Chapter 5
Sorption, Retention, and Release of Contaminