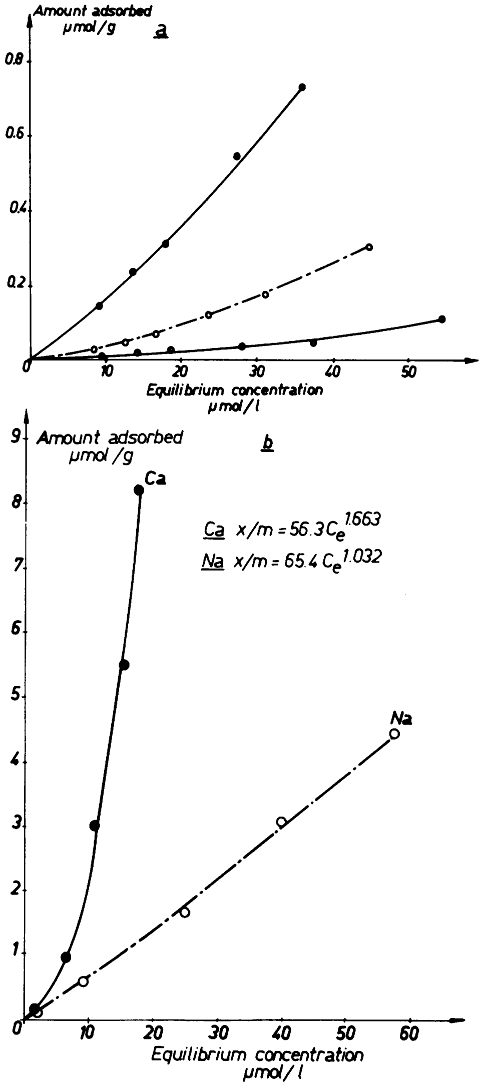


FIGURE 4. (*a*) Adsorption isotherm of Metolachlor on a sandy loam natural soil (●); after humic substances were removed by pyrophosphate + NaOH extraction (○); and after H_2O_2 treatment (◎). Redrawn from Kozak (*168*); (*b*) adsorption isotherm of methyl-parathion on Na- and Ca-montmorillonites. Redrawn from Bowman and Sans (*94*).

H-ISOTHERMS. H-isotherms are special cases of L-isotherms and are observed when the adsorbent surface possesses a high affinity for the adsorbed solute. Bipyridinium ions with clays and humic acids show this behavior (*4,18,19*). Examples of H-isotherms are given in Figure 6.

C-ISOTHERMS. C-isotherms correspond to a constant partition of the solute between the bulk solution and the adsorbent (*14*). Conditions favoring C-curves are a porous substrate with flexible molecules and region of differing degrees of solubility for the solute and

Table 2. Systems with L-isotherms.

Compounds	Adsorbents	Reference
Ionic		
2,4-D	Illite, sand, humic acid, pH 6	(*31*)
2,4-D, picloram	Humic acid, pH 3.3–3.6	(*44*)
Oxamyl	Na-kaolinite, illite, montmorillonite	(*65*)
Terbutryne	Humic acid	(*171*)
Benzidine	Sediments, soils	(*56*)
Neutral		
Simazine	Soils	(*2*)
Lindan	Soils	(*38*)
Fluridone	Soils	(*17*)
Atrazine	Soils	(*2*)
Atrazine	Ca-montmorillonite, pH 3	(*118*)
Napropamide	Soils	(*172*)
Chlortoluron	Soils	(*173*)
Bromacil	Soils	(*173*)
α-Naphtol	Soils	(*89*)
Nitrobenzene	Sediments, soils	(*38*)
Tebuthiuron	H, Ca-organic matter	(*174*)

solutes with higher affinity for the substrate than for the solvent allowing easy penetration in the substrate. These conditions are likely to be met with hydrophobic compounds and soil or sediment organic matter, as shown, e.g., with chlorinated organic compounds (*20*), dibenzothiophene (*21*), and nitrogen heterocyclic compounds (*22*). In spite of that, various other systems with mineral adsorbents and/or polar compounds are also characterized by C-isotherms. Table 3 and Figure 7 give some examples of such isotherms.

It happens frequently that adsorption isotherms are strictly L-curves but are very close to C-curves, which can be taken as approximate descriptions. For example, this is the case of the results of Felsot and Dahm (*23*) concerning organophosphorus and carbamate insecticides adsorbed on various soils.

General Comments. Adsorption of organic chemicals on soils, sediments, and their constituents reveals a great variety of systems and behaviors. No general rule can be derived from the reported results because of the wide range of variation of molecular properties and of adsorbent substrates. In addition, simple correspondence between the conditions advanced by Giles et al. (*14*) and experimental isotherms are not straightforward. This is mainly due to insufficient knowledge of the structure and surface properties of amorphous mineral and organic adsorbents and of their associations with clays.

Nevertheless, isotherms alone are certainly not able to describe completely the adsorption phenomenon. Thermodynamic and kinetic data, as well as any information about the molecular mechanisms, have to be used in order to provide more detailed descriptions.

Desorption Isotherms

Desorption has been much less studied than adsorption and it is not yet well understood. Desorption iso-

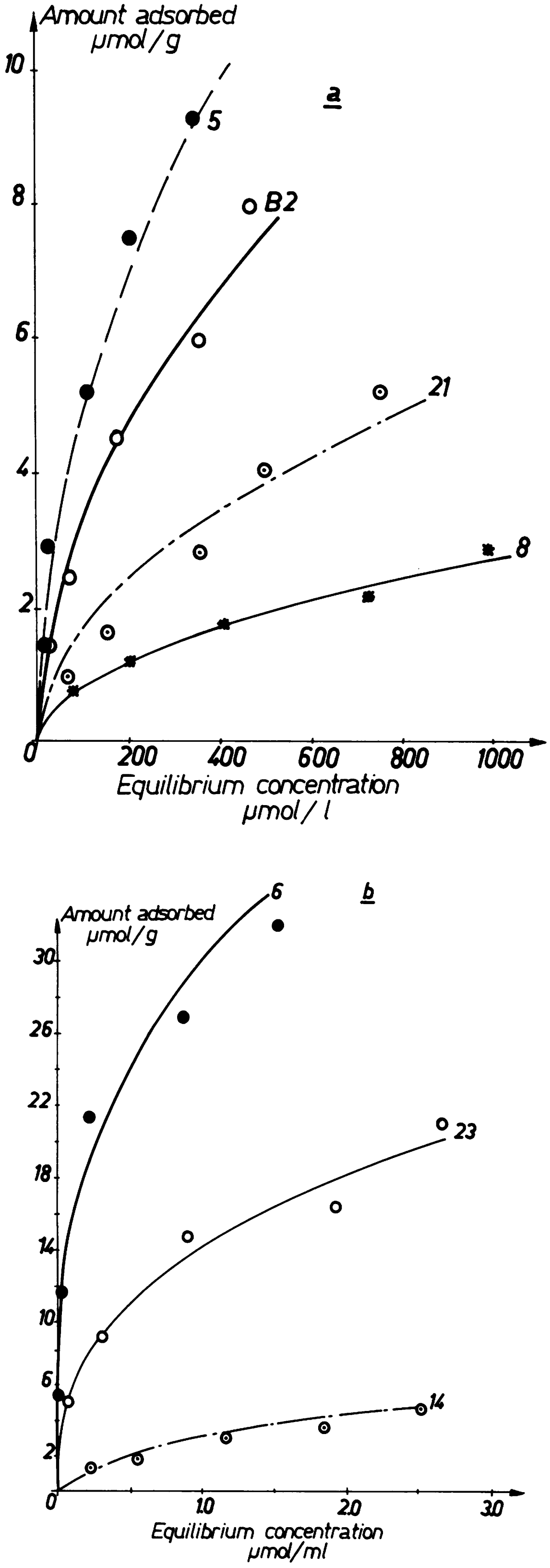


FIGURE 5. (*a*) Adsorption isotherm of benzidine on several soils and sediments; numbers refer to samples listed in Zierath et al. (*29*); (*b*) adsorption isotherm of α-naphtol on several soils and sediments; numbers refer to samples listed in Hassett et al. (*88*). Redrawn from Hassett et al. (*88*)

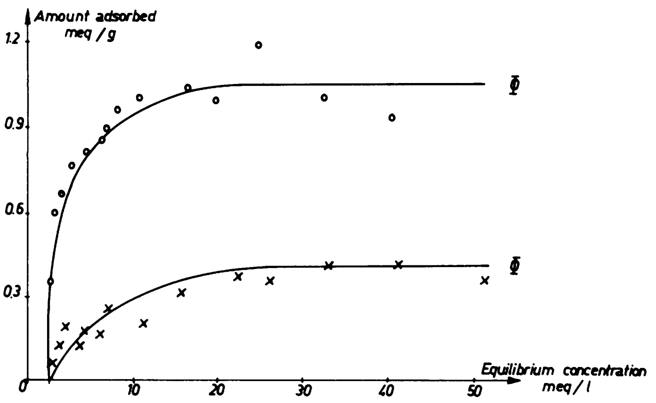


FIGURE 6. Adsorption of paraquat on Ca-humates in water (○) and in a $CaCl_2$ (0.666 N) solution (x). Redrawn from Burns et al. (*19*).

Table 3. Systems with C-isotherms.

Compounds	Adsorbents	Reference
Buthidiazol, fluridone, tebuthiuron	Ca-montmorillonite	(*174*)
Bromacil 2,4-D	Na-illite, silicagel Na-montmorillonite Alumina, silicagel	(*168*)
Fenuron, monuron	H (Al)-montmorillonite	(*175*)
Napropamide	Soil + organic matter	(*172*)
Bromacil	Peat soil	(*16*)

therms can generally be represented by a Freundlich type formula:

adsorption

$$q_a = K_{fa}C_e^{nfa}; \tag{10}$$

desorption

$$q_d = K_{fd}C_e^{nfd}$$

In the case of hysteresis, K_{fd} and n_{fd} are respectively different from K_{fa} and n_{fa}. A relation between adsorption and desorption parameters has been proposed by Hornsby and Davidson (*24*):

$$K_{fd} = (K_{fa})^{nfa/nfd} (q_{max})^{(1-nfa/nfd)} \tag{11}$$

This formula was later applied by van Genuchten et al. (*25*) for picloram and by O'Connor et al. (*26*) for 2,4,5-T desorption from soils. It shows that the shape of desorption isotherms depends on the adsorbed amount of solute before desorption (qm).

Experimental results frequently show a different q = f(C_e) relation for desorption as compared to adsorption. This phenomenon, called adsorption hysteresis, is not completely explained. It has been observed by several authors and references concerning this topic

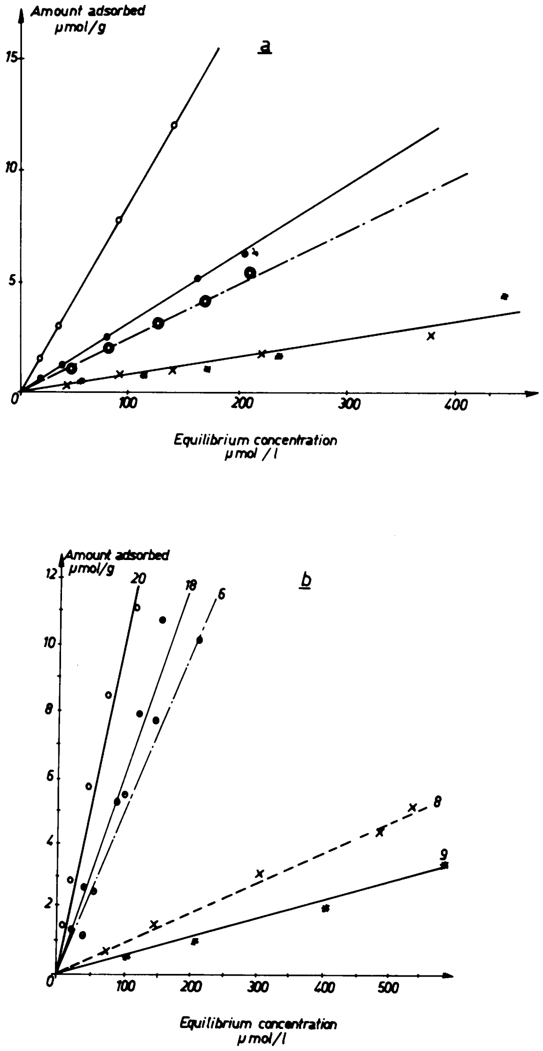


FIGURE 7. (*a*) Adsorption isotherms of fenuron and monuron on H(Al)-clays; fenuron-bentonite (○); monuron-bentonite (●); monuron-Camberteau montmorillonite (x); fenuron-Campberteau montmorillonite (*). Redrawn from van Bladel and Moreale (*173*). (*b*) Adsorption isotherms of dibenzothiophene on several soils and sediments; numbers refer to samples listed in Hassett (*21*). Redrawn from Hassett et al. (*21*).

Table 4. Systems showing adsorption hysteresis.

Compounds	Adsorbents	Reference
Napropamide	Soils	(*172*)
Organophosphorus compounds	Na, Ca, Fe-montmorillonites	(*95*)
Organophosphorus, carbamate insecticides	Soils	(*23*)
2,4-D	Soils	(*176*)
2,4,5-T	Soils	(*26*)
Terbufos, terbufos derivatives	Soils	(*177*)
Chlorsulfuron	Soils	(*178*)

have been given by Hamaker and Thompson (*2*) and Calvet et al. (*4*). Other references are listed in Table 4.

For adsorption of hydrophobic compounds on sediments, Di Toro and Horzempa (*27*) have shown that linear relations hold both for adsorption and desorption. Thus hysteresis was simply described in this situation. As will be shown, hysteresis is strongly dependent on the adsorption mechanism. However, when interpreting desorption data, it is advisable to consider secondary phenomena such as degradation or chemical fixation, which may be a source of erroneous observations.

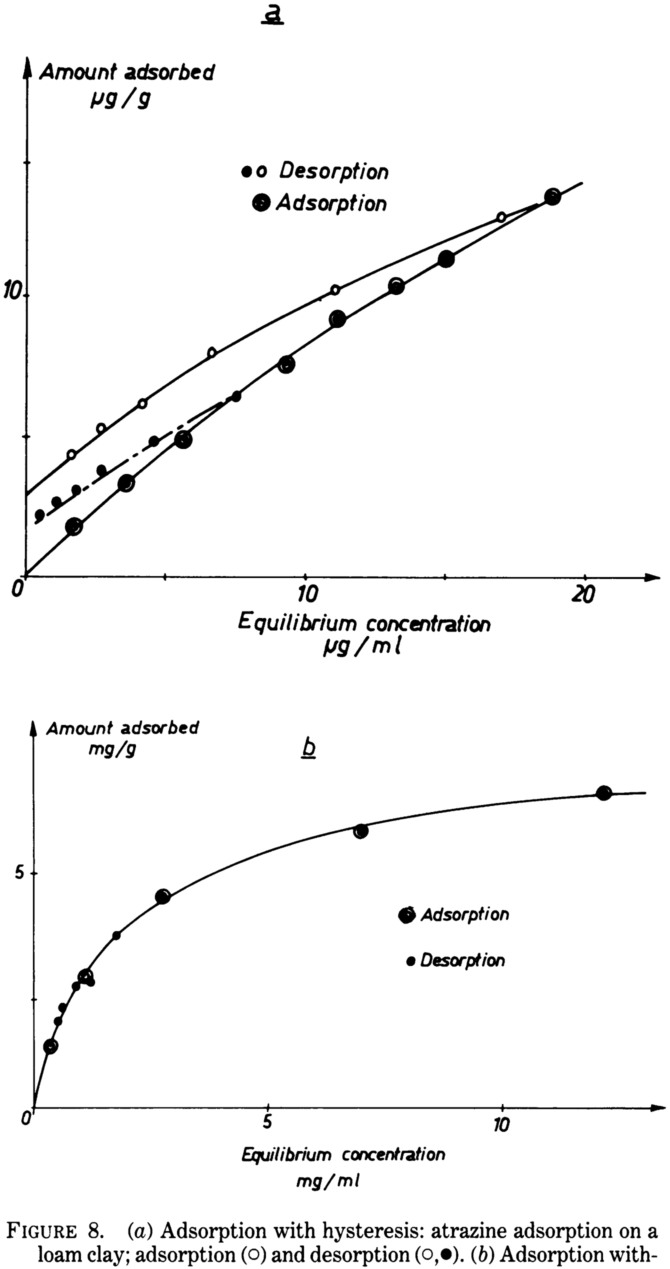


FIGURE 8. (*a*) Adsorption with hysteresis: atrazine adsorption on a loam clay; adsorption (○) and desorption (○,●). (*b*) Adsorption without hysteresis: propamocarbe adsorption on a clay soil; adsorption (○) and desorption (●). (Calvet, unpublished results).

Thermodynamics of Adsorption

Thermodynamic Characteristics. A detailed analysis of the thermodynamics of organic chemical adsorption is not the purpose of this paper. The aim here is only to give a summary of the approaches that are often followed by soil scientists interested in adsorption phenomena.

There are two kinds of thermodynamic characteristics. The first concerns the characterization of the process of adsorption (or of desorption) causing the system to pass from an initial state to a final equilibrium state. The thermodynamic characteristic is the Gibbs Free Energy change during adsorption. If K_e is the corresponding thermodynamic equilibrium constant, one has:

$$\Delta G = -RT \operatorname{Ln} K_e \ . \qquad (12)$$

A general expression of the adsorption reaction can be written as follows:

$$n_1S_{a1} + n_2S_{b2} \qquad n_2S_{a2} + n_1S_{b1} \qquad (13)$$

where a and b represent the adsorbed phase and bulk solution, and 1 and 2 represent the solvent and solute, respectively. n1 and n2 are the numbers of molecules involved in the process.

The corresponding equilibrium constant is given by:

$$K_e = \frac{(\gamma_{a2})^{n2}(\gamma_{b1})^{n1}}{(\gamma_{a1})^{n1}(\gamma_{b2})^{n2}} \, \frac{(C_{a2})^{n2}(C_{b1})^{n1}}{(C_{a1})^{n1}(C_{b2})^{n2}} \qquad (14)$$

where C_{ij} is the concentration and γ_{ij} is the activity coefficient. Unfortunately, this formula is difficult to apply because solute activity coefficients and concentrations in the adsorbed phase cannot be easily calculated.

In order to simplify the expression of K_e, the system is characterized for a limiting case corresponding to $C_{b2} \rightarrow 0$ and $C_{a2} \rightarrow 0$. Furthermore, it is assumed that the ratio of all the activity coefficients approximate unity, which is valid for small concentrations; the ratio concerning the solvent molecules is constant; and $n1 = n2 = 1$, that is, adsorption of one solute molecule entails the desorption of one solvent molecule.

With these assumptions, Eq. (14) reduces to:

$$K_e = \frac{C_{b1}}{C_{b2}} \frac{C_{a2}}{C_{a1}} \text{ or } K_e' = \frac{C_{a2}}{C_{b2}}, \text{ if } \frac{C_{b1}}{C_{a1}} = \text{constant} \qquad (15)$$

The concentration of solute in the adsorbed phase C_{a2} still remains to be expressed. For that purpose, Biggar and Cheung (*28*), and Moreale and van Bladel (*12*) have used a formulation proposed by Fu et al. (*29*). This leads to:

$$C_{a2} = \frac{(\rho_1/M_1)A_1}{S/Nq_a - (A_2/M_2) \times 10^6} \qquad (16)$$

where

A_1, A_2	respective cross sectional areas (cm^2/molecule)
M_1, M_2	respective molecular weights (g/molecule)
S	surface area of the adsorbent (cm^2/g)
q_a	amount adsorbed (g/g)
N	Avogadro's number
ρ_1	density of the solvent (g/ml)

Then the characterization consists of calculating the limiting value of the ratio C_{a2}/C_{b2} (thus of $K_{e'} = K_o$) by extrapolating a plot of C_{a2}/C_{b2} against C_{a2} to $C_{a2} = 0$. This leads to:

$$\Delta G_0 = -RT \, \text{Ln} \, K_0$$

$$\Delta H_0 = -R \frac{\partial(\text{Ln}\, K_0)}{\partial(1/T)}$$

$$\Delta S_0 = \frac{\Delta H_0 - \Delta G_0(T)}{T} \qquad (17)$$

Examples of application of this theoretical treatment were given by Biggar and Cheung (*28*) for adsorption of 2,4,5-T on soils and by Moreale and van Bladel (*12*) for adsorption of aniline molecules on soils. It is important to note that this implies a constant value of the enthalpy of adsorption.

The second concern is the characterization of the equilibrium of the system. As pointed out by Burchill et al. (*6*), this is done by envisaging a virtual process that takes place under equilibrium conditions with no change in the Gibbs Free Energy. In this case, $\Delta H_i = T\Delta S_i$, where the Δ represents the variations corresponding to the adsorption of a unit amount of substance under equilibrium conditions. ΔH_i is the difference, at equilibrium, between the partial molar enthalpy of the adsorbed solute and that of the solute in solution. Although it can be determined by calorimetric measurements, it is generally obtained from isotherm adsorption data for a given amount adsorbed (q) at a constant area (A) of the adsorbent and pressure (P). The enthalpy values so determined are called isosteric heat of adsorption. Then:

$$\Delta H_i = \frac{\partial(\text{Ln}\, C_{b2})}{\partial(1/T)}_{q,A,p} \qquad (18)$$

A more rigorous expression is obtained by using activities instead of concentrations.

A complete theoretical treatment was proposed by Mills and Biggar (*30*), who derived an expression of the differential heat of adsorption at constant spreading pressure. They emphasized that this characteristic represents the true difference in partial molar enthalpy of the solute between the adsorbed and the bulk phases. However, isosteric heats of adsorption have been more frequently determined. Some examples of systems to which this calculation was applied are given in Table 5.

Table 5. Systems for which isosteric heats were calculated.

Compounds	Adsorbents	Reference
2,4-D	Various adsorbents	(*31*)
Isocil, bromacil	Various adsorbents	(*168*)
Anilines	Soils	(*12*)
Azinphos-methyl	Smectites	(*62*)

Physical Meaning of Measured Thermodynamic Characteristics. Thermodynamic characteristics are both macroscopic and global. Even at low solute concentrations, several interactions have to be considered: solute-adsorbent surface, solute-solvent, adsorbent surface-solvent, and solvent-solvent. Calculated values must be interpreted carefully since, in general, they do not always give a direct characterization of the solute surface bond. Other information about the molecular and adsorbent properties and on the solute-adsorbent complex (e.g., IR data) are necessary.

Three main types of information may be provided by the analysis of thermodynamic characteristics. The first concerns the way in which isosteric heat of adsorption (or the differential heat) varies with the adsorbed amount, which is closely related to the shape of isotherms. A constant ΔH_i value would correspond to a Langmuir isotherm, whereas ΔH_i values exponentially decreasing with surface coverage would correspond to Freundlich isotherms (*6*). Examples of the latter situation are given by Haque and Sexton (*31*) and Burchill and Hayes (*6*). The second type of information deals with solute-surface interactions as shown by Biggar and Cheung (*28*) for picloram adsorption by soils. They found values of standard enthalpy of -20 kcal/mole at pH = 2.0 and of -5.3 kcal/mole at pH = 4.2. They interpreted this on the basis of molecular states of picloram. At pH = 2.0, picloram essentially occurs in protonated and dipolar forms ($pK_a = 3.4$) and can strongly interact with metallic cations on the surface. On the contrary, at pH = 4.2, most of the molecule is in anionic form causing a weaker interaction with the surface. The third type of information concerns the possible occurrence of other phenomena taking place simultaneously with adsorption. Thus a positive enthalpy was interpreted by Moreale and van Bladel (*12*) to be due to a diffusion process into soil particles and by Sanchez Martin and Sanchez Camazano (*63*) to be due to interlamellar swelling of clays.

The solvent relevant to environmental systems is water and thus solute-water interactions are important. They may be taken into account in two ways. In the first way, expressions for thermodynamic characteristics are written in terms of reduced solute concentrations C/C_o (C_o being the water solubility in the bulk solution). Under these conditions thermodynamic characteristics correspond to passage of the solute from the solid state to the adsorbed state (*30*). This procedure has been used by several authors to eliminate the effect of solute-solvent interactions. Some examples have been reported in Calvet et al. (*4*). However, it is unlikely to provide a real improvement of thermodynamic analysis. The second way to take into account solute-solvent interactions is illustrated by the case of hydrophobic compounds adsorption. This was sometimes described as a partition phenomenon between water and soil or sediment organic matter. The equilibrium thermodynamic constant is then expressed in terms of fugacity coefficients of the solute in water and in organic matter phase (*32*).

Kinetic Characteristics

Kinetic study of adsorption is important because it gives the times necessary to reach the equilibrium for adsorption and desorption that are required data for obtaining valuable isotherms and the energetic characteristics of molecular displacements and reaction near or on the adsorbent surface (which bring the solute in the adsorbed state).

Some works on this subject have been reported in previous reviews (*3,4,33,34*). From these and others cited below, it appears that adsorption rates are generally greater than desorption rates; for adsorption, equilibrium is often reached within 1 to 24 hr although it can take longer for some systems because other phenomena, such as chemical fixation, are acting after adsorption has been achieved.

Several theoretical treatments are proposed to modelize the kinetics of adsorption. Models can be classified into three categories: models based on the surface reaction only; models that take into account the surface reaction and the transport towards the surface and/or into the adsorbent aggregates; and black box models.

Surface Reaction Models

Instantaneous Reaction. Instantaneous reaction corresponds to the most simple situation. The rate of adsorption is given by:

$$\frac{\partial q_a}{\partial t} = \frac{\partial [f(C_e)]}{\partial t} \tag{19}$$

$f(C_e)$ is generally considered as a linear or as a Freundlich isotherm. Examples of the use of this model are given by Nkedi-Kizza et al. (*35*) and van Genuchten et al. (*25*).

Noninstantaneous Adsorption. Models describing noninstantaneous adsorption are widely used. They present various degrees of complexity depending on whether adsorption and desorption are described simultaneously or not.

MODELS BASED ON ADSORPTION RATE ONLY. A first-order kinetic model has often been applied, as in the works of van Genuchten (*25*), O'Connor et al. (*26*), and Nkedi-Kizza et al. (*35*). The corresponding equation is:

$$\frac{\partial q_a}{\partial t} = \alpha[KC^n - q_a] \tag{20}$$

where q_a and C are the adsorbed amount and the solution concentration, respectively; K and n are adsorption isotherm parameters, and α is the first-order rate constant.

This type of model was modified by several authors to account for the existence of two categories of adsorption sites. This was done assuming that either one category with instantaneous equilibrium is associated with another characterized by a first-order rate law (*36*) or two categories obeying a first-order rate law are present (*37,38*). Higher order kinetics have sometimes been observed (*12*).

MODELS BASED ON ADSORPTION AND DESORPTION RATE. Starting from a formulation proposed by Fava and Eyring (*39*), Haque and Sexton (*31*) and later Lindstrom et al. (*40*) derived a kinetic model having the following characteristics: it is applicable to sparingly soluble compounds and takes into account adsorption and desorption; it uses the concept of distance from the equilibrium, expressed as the fraction of adsorbed solute ϕ; ϕ is related to adsorption and desorption velocities that are derived from a general Langmuir approach; it introduces a sticking probability, function of ϕ; and it contains a free-energy variation term for adsorption and desorption, which is taken as a linear function of solute adsorbed fraction.

The model was applied by the authors to the adsorption of 2,4-D, isocil, and bromacil on several adsorbents. A numerical procedure is developed to allow the rate and energetic parameters to be determined from the $\phi(t)$ experimental curves. Another application was given by Bansal et al. (*41*) for the adsorption of oxamyl on illites, confirming that the model is useful for the simultaneous evaluation of adsorption and desorption rates.

A slightly simpler model, based only on adsorption rate and without a sticking probability function, was also used by Haque et al. (*42*), Haque and Sexton (*31*), and Leenheer and Ahlrichs (*43*).

Surface Reaction-Transport Models. Kinetic adsorption data frequently show two steps. The first, quite rapid, is probably due to a surface reaction; the second, slower, is attributed to a transport into the adsorbing aggregates. Such observations were given for example by Leenheer and Ahlrichs (*43*) and by Khan (*44*).

Several descriptions and models have been proposed in the literature. The simplest situation holds when adsorption is instantaneous (or nearly so), so that the rate-limiting step is the molecular diffusion into aggregates (or also into porous grains). This situation was observed by Weber and Gould (*11*) for the adsorption of several pesticides on active charcoal for which the amount sorbed was a linear function of the square root of time.

In order to obtain more realistic descriptions, the structure of the adsorbing medium has to be considered. From this point of view there are two kinds of systems: suspensions of particles that can be isolated or aggregated and three-dimensional porous media that can be either undisturbed soil cores or simply nonporous particles or aggregate packings.

The first situation, which corresponds to the classical slurry experiments, was recently described by McKay et al. (*45*) and by Miller and Weber (*38*). In the model proposed by McKay et al. for adsorption kinetics, three steps are described: solute diffusion from the fluid phase to the surface aggregate (several elementary particles associated together); adsorption on the surface; and diffusion into the aggregate. Equations of the model were solved numerically. An application is described for the adsorption of dyes on various adsorbents.

The model of Miller and Weber (*38*) is different in that the adsorption process is only described on the basis of solute transport. Two steps are involved: a molecular diffusion through a boundary liquid layer surrounding the soil particle and a molecular diffusion within the particle itself. According to the authors, experiments with lindan and nitrobenzene adsorption on soil suspensions are well described by the model.

The second kind of situation may be envisaged in two ways. In the first way, adsorption is taken as a source/sink phenomenon coupled with a transport equation, and its kinetics are simply described by an instantaneous or a first-order rate law. Numerous publications about solute transport in porous media illustrate this approach (*25*). However, from the adsorption point of view, it does not represent an improved description. A second way to describe adsorption kinetics in porous media with a moving liquid phase has been recently proposed by Akratanakul et al. (*46*), who also considered three steps (Fig. 9).

Three basic equations are written: *a*) the mass balance for ions in the bulk solution based on a two-dimensional analysis. The equation relates C, the concentration in the bulk solution, the hydrodynamic dispersion coefficient, the Darcian flux, and the volumetric water content; *b*) the mass balance for ions in the subsurface layer; since there is no bulk flow in this region, the equation only described a one-dimensional molecular diffusion; and *c*) the surface rate reaction; it takes into account an activation energy corresponding to a system that follows a Freundlich isotherm.

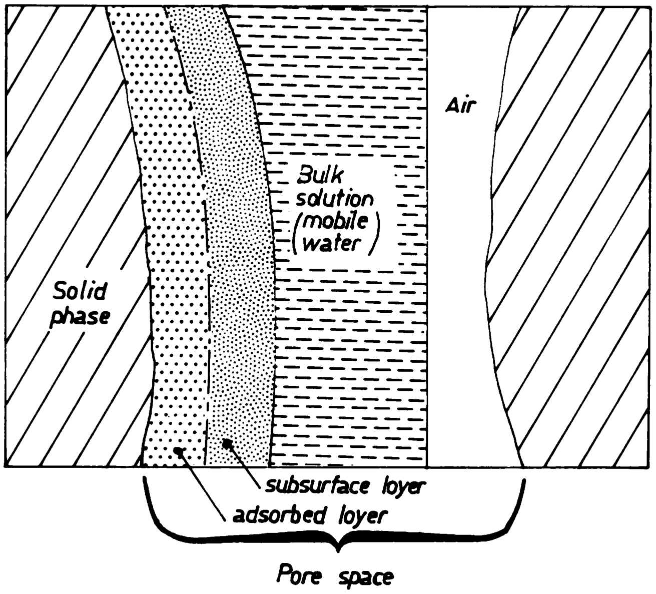


FIGURE 9. Schematic representation of the pore space used in the model of Akratanakul et al. (*45*).

Solutions of this system of equations are obtained with the following boundary conditions: no flux at the outer boundary of the bulk solution; at the subsurface layer/bulk solution boundary, the diffusion flux in the subsurface layer is set equal to the rate of solute transfer in the bulk solution to the subsurface layer; at adsorbed layer/subsurface boundary, diffusion flux in the subsurface layer is set equal to the rate of amount adsorbed.

An application for adsorption of Cd-cations shows that the diffusion across the subsurface layer is the rate-limiting step when the system is far from the equilibrium and that the adsorption rate increases with the pore water velocity (*47*). It would be interesting to apply this model to organic chemical-soil systems.

Black Box Models. Black box models constitute a very different approach to the kinetics of adsorption. From this point of view, the soil suspension can be represented as a system containing (*48*) two compartments, the solution phase and the soil particles or aggregates. Solute transfers take place between these two compartments; three compartments, one for the solution phase and two for the soil particles or aggregates. Transfers take place to and from the solution but not between the two soil compartments.

Rate constants values are calculated from experimental kinetic curves. According to the authors, the three-compartment model seems to give the better results. This kind of model is only useful for numerical descriptions of adsorption kinetics but does not allow physicochemical parameters to be evaluated. Nevertheless, it would be interesting to study the variations of the size of compartments with the soil composition and the chemical nature of the solute.

Adsorption Mechanisms

Adsorption and desorption isotherms, thermodynamic, and kinetic data cannot be fully understood unless the molecular mechanisms are known. According to the properties of solutes and substrates, several interaction mechanisms with the surface are possible: ion exchanges, interactions with metallic cations, polar interactions, charge transfers, and London-van der Waals dispersion forces/hydrophobic effect. Several reviews such as those of Mortland (*49*), Burchill et al. (*6*), Khan (*5*), and Theng (*50*) among others have been published on the subject, so only the principal features will be discussed in this chapter.

For a given system, the description of adsorption mechanisms is a difficult task because of the wide range of solute chemical structures and of adsorbent properties of soil constituents. In addition, direct experimental evidence of a particular mechanism is quite rare and one is often confined to propose a hypothesis. Nevertheless, the great body of published results allows some partial conclusions to be drawn.

Ion Exchanges

Ion exchanges can take place either between cations and negatively charged surfaces or between anions and positively charged surfaces. The first situation is the most frequent for organic chemicals and corresponds to the adsorption of organic cations on clays and humic substances. Organic cations of interest belong to two groups of compounds: compounds with a permanent charge such as bipyridinium herbicides (*5,18,51*); weak bases with pK_a values between 3.0 and 8.0 allowing ionization by protonation in normal soil pH range. This is the case of some triazine herbicides (*52,53*) and of some carbamate fungicides (*54*) oxamyl and dimecron (*55*) and benzidine (*56*).

Evidence of ion exchanges is given by adsorption competition between organic cations and other cations. Amounts of adsorbed diquat and paraquat decrease in the order: Na-humic acid > K-humic acid > Ca or Mg-humic acid, and also decrease with pH (*57*). Paraquat cations favor the desorption of tricyclazole cations from soil organic matter (*58*). Release of calcium cations upon adsorption of chlordimeform cations also demonstrates clearly the ion exchange mechanism as shown in Figure 10 (*59*).

Furthermore, it can be observed from Figure 10 that cations are partially adsorbed through another mechanism, which has not been described yet. The role of other interactions in cation adsorption has also been noted for paraquat and diquat (*60*).

Adsorption isotherms for organic cations are frequently of the H-type, revealing high solute-sorbent affinity (*18,59,61*). Langmuir isotherms have also been observed and appeared to be related to high competition (*13,57*). Organic anions can also be adsorbed through an ion exchange mechanism on oxides and hydroxides, but probably it is not the main mechanism for these compounds.

H-Bond Interactions

The chemical structure of adsorbed organic compounds and the nature of soil constituent surfaces allow hydrogen bonds to be formed. The corresponding interaction energy is of the order of 1–10 kcal/mole and is greater between oxygen and/or nitrogen atoms. Hydrogen bonds have been assumed to be responsible for adsorption in various systems, either directly through associations with functional surface groups or indirectly through associations with hydration water molecules of exchangeable metallic cations. Table 6 lists some systems for which hydrogen bonding have been assumed.

Interactions with Metallic Cations

Adsorbents in soils contain various cations as exchangeable ions or as constitutive units of crystalline and amorphous minerals, so there are many opportunities for organic molecules-metallic cations interactions. According to the electron acceptor power of cations, two types of interactions are possible: cation-organic dipole interactions, likely to occur with Na^+, K^+, Ca^{2+}, or Mg^{2+}; and coordination bonds with transition metallic cations.

Information about these interactions is generally obtained by comparing the effect on adsorption of various cations, and by analyzing infrared spectrometric data. Characteristic vibration frequencies of C=O, C=N and

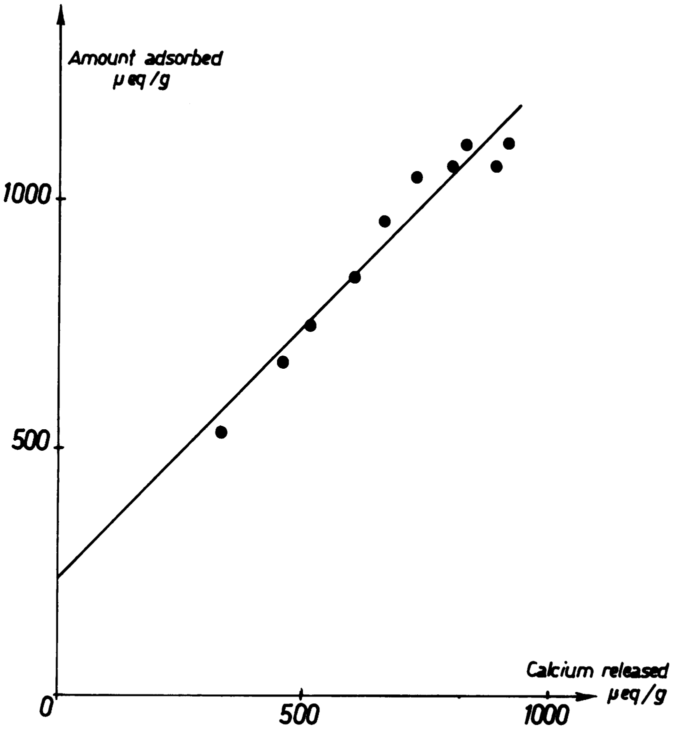


FIGURE 10. Variation of adsorbed amount of chlordimeform on Ca-humic acid against the calcium released in solution. Redrawn from Maqueda et al. (*58*)

Table 6. Systems for which hydrogen bonding is assumed.

Compounds	Adsorbents	Reference
Organic molecule HoH	Al-montmorillonite	(*116, 179*)
Carbamates		
Anilines	Montmorillonites	(*180*)
Phenol, *p*-nitrophenol	Montmorillonites	(*181*)
2,4-D	Montmorillonites	(*182*)
Malathion	Montmorillonites	(*64*)
Atrazine	Al-montmorillonite	(*123*)
Organic molecule HO		
Substituted phenol	Soils	(*75*)
N-Phenyl carbamates, acetanilides, anilines	Nylon	(*183*)
2,4-D	Silica gel, clays	(*31*)
Picloram	Soils	(*28*)
Atrazine	Humic acid	(*164*)
Atrazine	Cation exchange resin	(*110*)

P=S groups are modified upon interactions with metallic cations. This was observed for adsorption of oxamyl and dimecron on Cu, Cd, Zn, Mn, Co, and Ni-montmorillonites by Bansal (*55*) and for adsorption of phosmet and chloridazone on Na, K, Ca, Mg, Ba, and Ni-montmorillonites by Sanchez Martin and Sanchez Camazano (*62,63*).

However, direct interactions between the organic molecule and the cation can be precluded by water molecules as shown by the results of Bowman et al (*64*), who supposed that direct interactions between malathion molecules and cations only take place in dehydrated montmorillonites. When water molecules are involved in organic molecule-cation bonds, they participate in hydrogen bonding as previously described.

Coordination bonds can also be inferred from competitive effects of some organic ligands. An example is the decrease of oxamyl adsorption on Fe and Al-clays induced by humic acids (*65*).

Charge Transfers

Several authors have proposed charge transfers as a possible adsorption mechanism. Formation of a donor-acceptor complex between an electron donor molecule and an electron acceptor involves partial overlap of their respective molecular orbitals that allows electron exchanges ($\pi-\pi$ interactions). Chemical characteristics of both organic solutes and soil constituents may explain such interactions in the adsorption process. Two examples are relevant to this mechanism.

The first concerns the adsorption of diquat and paraquat molecules on montmorillonite for which Haque et al. (*60*) have observed some modifications of UV absorption spectra of the adsorbed molecules. The observed increase of the maximum absorption wavelength has been attributed to an enhanced electron delocalization, revealing a possible charge transfer.

The second example relates to adsorption of triazines and substituted ureas on humic acid (*66,67*). These herbicides are known to behave as electron donors in the chloroplast, leading to an inhibition of electron transport process in the photochemical pathway. Senesi and Testini have put forward the hypothesis that the same molecular constituents control the binding mechanisms in both the humic acid and the reactive sites in the chloroplast (*66,67*). The molecular constituents are thought to be conjugated quinone units and aromatic carbonyl groups. For instance, ESR data show an increase of free radical content of humic acid-herbicide molecule complex as compared to the humic acid alone. This was interpreted as an indication of charge transfers.

London-van der Waals Dispersion Forces/ Hydrophobic Effect

Adsorption of many organic chemicals is mainly due to soil organic matter, particularly for hydrophobic compounds. This was explained either in terms of solute partition between water and organic matter or in terms of solute adsorption.

Partition between two liquid phases is a three-dimensional process and has been considered by several authors as the main mechanism accounting for hydrophobic retention of chemicals in soils and sediments (*20,32*). Arguments supporting this theory are based on thermodynamic analysis, solute solubility, lipophilic character, and the existence of a linear relationship between adsorbed amounts and equilibrium bulk phase concentrations. However, such a relationship cannot univocally correspond to particular systems as shown by adsorption isotherms given in Figure 7 and as discussed by Mingelgrin and Gerstl (*68*). In addition, owing to the nature of humic substances and organomineral associations in the soil, it seems unlikely that soil organic matter may be described as a hydrophobiclike liquid phase.

Physical adsorption on organic matter is probably a more satisfactory explanation. Following the considerations of Hamaker and Thompson (*2*), the adsorption mechanism can be described on the basis of two phenomena: *a*) Hydrophobic molecules-water interactions. A hydrophobic molecule has no affinity for water; its introduction into liquid water causes water molecules to rearrange and to form an icelike structure around it. In spite of the negative enthalpy variation of this process, the corresponding entropy variation is highly negative (increased order), which is unfavorable. Thus, the spontaneous tendency of the system is to evolve toward a state where the hydrophobic solute is expelled from the liquid water. This is the hydrophobic effect. *b*) Physical adsorption on organic matter. The solute can be easily expelled if water is in contact with an adsorbent possessing hydrophobic surfaces that can adsorb hydrophobic compounds through London-van der Waals dispersion forces. Such interactions are usually weak (1–2 kcal/mole), but they may be magnified by the hydrophobic effect. The energy involved in the hydrophobic adsorption process arises mainly from the configurational rearrangement of water molecules as hydrophobic species come together, leading to a decrease of the water-hydrophobic interface area. Although the resulting attraction between solute and solid surface has the same range as London-van der Waals dispersion forces, it is an order of magnitude greater (*69*).

Analogy between this adsorption mechanism and reverse-phase liquid chromatography (RPLC) has been stressed by Rao et al. (*70*) and by Woodburn et al. (*71*). The theoretical basis of RPLC is the solvophobic theory that uses the hydrophobic and polar surface areas (HSA and PSA, respectively) as principal variables (*72,73*). Solutes for which PSA is small or inexistent are thus adsorbed from an aqueous solution through London-van der Waals dispersion forces/hydrophobic effect (e.g., polycyclic aromatic hydrocarbons, alkylbenzenes, halobenzenes). Accordingly, surface area of organic molecules is a fairly important characteristic as discussed by Sabljic (*74*) who proposed a description of adsorption in terms of molecular topology using a connectivity index (parameter well correlated to molecular surface area).

However, it should be noted that organic chemical, and especially pesticide and herbicide, adsorption on soils and sediments is not as simple as the reversed-phase chromatography. In that process the solid organic phase consists only of alkyl chains that make a stationary phase totally (or nearly so) hydrophobic. The solid phase in soils does not present the same features, since organic matter contains some polar and ionizable groups. Thus, adsorption of molecules possessing polar and nonpolar groups involves one or several mechanisms described above. This is a complicated situation, which probably explains the lack of definite descriptions of organic chemicals adsorption on soils and sediments.

Factors Affecting Adsorption

Several factors affect organic chemical adsorption on soils and sediments: molecular properties of adsorbed compounds; properties of adsorbents; and liquid-phase characteristics (composition and water content of adsorbing medium). Adsorption also depends on temperature, as shown by thermodynamic and kinetic descriptions. Increases in temperature generally cause adsorbed amounts to decrease and adsorption and desorption rates to increase.

Molecular Properties

Molecular properties may be classified into three categories related to the electronic structure, the partition coefficients, and the size and shape of molecules.

Electronic Structure. The nature of constituent atoms and of functional groups determine electronic structure. Three aspects have to be considered: the polarity depending on electron distribution; the polarizability representing the ease with which the electronic cloud is deformed in an electric field; and the charge delocalization being a consequence of the presence of π electrons.

The magnitude of permanent and induced electric dipoles is fixed by the polarity and the polarizability, respectively, which appear to play a part in adsorption mechanisms, particularly for interactions with metallic cations.

Charge distribution has a major influence on the binding of molecules to adsorbent surfaces. Charges in aromatic and conjugated aliphatic structures are delocalized. This delocalization is important for adsorption of pyridinium and bipyridinium compounds, protonated triazines, aromatic, and pseudo-aromatic molecules. For instance, adsorption through charge transfers and hydrogen bonds is greatly affected by charge delocalization. Four examples will illustrate these effects.

Adsorption of phenols and substituted phenols (basic structure of many hazardous organic chemicals) is closely related to the electron donor power and position of ring substituents (*75*). Table 7 shows that: *a*) Adsorption increases with the electron donor power whatever the position, *ortho*, *meta*, or *para*. This is due to the increased ability of phenol OH to act as proton acceptors and thus to form hydrogen bonds. *b*) Adsorption is lower when the substituent is in the *ortho* position because steric hindrance of H-bond formation. *c*) The *ortho* position of NO_2 favors intramolecular hydrogen bonds and decreases water solubility, thus increasing adsorption.

Table 7. Effect of the nature and position of ring substituents: values of Freundlich constant *K* (*75*).

Position	NO_2	Cl	OCH_3	OH
ortho	3.05	1.37	1.07	0.59
meta	1.42	1.78	0.94	0.92
para	1.48	1.88	1.60	1.31

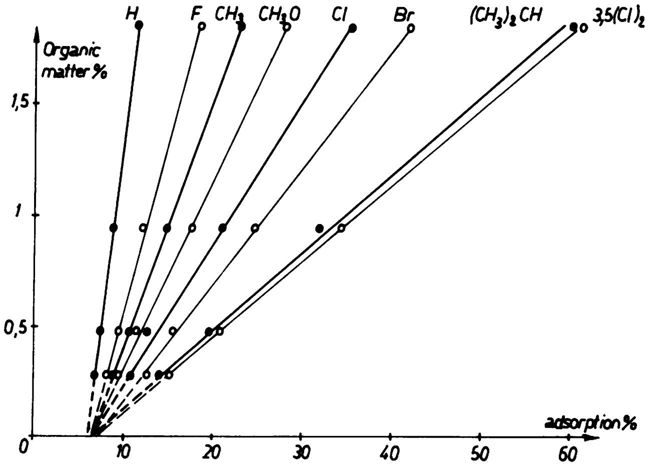


FIGURE 11. Variation of adsorption of propyzamide and of its derivatives against soil organic matter content. Ring substituents are indicated on the top of the figure. Redrawn from Bastide et al. (*75*)

The adsorption of propyzamide and its derivatives are also well correlated to the electron donor power of the ring substituent as illustrated in Figure 11 (*76*). The presence of chloride substituent on phenyl ring of substituted ureas increases their adsorption (*77*).

Studying adsorption of aromatic carbamates, Pussemier (*78*) found linear relationships between the logarithm of the Freundlich adsorption constant K_{fa} and the charge transfer constant C_T. C_T is a measure of π electron density on aromatic ring and is defined as:

$$C_T = \log \left[\frac{k(R)}{k(H)}\right] \tag{21}$$

where k(R) is the association constant for the formation of a charge transfer complex between tetracyanoethylene and the substituted compound (R) and k(H) is the same constant for the parent compound.

Another aspect of the role of the electronic structure is clearly shown by the different behavior of mesomeric forms of a molecule. Energetic characteristics for the adsorption of beta and gamma isomers of HCH on mineral surfaces are different (*30*) and adsorption on silica of 2-chlorothiopyrimidine is less than that of the 4-chloro isomer (*79*).

Ionization. Ionization of organic molecules is directly dependent on their electronic structure. Some compounds, such as quaternary ammoniums (e.g., diquat, paraquat) are strong bases and always occur in cationic form in soils and sediments. Accordingly, they act as cations and are adsorbed by ion exchanges.

Other compounds are weak bases and weak acids; their ionization depends on ionic composition of the liquid phase, especially its pH. A basic characteristic of these compounds is their pK_a values, some examples of which are given in Table 8. Weber (*80,81*) has used UV spectrometry for the determination of such values. Taking into account the normal pH range of cultivated soils, weak bases or acids may be ionized in appreciable amounts if their pK_a values are about 4.0 to 6.0. However, as pointed out by Feldkamp and White (*53*) and further illustrated by Browne et al (*82*) and by Terce (*83*), ionization of weak bases such as triazines is modified by an adsorbent phase. The reason is that the equilibrium:

$$M^+ + H^+ \rightleftarrows MH^+ \qquad M = \text{organic molecule} \tag{22}$$

is displaced toward the formation of MH^+ as a result of its adsorption. The amount of the adsorbed species is thus greater than the amount that would be deduced from the pK_a values. This has lead Feldkamp and White (*53*) to define an apparent pK_a (Table 8).

The nature of functional groups has a marked influence on molecule ionization. For protonation of triazines, examples have been given by Weber (*80*). On the other hand, acid dissociation of monohydroxybenzene derivatives increases with the electron withdrawal power of the substituent in accordance with the Hamett constant (*84*).

Partition Coefficients. As emphasized by Briggs (*85*), important environmental properties are partition coefficients: water solubility, organic solvent solubility, bioconcentration, and soil adsorption. Any pair of them should be related by a Collander equation of the form:

$$\log K_1 = a \log K_2 + b \tag{23}$$

K_1 and K_2 are partition coefficients (a and b are constants).

Table 8. Examples of pK_a and pK_a-eff values.

Type of molecule	Compounds	pK_a	pK_a-eff
Weak base	Atrazine	1.68	2.8 -6.9 (*82*)
	Simetone	4.10	5.6 -6.15 (*53*)
	Prometryne	4.05	4.78-5.32 (*53*)
	Terbutryne	4.30	
	Atratone	4.20	
	Aminotriazole	4.17	
Weak acid	Picloram	3.50	
	2,4-D	2.64-3.31	
	2,4,5-T	3.14	

These partition coefficients vary over a wide range of values up to seven orders of magnitude, and they could be useful to predict the behavior of organic chemicals in the environment. Relationships for bioaccumulation have been reviewed by Esser (*86*). For adsorption on soils and sediments, the works most frequently cited are those of Karickhoff (*32*), and Karickhoff et al. (*87*), Felsot and Dahm (*23*), Chiou et al. (*20*), Briggs (*85,88*), and Hassett et al. (*89*). The corresponding relations between partition coefficients will be given later.

Water Solubility. Water solubility can be considered as a partition coefficient between water and the solid compound. For organic chemicals, this characteristic varies considerably, from a fraction of a microgram to several grams per liter. Published results show that definite relationships with adsorption are not always clear.

Starting from a thermodynamic reasoning, Karickhoff (*32*) derived a relation that he found to adequately describe adsorption data for hydrophobic compounds. In addition, many other observations seem to confirm a negative adsorption-water solubility correlation (*90–93*). On the contrary, some experimental results do not show any similar relationships. Such is the case of napropamide and bromacil (*94*), organophosphorus compounds (*95*) and substituted ureas (*77,96*). Although experimental information does not allow a precise conclusion to be drawn, it appears that the inverse relation between water solubility and adsorption does not hold systematically for polar compounds even though it is probably a good working basis for weakly polar and nonpolar molecules.

Partition Between Water and Organic Solvent. Ward and Holly (*97*) have found the adsorption coefficients of triazines to be linearly related to water-cyclohexane partition coefficients; however, the literature shows that the water-octanol partition coefficients are the most widely used. This is based theoretically on an analogy of interactions between organic solute and octanol on one hand, and organic solute and soil and sediment organic matter on the other hand. Such an approach is only valid if the mineral constituents do not play any important part in the adsorption process. In addition, as pointed out by Brown and Flagg (*98*), adsorbate dissociation, protonation, and chemical interactions with surfaces may cause deviations from this behavior. Many relations between adsorption coefficients and water-octanol partition coefficients have been published; they will be given later.

Size of Adsorbed Molecules. The size of a molecule can be involved in adsorption through the molecular volume and the surface area. The molecular volume is related to water solubility and probably in some ways to adsorption. This was confirmed by Lambert (*15*) for adsorption of phenyl ureas. He observed a linear relationship between adsorption coefficients and the parachor. Hance (*99*) has also proposed a similar description, introducing a modification to take into account the effect of hydrogen bonds. In the same way, Karickhoff (*32*) derived a linear equation, relating the logarithm of water-octanol partition coefficient to the parachor, which includes a parameter depending on the chemical structure.

The surface area is a basic characteristic of the London-van der Waals dispersion interactions. From the adsorption point of view, this was accounted for by molecular topology (*74*). The first-order connectivity index is a parameter correlated with molecular surface area and related to adsorption coefficients. Sabljic found this to provide a better equation for the description of halogenated hydrocarbons adsorption on soils than the water solubility and octanol-water partition coefficient did.

Properties of Adsorbents

Properties of adsorbents and those of organic molecules are complementary. Adsorption on soils and sediments is due to mineral and organic constituents, and it is often difficult to clearly separate their roles because they are always associated. It is thus necessary to study much simpler systems to obtain more precise information about the adsorptive properties of the constituents. This can be done by performing experiments either with pure mineral or organic substrates or with fractions extracted from the soil or the sediment. In the first case, results are obtained for model surfaces and are useful for the analysis of adsorption mechanisms. In the second case, results concern, theoretically, the constituents as they occur in the natural medium. Nevertheless, the possible modifications resulting from the extraction procedures may lead to misinterpretations.

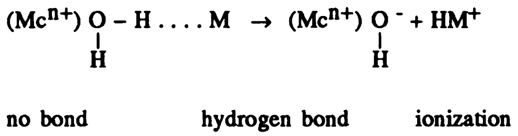
Mineral Adsorbents. The mineral adsorbents involved in the adsorption process of organic chemicals are clays, oxides, and hydroxides. Other minerals do not appear to be efficient. For instance, Hudson-Baruth and Seitz (*100*) observed no adsorption of phenol derivatives on carbonates.

Clays and clay minerals certainly play a great part in the adsorption of organic cations, but their importance in natural systems for nonionic molecules is difficult to assess. Some observations show that the effect of mineral fraction is only dominant in soils with high clay content and low organic matter content (*89,101*).

CLAYS. The most studied clays are montmorillonites, kaolinites, and illites, as far as adsorption is concerned. They possess different adsorptive properties, but no general rules can be set as to their relative adsorption power (*4*). A possible reason for this is that adsorbed amounts are generally small owing to low solution concentrations encountered for organic chemicals. Thus, adsorption is likely to occur on external surfaces of clay particles rather than in interlamellar space. Of course, this is not necessarily the case for organic cations. Interlamellar localization of organic molecules is only observed with high solution concentrations and frequently when adsorption takes place from organic solvents [e.g., adsorption of phosmet by montmorillonites (*62*)]. The S-shaped isotherms frequently observed with montmorillonites could be a consequence of adsorption on external surfaces, essentially on lattice edges.

Adsorption on clay surfaces is mainly due to exchangeable cations. Some adsorption could also result from interactions between organic molecules and OH groups on the lattice edges and on basal planes (for kaolinite), but there is no evidence for this in the literature.

Exchangeable cations may be involved in adsorption in two ways. They may compete for negative charges with organic cations, and they may behave as adsorption sites. Competition was previously discussed. On the other hand, adsorption of unionized molecules is probably essentially due to interactions with exchangeable cations. As already mentioned, exchangeable cations can participate in the bonding of organic molecules directly through dipole-cation interactions and coordination bonds and indirectly through their hydration water and hydrogen bonds. It is well known that water molecules are highly polarized in the cation electric field and may dissociate, thus allowing organic molecules to be protonated (*102*). Accordingly, all degrees of hydrogen bonding are possible between no bond and a complete ionization:



$$(\mathrm{Mc}^{n+})\,\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}-\mathrm{H}\ldots\mathrm{M} \rightarrow (\mathrm{Mc}^{n+})\,\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}{}^{-}+\mathrm{HM}^{+} \qquad (24)$$

where Mc is a metallic cation and M an organic molecule.

Table 9 gives some observations about the influence of exchangeable cations together with assumed adsorption mechanisms.

Anionic molecules are generally weakly adsorbed on pure clays, as shown by Hamaker et al. (*103*) for picloram and by Haque and Sexton (*31*) for 2,4-D. Various unionized molecules can be adsorbed on clay surfaces, but highly hydrophobic compounds cannot, as observed by Urano and Morata (*104*) for chlorinated organic mole-

Table 9. Effect of exchangeable cations (decreasing order of adsorption).

Compounds	Effect	Type of bond	Reference
Linuron	Fe > Co > Cu > Ni > Ca	Coordination	(*184*)
Linuron	Al > Cu > Ni > Mg	Coordination	(*185*)
Monuron	Al > Mg >	Hydrogen bond	(*12*)
Fenuron	Ca > Na		
Picloram	Cu > Al > Zn > Fe	Coordination	(*4*)
Atrazine	Fe > Al > Ca	Coordination	(*186*)
Organophosphorus insecticides	Fe > Ca > Na	Cation-dipole	(*95*)
Terbutryne	Fe > Al > Ca	Coordination	(*186*)
Metabenzthiazuron	Al > Fe > Ca	Coordination	(*186*)
Malathion	Fe > Al > Cu > Ca > Na	Hydrogen bond	(*64*)
Glyphosate	Al > Ca > Na	Coordination	(*117*)
Oxamyl	Ca > Mn > Cu >	Cation-dipole	(*55*)
Dimecron	Zn > Co > Ni	Coordination	

cules brought into contact with montmorillonite and kaolinite clays.

OXIDES AND HYDROXIDES. Oxides and hydroxides have been less extensively studied than clays. Their role in adsorption has probably been underestimated because they are widespread minerals, even under temperate climates, and they often have a high surface activity.

Table 10 illustrates the effect of amorphous hydroxides on clay adsorption of unionized and weak base molecules. Greater amounts of organic molecules are adsorbed on the clay hydroxide complex as compared to the clay alone. On the contrary, crystalline hydroxides are less efficient except for anionic molecules. This is clearly shown in Figure 12, where adsorption of picloram is represented as a function of pH (*103*). The relatively high adsorption on aluminum and ferric oxides, even at pH greater than 5.0 (pK_a = 4.1), emphasized the role of Al and Fe cations in the adsorption process.

Organic Adsorbents. Many works show that adsorption of organic chemicals in soils and sediments is often mainly due to organic matter. Several reviews have been published on the subject (*2,105,106*).

Two main difficulties are encountered in the description of adsorption on organic matter. The first one comes from the lack of a clear understanding of the structure and properties of organic constituents. From published works, features such as carboxylic and phenolic groups, aromatic structures are essential for describing adsorption of organic chemicals (*107,108*). In this field, an interesting model of humic substances was recently proposed by Wershaw (*109*) to account for their interactions with hydrophobic pollutants. In this model, humic substances are viewed as molecular aggregates resembling micelles or membranes where the inside is hydrophobic and the outside is hydrophilic. Roles of other models, such as those based on the concept of physically and chemically protected humic substances have been discussed by Chassin and Calvet (*110*).

Table 10. Adsorption of several herbicides by Al-montmorillonite and Al-hydroxide (*186*).

	Al-montmorillonite		Al-montmorillonite + NaOH		Al-hydroxide	
Compounds	qa[a]	pH	qa	pH	qa	pH
Atrazine	0.37	6.0	2.70	7.4	0.50	6.2
Terbutryne	2.40	5.8	2.25	7.5	0.45	6.2
Methabenzthiazine	2.80	6.1	2.90	6.8	0.30	6.2
Diuron	0.08	6.0	0.43	7.3	0.20	6.2
Picloram	0.00	5.3	1.40	7.3	0.20	6.2

[a] qa = mole/gram.

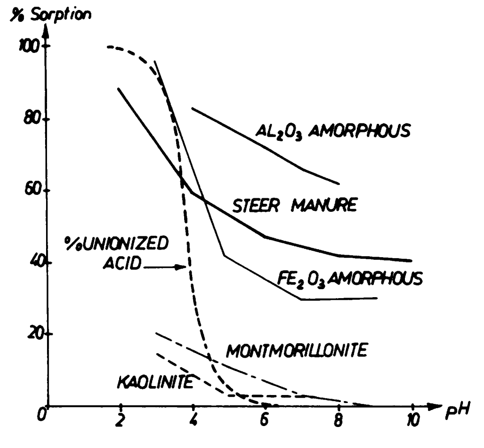


FIGURE 12. Adsorption of picloram on several adsorbents as a function of pH. Redrawn from Hamaker et al. (*102*).

The second difficulty lies in the possible confusion between real adsorption and chemical fixation. The latter leads to the retention of molecule through covalent bonding, a quite frequent phenomenon (*5,111–113*). This will not be discussed here because the review is limited to adsorption.

Evidence for the Role of Organic Matter. Analyzing many experimental results, Hamaker and Thompson (*2*) stressed the role of organic matter by proposing to refer adsorption coefficient to the soil organic carbon content, or to the soil organic matter content. They define new coefficients according to the formula:

$$K_{oc} = \frac{K}{O\ C} \qquad K_{om} = \frac{K}{O\ M} \tag{25}$$

where OC and OM are the organic carbon and organic matter contents.

These coefficients appear to be less variable for adsorption of a given molecule; they are now widely used. On a theoretical ground such coefficients imply that organic matter behaves in the same way with the same thermodynamic characteristics whatever the soil and that the adsorption isotherm is linear (*32*). Since these two conditions are not always fulfilled, it is frequently observed that K_{oc} values do vary within a factor of 2 to 10.

Many works have reported correlations between adsorption coefficients and organic carbon (or matter) content. They will be given in the following section. Several references can be found in Stevenson's paper (*106*) for various compounds. Other references are Felsot and Dahm (*23*) for organophosphorus and carbamate compounds, Hassett et al. (*21*) for dibenzothiophene, and Moreale and van Bladel (*91*) for some herbicides and insecticides. Although these correlations demonstrate the role of organic matter, they are not of general value and have to be handled with care. The reason is that the simple correlations with the organic carbon content does not hold for all systems. Relevant to this limitation are the observations of *a*) Hassett et al. (*89*) for α-naphtol who obtained a good correlation when soil organic content was greater than about 1%; *b*) Reddy and Gambrell (*114*) for 2,4-D and methyl parathion, who showed that organic matter is an important factor when organic carbon content is greater than 0.5%; *c*) Weber et al. (*17*) for fluridone, who had to take into account both organic carbon content and clay content in order to get good predictions; and *d*) Calvet et al. (*4*) who concluded from published results that organic carbon content should be greater than about 2% to obtain good correlations for adsorption of some triazines and substituted ureas. Figure 13 gives two illustrations of the adsorption-organic carbon content relationships.

Adsorption on Organic Matter Fractions. REMOVAL OF FRACTIONS. It has been thought that it would be interesting to study the possible role of organic matter components by examining the effect of their removal. This has been done sometimes with specific solvents able to extract a given fraction (lipids, wax). However, the interpretation of results is not easy because of the difficulty in making a clear distinction between the actual effect on adsorption of a fraction and the effect of the solvent itself on the soil constituents. Some indications may still be obtained, as shown in Table 11.

HUMIC SUBSTANCES. Humic substances are certainly the most efficient fraction of soil organic matter as adsorbent for organic molecules. Possible binding mechanisms are ion exchanges, hydrogen bonds, charge transfers, and London-van der Waals dispersion forces/hydrophobic effect. It is, however, difficult to attribute a relative importance to each of them. It seems clear that cationic molecules are principally adsorbed by ion exchanges involving carboxylic and phenolic groups, that highly hydrophobic molecules interact through a London-van der Waals dispersion forces/hydrophobic effect, and that the adsorption of neutral polar molecules has not been fully described. Two types of studies have been conducted to obtain more information about this.

The first type of study consists of blocking some functional groups using appropriate chemical treatments. Methylation procedures are applied with methanolic HCl (to block COOH), diazomethane (to block COOH and phenolic OH) and dimethylsulfate under alkaline conditions (to block phenolic OH). Table 12 gives an example of results which can be obtained.

Globally, blocking carboxylic groups and phenolic OH entails a reduction of adsorption, but more detailed interpretation may be misleading. As pointed out by Stevenson (*106*), methylation procedures are not specific enough because of the wide range of pK values of acidic functional groups.

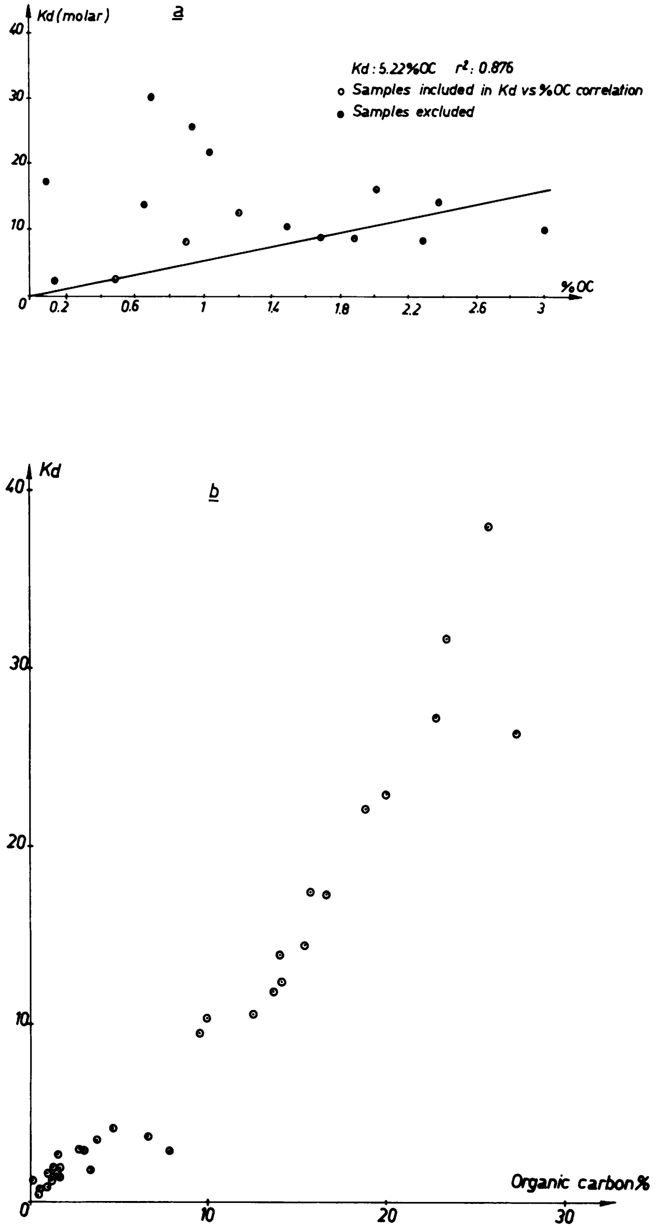


FIGURE 13. (*a*) Relationships between the adsorption coefficient and the soil organic carbon content. Redrawn from Hassett et al. (*88*). (*b*) Adsorption coefficient of atrazine (μmole adsorbed/μmole/mL) as a function of the soil organic carbon content. After Walker and Crawford (*190*).

Table 11. Adsorption of several herbicides on Fe-montmorillonite and Fe-hydroxide (*186*).

	Fe-montmorillonite		Fe-montmorillonite + NaOH		Fe-hydroxide	
Compounds	qa[a]	pH	qa	pH	qa	pH
Atrazine	0.94	4.6	1.50	5.7	0.32	7.5
Terbutryne	2.50	5.0	2.40	5.8	0.29	7.5
Methabenzthiazuron	2.05	5.0	2.10	5.9	0.25	7.5
Diuron	0.11	4.9	0.25	5.7	0.20	7.5
Picloram	0.02	4.4	0.25	5.7	0.20	7.5

[a] qa = mole/gram.

The second type of study relies on adsorption experiments with model organic adsorbents. Although they may be far from natural organic adsorbents, they are interesting because they allow the adsorption properties of given sites to be easily studied. An example of a model used for understanding humic substances properties is given by Chassin and Calvet (*110*). Figure 14 represents the adsorption isotherms of atrazine on a

Table 12. Effect of the removal of various fractions of the soil organic matter: adsorption of dinitroanilines (*187*).

Treatments	Fraction removed	Effect on adsorption, %
Ether	Wax, lipids	+ 22
Ethanol	Resins	+ 34
Water	Polysaccharides	+ 0.8
2% HCl	Hemicelluloses	+ 30.2
80% H_2SO_4	Cellulose	+ 77
35% H_2O_2	Organic matter	− 21.3
Na-dithionite bicarbonate, Na-citrate	Free Fe-oxides	+ 44
Na-dithionite bicarbonate, Na-citrate, 35% H_2O_2	Free Fe-oxides, organic matter	+ 576.5

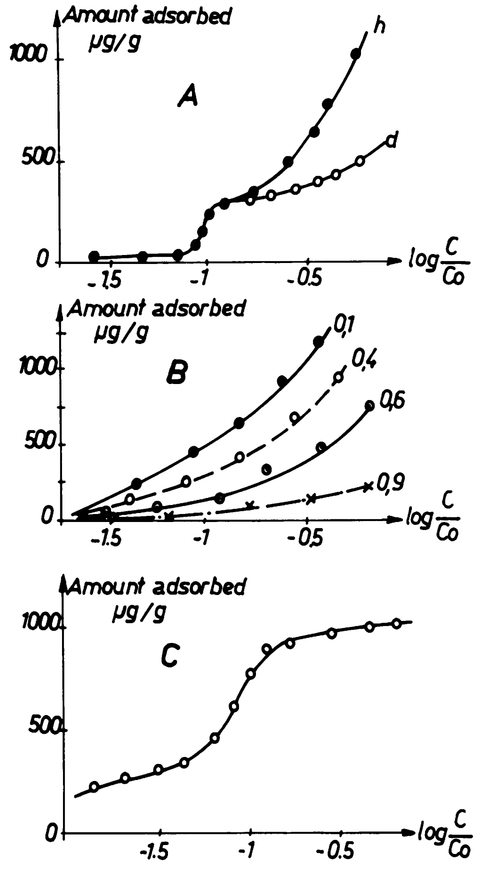


FIGURE 14. Adsorption of atrazine (*A*) on dehydrated (d) and nondehydrated (h) humic acid; (*B*) on cation exchange resin -numbers refer to ionized fraction of COOH groups; and (*C*) on graphite. From Chassin and Calvet (*109*).

humic acid (dehydrated or not) on a cation exchange resin with various degrees of ionization and on graphite.

As carboxylic groups of the exchange resin are ionized, amounts of adsorbed atrazine decrease markedly. This shows that unionized COOH are involved in the adsorption mechanism, probably by forming hydrogen bonds. The adsorption isotherms on the nondehydrated humic acid present two parts, one of the same general shape as that observed for resin and disappearing upon dehydration. According to Chassin (*110*), the dehydration treatment favors intramolecular hydrogen bonding, and therefore decreases the number of available adsorption sites. The second part of the adsorption isotherm remains after dehydration and resembles the adsorption isotherm on graphite. It was thus suggested that adsorption of atrazine on humic acids is due to both hydrogen bonds with unionized COOH groups and to charge transfer complexes. The latter mechanism would remain after the humic acid has been dehydrated. Such a behavior is likely to occur in the soil, mainly in the surface horizons.

Other uses of adsorbent models are those of Leenheer and Ahlrichs (*43*), who observed that carbaryl and parathion were more adsorbed on hydrophobic resins than on cation exchange resins, and those of Bouchard and Lavy (*115*), who found no adsorption of hexazinone on cellulose from water solutions, but found some adsorption with hexane solutions and polystyrene in water. Some results are also given in Tables 13 and 14.

All these observations support the fact that adsorbents with high aromatic character are efficient toward adsorption, even for polar compounds if these compounds possess an aromatic ring.

Organic Matter in Soils. The characterization of the different fractions of organic matter or of organic polymers that can be found in the soil is certainly an important step in better understanding of adsorption. Characterization of the fractions is certainly not sufficient because organic matter in soils undergoes various biochemical transformations and is generally associated with mineral constituents.

Table 13. Effect on the adsorption off atrazine of the removal of different functional groups from humic acid (*164*).

Treatment	Removed groups	Adsorbed amount, %
0	—	100
Diazomethane	-COOH ; phenol -C-C--C = C ‖ ǀ O OH -N-C-,O-C-COOH ǀ ‖ ǀ H O H	27
Dimethylsulfate	All groups except COOH	54
Ca-acetate	-COOH	14

Table 14. Freundlich adsorption constants for three herbicides on various organic adsorbents (*188*).

	Trifluraline			Triallate			Diallate	
Adsorbents	*K*	*n*	pH	*K*	*n*	pH	*K*	*n*
Cellulose	56	1.00	6.1	21	0.96	6.3	38	0.80
Cellulose triacetate	1000	1.38	4.4	190	1.06	4.6	195	0.73
Active carbon	115000	1.51	9.4	65000	1.45	9.6	350000	1.58
Peat	13500	1.41	3.8	710	0.94	4.0	1080	0.67
Wheat straw	830	1.04	6.00	365	1.04	6.2	530	0.68

Examples of the consequences of such processes are given in the following tables. Table 15 shows the change of adsorptive properties due to humification of some organic materials. The change occurs in a way that depends strongly on both the chemical structure of the organic molecule and the type of plant tissues. In Table 16 several results concerning the effect of associations between humic acids and clays are presented. They clearly demonstrate the nonadditivity of adsorbent properties.

Characteristics of the Liquid Phase

Ionic Composition. Ionic composition may have an influence on adsorption through the pH and the amount of mineral ions in solution.

EFFECT OF PH. Effects of pH have been studied in many works. They are schematically represented in Figure 15. Curves A of Figure 15 can be observed in three situations:

a) Adsorption of weak bases on negatively charged adsorbents as triazines on montmorillonites (*53,116*) and benzidine on soils (*56*). The explanation lies simply in the effect of pH on molecule protonation. As pH decreases, the proportion of protonated molecules (thus of organic cations) increases and so does adsorption by cation exchanges.

b) Adsorption of weak acids as neutral molecules on negatively charged adsorbents. Examples are adsorption of picloram on various adsorbents (*28,103*), adsorption of bromacil on soils (*16*), and adsorption of glyphosate on several mineral adsorbents (*117*). In these situations, the proportion of neutral molecules increases as pH decreases, resulting in an increased adsorption.

c) Adsorption of neutral molecules on adsorbents whose surface properties are modified in acid media. Two examples are relevant to this case. The first deals with adsorption of metabenzthiazuron on Ca-montmorillonite, with the binding of the molecule probably due to complexation with Al cations that are removed from the clay lattice under acid conditions (*118*). The second concerns the adsorption of atrazine on a cationic exchange resin within a pH range where the molecule remains neutral (*110*) (Fig. 14).

Curves B of Figure 15 are generally observed with weak bases (*54,116,119,120*). The pH corresponding to the adsorption maximum is sometimes nearly equal to the pKa of the molecule. It is not a general rule, as shown by Calvet et al. (*4*) from published values. The interesting point is the decrease of adsorbed amount below a given pH. This behavior can be attributed to a competition for adsorption sites between protonated molecules and H^+ and/or Al^{3+} ions. It can also be due to the repulsion of protonated molecules by preventing the formation of a complex. Oxamyl and dimecron adsorption on montmorillonites may be explained in this way (*55*).

Curves C of Figure 15 correspond to an increased adsorption with increasing pH. They are observed with weak bases that are essentially adsorbed as neutral molecules. This occurs for instance when molecules are adsorbed through London-van der Waals dispersion forces hydrophobic effect as for adsorption of simazine and atrazine on active charcoal (*121*). Curves C are also observed when molecules are bonded by complexation with a metallic cation as for terbutryne on Al-montmorillonite (*122*). In the latter case, protonated molecules are not able to compete with Al-cations and thus to be adsorbed. When interpreting the effect of pH on adsorption, one must be aware that pH variations can influence the solute molecule as well as the adsorbent.

EFFECT OF THE NATURE AND CONCENTRATION OF MINERAL CATIONS. Several results have been reported previously by Calvet et al. (*4*). Examination of published data shows that for neutral molecules, increasing ionic force above unity increases adsorption. When ionic force is below unity no general trend was observed. Data also show that for cationic molecules, increasing ionic force causes a reduction of adsorption as a result of cation competitions for adsorption sites.

Presence of an Organic Solvent. Adsorption of organic pollutants from mixed aqueous solvent solutions is interesting from two points of view. First, it may be useful to assess the behavior of hydrophobic compounds in soils and waters. Second, it may provide a nice tool for analysis of adsorption mechanisms. This was recently emphasized by Rao et al. (*70*) in a study of hydrophobic compounds from solvent mixtures. In such a case, varying the solution composition entails variations of solute solubility and adsorption on hydrophobic surfaces. This can be explained on the basis of solvophobic theory.

In addition, it was shown that solvent mixtures appear to be useful for the study of polar molecules. For

Table 15. Adsorption constant of several compounds on various organic adsorbents: *K* (mL/g) (*189*).

Adsorbents	Carbendazim	Fluometuron	Trimefon	Nuarimol	Triarimol	Fenarimol	SD, $p = 0.05$
Pepper lignin	700	813	1122	1288	2691	2300	46.6
Cotton lignin	800	400	513	537	1349	1100	37.7
Pine lignin	590	160	224	270	457	660	24.7
Cellulose	4	6	6	7	20	20	2.7
Ethylcellulose	36	70	78	73	96	102	14.6
Protein (BSA)	7	8	8	125	203	211	11.9
Polygalacturonic acid	0	0	0	0	0	0	0
SD, $p = 0.05$	21.3	17.1	19.9	18.7	31.2	28.9	

Table 16. Example of variations of adsorption properties due to the organic matter evolution (*4*).

			Evolution of plant materials incorporated into a soil			
	Evolution of a peat		Linear adsorption coefficient			
	Freundlich coefficients		Wheat straw		Lucern	
State	Linuron		Diuron	Terbutryne	Diuron	Terbutryne
Initial	$K_f = 24$	nf = 0.922	9.3	20	8.3	36
Humified materials	$K_f = 297$	nf = 0.671	16.3	28	6.0	8

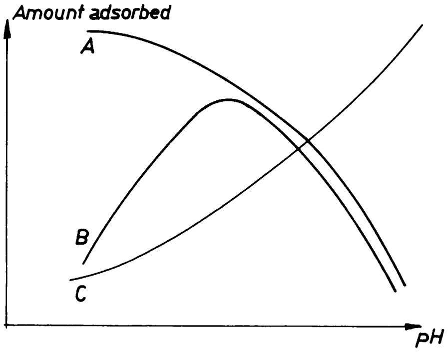


FIGURE 15. Possible variations of adsorbed amounts as a function of pH.

instance, Calvet and Terce (*123*) were able to describe the role of water molecules in atrazine adsorption on Al-montmorillonite and ascribe the binding mechanism to the formation of hydrogen bonds with hydration water molecules of Al cations.

Water Content of Adsorbing Medium

Under natural conditions, adsorption of organic molecules often occurs in water-unsaturated media. Soil water content is thus a factor that has to be taken into account since it can influence the amount of adsorbed compound. When adsorption takes place directly from the gas phase on the adsorbent surface, binding sites may be inaccessible if they are covered with water. In this case, the amount of adsorbed molecule decreases as soil water content increases, as shown by Arvieu (*124*) for methyl bromide adsorption on a sandy soil (Fig. 16) and by Call (*125*) for adsorption of ethylene.

The effect of soil water content on adsorption from the liquid phase has been less studied, probably because experiments are difficult to design. It has been reported that adsorption coefficients increase as water content decreases. This was noted by Yaron and Saltzman (*126*) for parathion adsorption from hexane solutions, by Hance (*127*) for atratone and monuron adsorption from 2,2,4-trimethylpentane solutions and van Bladel and Moreale (*128*) for adsorption of aniline from benzene solutions. Interpretation of such results is not easy, because it is difficult to separate the role of water molecules and the role of solvent-adsorbent interactions.

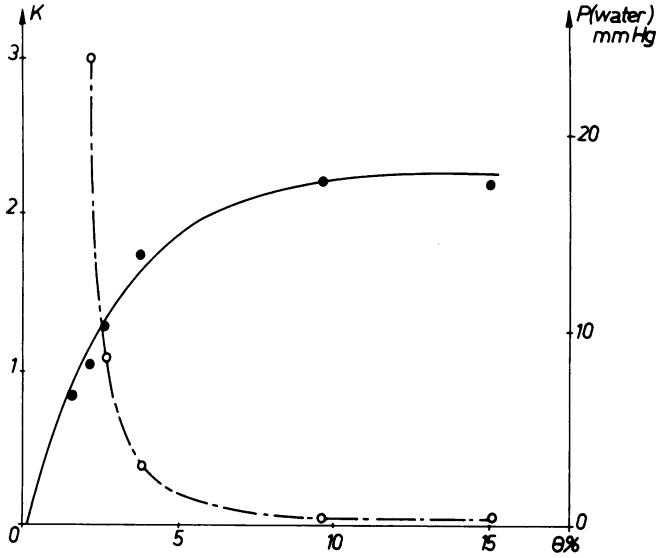


FIGURE 16. Adsorption of methylbromide on a sandy soil (○) and equilibrium water vapor pressure (●) against the volumetric water content of the soil. K in (mole/kg)/(mole/L air). From Arvieu (*122*).

The water content of an adsorbing medium must also be taken into account for laboratory measurements where adsorption is determined using adsorbent suspensions. This will be discussed later.

Evaluation of Adsorption

The evaluation of adsorption presents two aspects: the determination of amounts of adsorbed solute and the prediction of adsorption behavior. The first is a necessary step in adsorption studies for obtaining adsorption curves. The second corresponds to the need of people interested in environmental problems and wishing to estimate the fate of a given chemical brought into the soil or aquatic systems. Since experimental characterization of adsorption is time consuming and requires well-equipped laboratories, there has been a growing need for convenient tools during the past decade. Several relationships have been proposed to express adsorption coefficients as a function of various parameters that are easy to evaluate.

Measuring Adsorption

Batch Adsorption Measurements. Batch measurements are certainly the most frequently used procedure in adsorption studies. A given amount (m) of adsorbent is mixed with a given volume (V) of a solution of known concentration (C_o). After an appropriate time determined from kinetic data, the solid and the liquid phase are separated, and the bulk solution equilibrium concentration (C_e) is measured.

Separation of the solution is generally obtained by centrifugation, but other techniques have been used sometimes. Burns et al. (*19*), Savage and Wauchope (*129*), Hance and Embling (*130*) have employed the extraction membrane apparatus that is commonly used in soil physics to determine characteristic water retention curves. This could be convenient for the study of the water content effect on adsorption. The difficulty comes from the low collected volumes of solution and from a possible undesirable adsorption on the microporous membrane. Gel filtration is also a means for separating the equilibrium solution. It was applied first by Khan (*131*) and Burns et al. (*19*) and more recently by Madhun et al. (*132*). This technique seems to be convenient for humic and fulvic acid studies. Some conditions must be fulfilled to yield reliable results: no equilibrium modifications due to gel filtration; no interaction between the gel matrix and the adsorbent; and the gel porosity must allow a good separation of adsorbed and free solute. These conditions probably limit the use of this technique.

Filtration of suspension using filter paper disks in hypodermic syringes (*133*) or microporous membranes (*134*) are other techniques.

Once the solution concentration is obtained, amounts adsorbed are simply calculated with the following formula:

$$q = \frac{V(C_o - C_e)}{m} \tag{26}$$

Units of q depend on the units used for C_o and C_e and it is necessary to be careful in comparing data from different authors and paying attention to the units used. To facilitate the comparisons between different works, Bowman (*135*) suggested to express experimental results in mole per gram.

Flow Experiments. Adsorption data can also be determined from breakthrough curves obtained when a solution flows through a column of an adsorbing porous media. The procedure is not straightforward, as the corresponding mathematical formulation is complex and difficult to use without computers.

By assuming instantaneous equilibrium, linear isotherm, no hysteresis, and no liquid stationary phase, it is possible to evaluate approximately the adsorption coefficients from elution curves (*136*).

Factors Influencing Adsorption Measurements. Several factors may have an influence on adsorption measurements, and it is worth examining their mode of action. They can be classified into three groups: interfering phenomena, pretreatments of adsorbing materials, and the solid-phase concentration in suspension.

INTERFERING PHENOMENA. The calculation of adsorbed amounts described above implies that only adsorption is causing the decrease of solute concentration in the liquid phase. However, several phenomena may interfere and produce erroneous data.

Degradation. Degradation of organic chemicals may be due to chemical decomposition or to biological transformations. It is known, for instance, that clays and humic substances favor the hydrolysis of atrazine (*105*). Modifications due to adsorption can influence adsorption and desorption. An interesting illustration is given by Koskinen et al. (*137*) for 2,4,5-T adsorption desorption studies on soils. They observed that biodegradation could partially account for the apparent hysteresis as shown by measurements of CO_2 evolved during the experiment. This was further confirmed by performing studies under N_2 atmosphere to prevent aerobic transformations (*138*). Apparent hysteresis reduction obtained when degradation is taken into account is illustrated in Figure 17.

Adsorption on Glass. Adsorption on glass was noted by Bowman and Sans (*139*) for organophosphorus compounds, and especially for dieldrin, and by Russel and McDuffle (*140*) for phthalate esters. This is an opportunity to say that any material which may be brought into contact with the organic chemicals under study must be tested for its adsorption properties.

Volatilization and Precipitation. These phenomena are likely to occur with solutes having high vapor tension and very low solubility, respectively. The former is more easy to control than the latter, but undoubtedly they can seriously complicate experiments. An example of precipitation is given by Shin et al. (*141*) for adsorption of DDT on various adsorbents.

PRETREATMENTS OF ADSORBING MATERIALS. Several pretreatments are frequently applied to adsorbing materials. The main objectives of these pretreatments are to separate some fractions or to limit the possible biodegradation of added chemicals by sterilization.

Measuring adsorption on particle size separates may lead to very different characteristics from those corresponding to the whole material. Karickhoff and Brown (*142*) have studied adsorption of paraquat on particles of different sizes separated from sediments. They found the clay fraction to be more effective and the adsorbed amounts to be correlated with the exchange capacity of individual size fractions (Fig. 18).

A similar situation was reported by Nkedi-Kizza et al. (*143*) for diuron and 2,4,5-T adsorption on soils. They found that adsorbed amounts were closely related to the organic carbon content of the fractions. These two examples show that one must be aware of the possible consequences of a granulometric separation of a soil or a sediment material.

Because degradation could be misleading, it could be advisable to sterilize the adsorbents. Sterilization is most frequently achieved by autoclaving. This treatment has been observed to decrease the amounts of

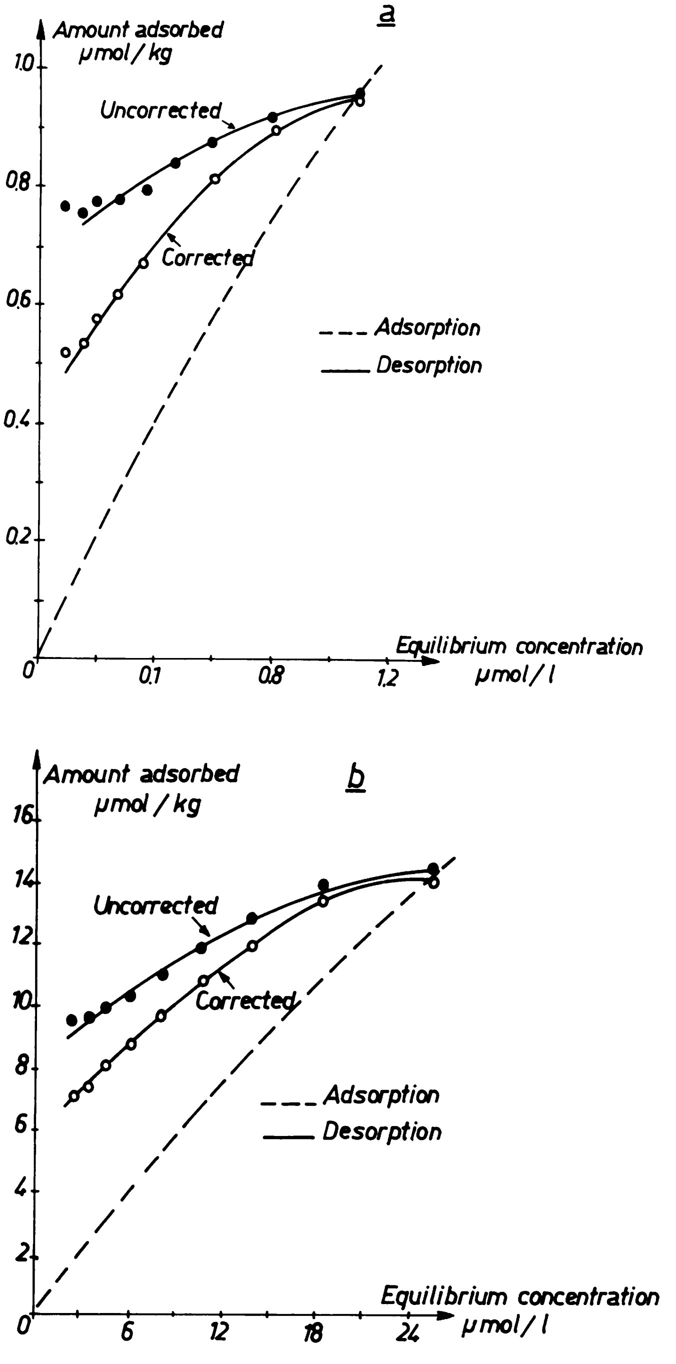


FIGURE 17. Desorption of 2,4,5-T; impact for correction of 2,4,5-T degradation at two concentrations, 2 mole/ L (*a*) and 39 mole/L (*b*). From Koskinen and Cheng (*136*).

2,4,5-T adsorbed on soils (*137*). Calvet and Lefebvre-Drouet (*144*) have also studied this effect on atrazine adsorption on several soils. They found that Freundlich parameter K_f decreases and nf increases upon heating and that the higher the organic carbon content, the greater the modification. The maximum change as compared with untreated soils was 30% for K_f and 20% for nf. These variations are negligible if one needs an order of magnitude, but they are not for mechanism studies.

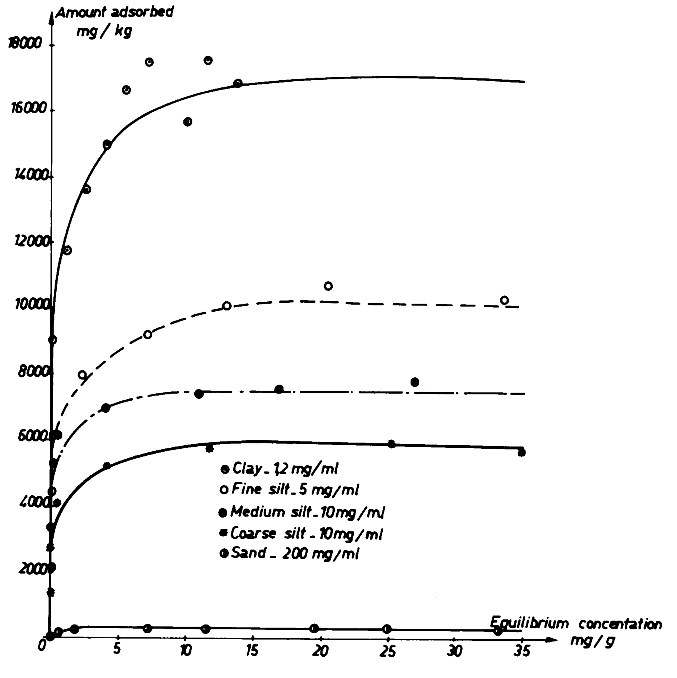


FIGURE 18. Adsorption isotherms of paraquat on several particle size separates. Redrawn from Karickhoff and Brown (*140*).

SOLID-PHASE CONCENTRATION. According to several observations, solid-phase concentration may affect the adsorption; the smaller the concentration, the greater the adsorbed amount per unit mass adsorbent. This was shown with soils as adsorbing materials by Grover and Hance (*145*) for linuron, Koskinen and Cheng (*146*) for 2,4,5-T, Bowman and Sans (*139*) for organophosphorus compounds and Calvet and Lefebvre (*144*) for atrazine. With dilute suspensions of montmorillonite and kaolinite, atrazine and terbutryne adsorption are also dependent on clay particle concentration (*83*). This may be explained either in terms of effect of water on the solid phase or in terms of adsorption mechanisms.

Diluting a suspension of particles increases both the destruction of microaggregates and the solid-water interface area, thus favoring adsorption (*145*). Another explanation lies in the possible modification of the equilibrium between free protons and protonated molecules causing an increase of adsorption as shown by Terce (*83*) for terbutryne-montmorillonite systems.

For hydrophobic compounds, Mackay and Powers (*147*) suggested that the particle concentration effect has to be explained on the basis of adsorption mechanism. Hydrophobic molecules do not interact strongly with solid surfaces and enhanced desorption may result from solid particle collisions. Since their number increases with particle concentration, adsorption also decreases.

Prediction of Adsorption Coefficients

Many relations have been obtained from both experimental and theoretical considerations. They concern various parameters characterizing the adsorbent phase as well as the solute.

Relations with Soil or Sediment Composition. The most frequently used parameter is the organic matter content (or the organic carbon content), which appears to be well correlated with the linear adsorption coefficient. On the contrary, this is not the case for the clay content. Table 17 lists some published relations.

A general trend appears clear—the increase of adsorption with the organic matter content. This information, however, is not very useful for the description of mechanisms. For prediction purposes these relations are doubtful because they are essentially specific for a molecule or a group of molecules. In addition, it is also likely that such relations only hold within a series of similar soils.

Relations with Partition Coefficients. Bases for the use of partition coefficients have been given in the portion dealing with adsorption mechanisms. Tables 18 and 19 give some relations collected from literature for water solubilities and water-octanol partition coefficients, respectively.

K_{oc} and K_{om} certainly increase as water solubility decreases according to the quoted relations. Furthermore, it appears that their parameters are not too variable from one relation to another so that a possible unique equation could be proposed for approximate predictions. The same comments hold for the relation with K_{ow}.

Relations with Structural Parameters. Three kinds of parameters have been related to adsorption coefficients: charge transfer parameters: Hansh constant, and charge transfer constant (*78*); molecular volume, which is accounted for by the parachor used by Lambert (*15*) for substituted ureas. Other authors have introduced some corrections in order to take into account the role of hydrogen bonds (*99*), or the nature of the chemical structure (*85*); molecular surface area, which is correlated with the first-order connectivity index. This index has been shown to allow a good prediction of adsorption coefficients (*74*). All of these parameters have been used in several relations, some of which are listed in Table 20.

Consequences of Adsorption

Composition of the soil solution and of the soil atmosphere is greatly influenced by adsorption/desorption. As a consequence, these phenomena influence transport, degradation, and biological activity of organic chemicals; thus they play an important role in their environmental fate.

Influence of Adsorption on Transport

Since the mobility of adsorbed molecules is very low, the transport of chemicals in soils and sediments only occurs in the fluid phase. Thus, from a general point of view, the mass transport of chemicals decreases as adsorption increases. In water-unsaturated soils, the relative contribution of the transport in the gas phase and the transport in the liquid phase depends on the partitioning of the compounds between the two phases. Fumigants and compounds having a high vapor tension are significantly transported in the gas phase. Descriptions of the influence of adsorption on gaseous molecular diffusion have been given by Graham-Bryce for disulfoton (*148*) and by Bode et al. for trifuralin (*149*).

Numerous works on solute transport have been published, and many references are reported in the reviews mentioned earlier. Experimental results for various compounds show a close relation between the depth of leaching and adsorption coefficients. Table 21 gives a schematic view of this relation. Although the reported values are only approximative, it is apparent that adsorption is an important factor for mass transport.

Several theoretical studies have been developed and have lead to more or less complete descriptions of solute transport in soils and model porous media. However, they do not provide practical tools because of their complex mathematical formulation, and because they are often derived for simplified initial and boundary conditions, as compared to field conditions. Nevertheless, they are useful to soil scientists since they emphasize the need for detailed knowledge about adsorption-desorption processes. Also they give a theoretical framework for the description of transport. Examples of adsorption-transport modeling can be found in the publications of van Genuchten (*25*), Leistra and Dekkers (*37*), Leistra et al. (*150*), and Bromilov and Leistra (*151*).

Simplifications have been introduced to obtain models providing approximate descriptions of the fate of chemicals in natural systems. Such is the case of a recent model proposed by Jury et al. (*152*), who considered all the involved phenomena with simplified formulations. For instance, adsorption is described with linear iso-

Table 17. Adsorption of atrazine and terbutryne on Ca-humate, Ca-montmorillonite complexes (*4*).

	Adsorbents			Adsorption coefficients	
Herbicide	Montmorillonite, %	Humate, %	pH	*K*	*n*
	100	0	7.8	11.7	
Atrazine	0	100	7.4	59.0	
	85	15	7.6	14.0	
	100	0	3–3.2	0.011	2.74
Terbutryne	0	100	3–3.2	0.71	0.90
	75	25	3–3.2	0.38	1.51

Table 18. Examples of relations between the adsorption constant and the soil organic matter (or carbon) content.

Compounds	n	Relations	Reference
Acetophenone	14	$K = 0.04 + 0.32$ (OC%)	(*101*)
Dibenzothiophene	14	$K = 0.1123$ (OC%)	(*21*)
Atrazine	74	$K = (0.5 \pm 0.4) + (0.6 \pm 0.2)$ (OM%)	(*4*)
Simazine	25	$K = (3.7 \pm 0.4) + (1.6 \pm 0.4)$ (OM%)	(*4*)
Diuron	12	$K = (0.4 \pm 0.4) + (11.0 \pm 0.6)$ (OM%)	(*4*)
Dibromoethane	22	$K = 12.81 + 2.75$ (OM%)	(*125*)
Fluridone	18	$K' = -0.004 + 0.007$ (% Clay) $+ 0.029$ (OC%)	(*17*)
Chlortoluron	9	$K = 0.06 + 0.62$ (OM%)	(*88*)

[a] n = number of observations. K in mL/g; K' in mmole/kg; OC, organic carbon; OM, organic matter.

Table 19. Examples of relations between adsorption coefficient and water solubility.[a]

Compounds	Relation	Reference
α-Naphtol	$\log K_{oc} = 4.273 - 0.686 \log S_w$	(*89*)
Various compounds	$\log K'_{om} = 2.75 - 0.45 \log S_w$	(*91*)
Aliphatic aromatic chlorinated compounds	$\log K_{om} = (4.040 \pm 0.038) - (0.557 \pm 0.012) \log S_w$	(*20*)
Cyclic aliphatic aromatic compounds	$\log K_{oc} = -1.405 - 0.921 \log X_{sw} - 0.00953$ (mp, 25)	(*32*)
Various pesticides	$\log K_{om} = 3.8 - 0.561 \log S_w$	(*92*)

[a] K'_{om}, mean values over several soils; S_w, water solubility; X_{sw}, fractional solubility; mp, melting point.

Table 20. Examples of relations between the adsorption coefficient and the octanol-water partition coefficient.[a]

Compounds	Relations	Reference
Substituted ureas simazine	$\log K_{om} = 0.69 + 0.52 \log K_{ow}$	(*85*)
Propizamide and derivatives	$K_{oc} = 0.619 + 6.69 \log K_{ow}$	(*76*)
α-Naphtol	$\log K_{oc} = -0.317 + \log K_{ow}$	(*89*)
Triazine, *p*-toluidine	$\log K_{oc} = -0.006 + 0.937 \log K_{ow}$	(*98*)
Bromacil, diuron chlortoluron	$\log K_{oc} = -0.40 + 1.23 \log K_{ow}$	(*93*)
Aromatic chlorinated compounds, PCB	$\log K_{oc} = -0.779 + 0.904 \log K_{ow}$	(*190*)
Aromatic hydrocarbons	$\log K_{oc} = -2.53 + 1.15 \log K_{ow}$	(*191*)
Various pesticides	$\log K_{om} = 4.4 + 0.72 \log K_{ow}$	(*92*)

[a] K_{ow}, octanol-water partition coefficient.

therms without hysteresis and expressed with K_{oc} coefficients. As was shown by several simulations, the model provides a convenient tool to classify organic compounds according to the main features of their behavior (*153*,*154*). So, mass transport is evaluated using a parameter called the convective time t_c, defined by the authors as:

$$t_c = \frac{(\rho_b f_{oc} K_{oc} + \Theta + aKH)L}{J_w} \tag{27}$$

Table 21. Examples of relations between the adsorption coefficient and some molecular parameters.

Parameters[a]	Relations	Reference
Hansh constant, π Transfer constant, CT	$\log K = 0.59 + 0.31 \pi + 0.84 CT$ 4°C pure water	(*78*)
First-order connectivity index, χ	$\log K_{om} = (0.55 \pm 0.02) \chi + (0.45 \pm 0.12)$	(*74*)
Parachor P Hydrogen bond, N	$\log K = (P - 45N)\, 0.0067 - 0.65$	(*99*)
Parachor P solubility Sw organic carbon content	$\log K = 0.915 \log K_{oc} - 1.397 \log S_w - 0.031P + 25.108$	(*23*)
Parachor P chemical structure, n	$\log K_{ow} = 0.0062(P - 100n) + 0.41$	(*85*)

[a] N, number of sites in a molecule that can participate in the formation of hydrogen bonds; n, parameter that depends on the chemical structure; this expression may be used in relations given in Table 20.

Table 22. Relation between leaching and adsorption; log K_{ow} corresponds to K for two soil organic matter contents (*88*).

K	Maximum leaching, 25-cm rainfall	log K_{ow} 1% OM	log K_{ow} 2% OM
0.1	Most below 20 cm	0.6	−0.3
0.5	Down to 20 cm	1.9	1.0
1	5–10 cm	2.5	1.6
10	Little below 5 cm	4.4	3.5
100	No significant leaching	6.3	5.4

where

ρ_b	bulk medium density
f_{oc}	fraction of organic matter
Θ	volumetric water content
a	volumetric air content
KH	Henry's Law constant
J_w	water flux
L	distance corresponding to t_c

Therefore, the convection time and the adsorption coefficient are linearly related. Table 22 gives some calculated values for a transport distance of 10 cm.

The model proposed by Jury et al. could probably be useful for screening procedures. Furthermore, it provides a general picture of the fate of a given chemical in natural environments, at least as a first approximation.

Transport of adsorbed solute may also occur when adsorbing particles can be displaced; such is the case under two circumstances. The first is the vertical migration of dispersed clays in the soil profile, which has been shown to induce the transport of adsorbed paraquat and DDT (*155*). The second circumstance is the surface runoff, which may be responsible for some mass transport of chemicals. Reported observations show that amount of solute transported through particle movements are small. Nonetheless, this type of transport should be taken into account in highly fissured soils such as vertisols.

Effect of Adsorption on Biological Activity

It is well known that herbicide doses that are applied in soils with high organic matter content are higher than the normal application rates. The reason is that herbicide concentration in the soil solution, and thus herbicide bioactivity decreases as adsorption increases. Most of experimental results deal with herbicides because experiments are easier to execute with plants than with other living organisms.

Figure 19 gives two illustrations of bioactivity-adsorption relationships. The first represents the relationship between the herbicide-induced inhibition of chlorophyll production by green algae (chorella) as a function of adsorption coefficients measured in various soils (*144*). The second shows the influence of soil organic matter content on the dose rate of trifluralin required to produce 90% reduction in fresh weight of wild oat plants (*156*).

Field experiments concerning the effect of adsorption on bioactivity are quite rare, so it is difficult to extrapolate laboratory and greenhouse studies. Only some qualitative correlations have been observed between adsorption and bioactivity in the field. Examples are the reduction of weed control by several herbicides when organic matter is added to the soil (*157*) and the negative correlation between the antifungal activity of carbendazim against *Rhizoctonia solani* and soil clay content, organic matter content, and CEC (*158*). Nevertheless, the effect of adsorption shows a general trend, whatever the nature of the living organism under consideration. The greater the adsorption, the smaller the bioactivity because the amount of a chemical able to be absorbed is fixed by the composition of the gas and the liquid phases, depending on its distribution between the soil atmosphere or the soil solution and the solid phase.

However, works on bioactivity-adsorption relationships are not very numerous in spite of the importance of the subject. Two questions remain without satisfactory answers: Are the adsorbed molecules potentially bioactive? In other words, are adsorbed molecules degraded on the surface of soil constituents? Effectively, for some chemicals, adsorption may lead to transformations, resulting in the disappearance of the bioactivity for instance, the hydrolysis of triazine herbicides. The second question concerns the bioavailability of adsorbed molecules, which certainly depends strongly on the kinetics of desorption and the possible presence of a hysteresis phenomenon. Nothing can be said about this subject, as no relevant data can be found in the literature. This represents an interesting subject for future research.

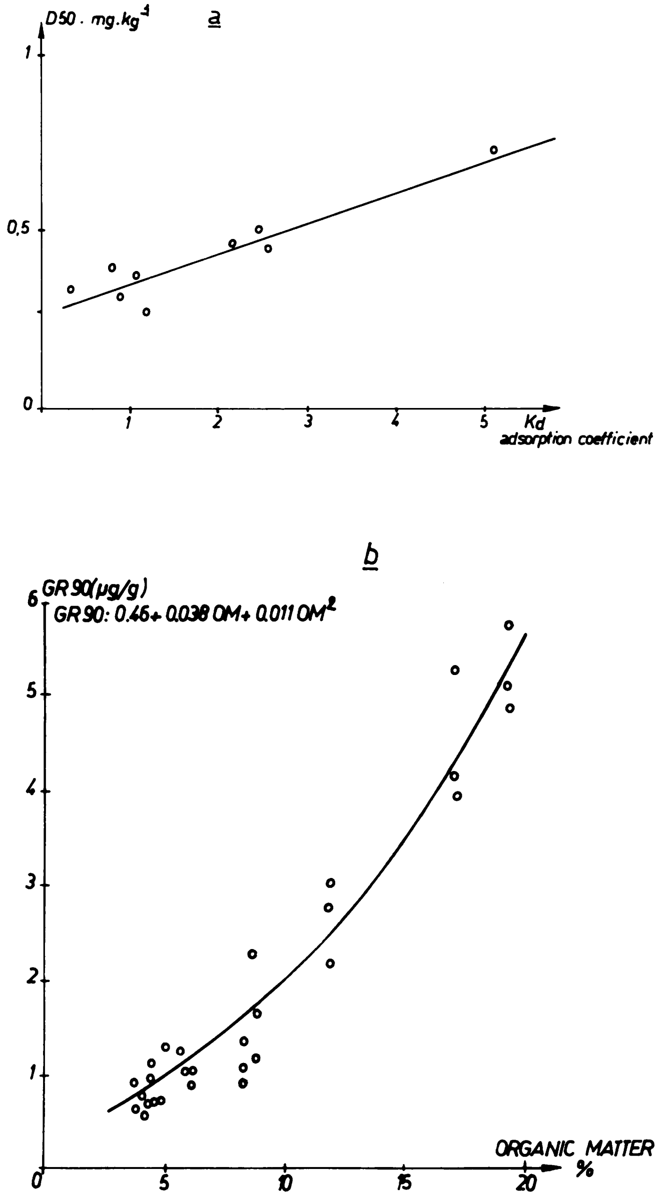


FIGURE 19. (*a*) Relation between the dose of atrazine producing a 50% reduction of chlorophyll production by green algae and adsorption coefficient. From Calvet and Lefbvre-Drouet (*142*). (*b*) Effect of organic matter on the dose of trifluralin producing a 90% reduction in weight of wild oat plants. From Moyer (*152*).

Adsorption and Degradation of Organic Chemicals

Degradation of organic chemicals in soils and sediments may be due to chemical and biological transformations. Since the causes of these phenomena are different, the effect of adsorption on degradation is variable, depending on the nature of the transformation.

Effect of Adsorption on Chemical Degradation. Chemical degradation can take place either in the soil solution or in the adsorbed phase. Several observations show that adsorbents such as clays and humic acids are able to catalyze some transformations mainly through two mechanisms: free radical reactions and protonation-hydrolysis reactions. The first mechanism was reviewed by Dragun and Helling (*159*), who examined 93 compounds. They proposed a classification of chemicals into four groups according to the chemical structure and water solubility, which was thought to be related to the compound reactivity. The second mechanism was studied by several authors on the basis of results showing the enhanced proton activity of adsorbed water (*160*). It was shown that aliphatic and aromatic amines are transformed at the surface of montmorillonite particles, resulting in the formation of ammonium ions and hydroxylated compounds (*161*).

Triazine molecules are also degraded through a protonation-hydrolysis mechanism, as described by Brown and White (*52*) and Cruz et al. (*162*). Assumed reactions are represented in Figure 20 together with infrared spectra obtained for triazine-soil systems. The absorption band that develops at about 1750 cm^{-1} corresponds to C=O groups vibrations and clearly demonstrates the hydrolysis of adsorbed triazine molecules. Other chemicals such as organophosphorus compounds may also be degraded on clay surfaces (*163*).

Humic and fulvic acids have been observed to favor the hydrolysis of triazine molecules (*164*). In a recent study, Gamble and Khan (*165*) obtained experimental results that improved the knowledge of the mechanism of humic substance catalytic action. They attributed this action to the hydrogen ions and to the undissociated carboxyl groups.

Effect of Adsorption on Biological Degradation. Adsorption-biological degradation relationships are more difficult to describe because observations are sometimes contradictory. Adsorption on clays decreases the rate of degradation, as shown by Soulas (*166*) for atrazine. This is probably due to the inaccessibility of adsorbed molecules to enzymatic systems produced by soils microorganisms.

Effect of adsorption on organic matter is more difficult to assess because two types of results are often reported, as shown by information presented in Table 23 (*167*). On one hand, organic matter behaves as an adsorbent and thus it reduces the rate of degradation. On the other hand, organic matter acts as a nutritive substrate for microorganisms and favors the degradation. Effect of adsorption on organic chemicals in soils is difficult to predict since several phenomena can interfere in a complex way.

Concluding Comments

Are experimentally determined adsorption coefficients useful for understanding the behavior of organic chemicals in natural systems? A definite answer cannot be given today, but a partial one can be proposed from the analysis of laboratory conditions, as compared to field conditions.

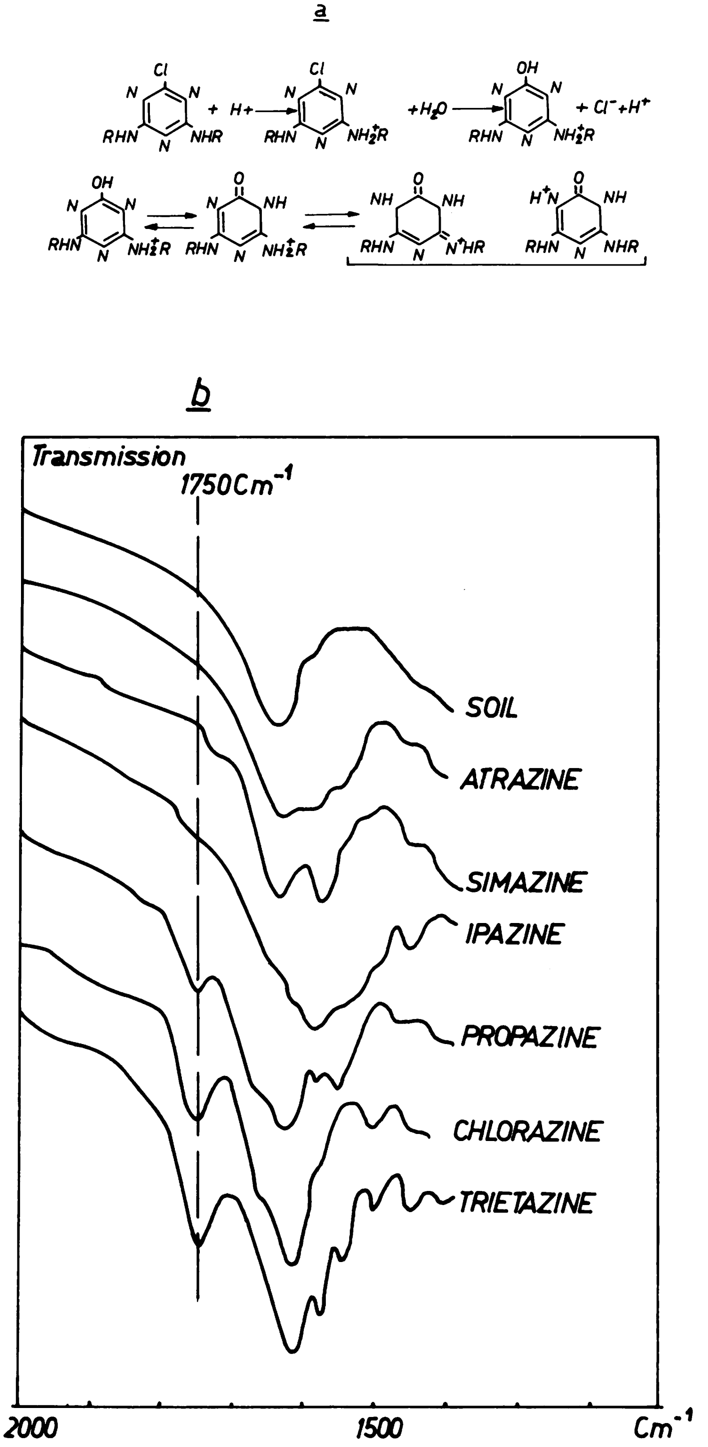


FIGURE 20. Triazine hydrolysis; assumed reactions (*a*) and observed infrared spectra (*b*). From Cruz et al. (*160*).

Most experimental results have been obtained with suspensions as adsorbing media. In such situations, soil or sediment materials are more or less dispersed in an aqueous phase as either microporous aggregates or nonporous particles. Aggregates are made of clays, metallic oxides and hydroxides, and organic polymers (often essentially humic substances) associated together. Nonporous particles are frequently formed by dispersed clays. On the contrary, in the field, soils are structured

Table 23. Some calculated values of the convection time according to Jury et al. (*154*).

Compounds	K_{oc}, mg^3/kg	t_c, days
2,4-D	0.02	6
Carbofuran	0.028	8
Nitrobenzene	0.071	15
Atrazine	0.16	31
Prometryne	0.61	105
Lindan	1.30	222
Triallate	3.60	611
Parathion	11.00	1800
Phenanthrene	23.00	3884
DDT	240.00	41000

Table 24. Effects of organic matter on degradation (*167*).

Compounds	Effect attributed to organic matter	Cause
Monuron	Increase	Increase of microbiological activity
TCA		
Chlorprophame		
Naptalame		
2,4-D		
Monuron	Increase	
Linuron		
Diphenamide		
Picloram	Decrease	Adsorption
Atrazine		
Diuron		
Paraquat		
Dalapon	No effect	
Linuron		

porous media, and adsorbing surfaces constitute the walls of micropores and macropores. What are the differences between these two situations as far as adsorption is concerned? One can tentatively answer by considering two points of view: that of surface properties and that of surface accessibility.

In suspensions, surface properties may be modified in two ways. First, the dissolving action of water causes the passage in solution of mineral salts and hydrosoluble organic compounds. Second, in very dilute suspensions, the electric charge of solid surfaces may vary with the ionic composition (ionic force and pH) of the liquid phase. As a result, adsorbing surfaces cannot be strictly the same in suspension as they are in the field. Unfortunately, one is limited to speculations because there are no observations relevant to this question. A possible avenue for future research would be to design experiments allowing adsorption characteristics to be determined for porous adsorbent media.

Accessibility of adsorbing surfaces is of course different in suspensions as compared to the field and this may greatly modify the kinetics of the adsorption process. In a structured, porous medium such as soil, the liquid phase has roughly two parts: one is mobile and the other is immobile. Transport and thus accessibility to the surfaces of macropores depend on both mass flow and molecular diffusion for the mobile phase. On the contrary, accessibility of surfaces of micropores is only controlled by molecular diffusion in the immobile phase. As briefly discussed earlier, this situation is complex and difficult, but it is more realistic. In suspensions, the adsorbing surfaces at the periphery of particles or aggregates are readily accessible. The other fraction of the surface at the walls of micropores in aggregates, although less accessible, may probably be attained rather rapidly because the size of aggregates is generally small ($< 100\ \mu$m). Thus, the kinetics of the adsorption process (transport + adsorption) are certainly different in suspension, as compared to the field. This analysis strongly supports the need for simultaneous studies of adsorption and transport in adsorbing media having the same structure or nearly the same as that of the soil in the field.

Are adsorption and desorption isotherms useful? The answer is certainly "Yes," but it is worth specifying clearly which uses of equilibrium and kinetic characteristics are valuable. These characteristics allow understanding of the mechanisms of adsorption and lead to detailed descriptions. They are necessary for any generalization based on satisfactory physical data. Although there are many results concerning various organic chemical-adsorbent systems, knowledge of the mechanisms of solute surface interactions is often limited to hypothetical descriptions. As pointed out by Burchills et al. (*6*), it would be advisable to study model systems allowing unambiguous interpretation. Furthermore, adsorption isotherms may have another application; they also provide a means for the study of soil and sediment constituents. However, a direct utilization of adsorption data specifying the characteristics of transport in the field is generally not possible. To do this, it is safer to correlate adsorption coefficients with the transport characteristics in natural situations. But this does not provide a complete description of transport-adsorption processes.

What about the correlations between adsorption coefficients and parameters such as the organic matter or organic carbon content, water-octanol partition coefficients, and water solubility? At first, it is necessary to recall the assumptions underlying the derivation of these relations: Adsorption isotherms are linear. That is to say that adsorption coefficients are considered as water-solid surface partition coefficients. The London-van der Waals dispersion forces/hydrophobic effect is the main adsorption mechanism. Interactions between solutes and solid surfaces and between solute and octanol are similar.

As previously discussed, it has been shown that these assumptions are not verified in many systems. Therefore, it would be safe to use these correlations with care because they are essentially pertinent for the systems where they are obtained, and extrapolations are not necessarily justified. These correlations should only be taken as operational tools to obtain rough evaluations of adsorption coefficients. The question is whether it is always sufficient to have a prediction within a factor of 2 to 10 or if some situations require more accurate values to be described adequately.

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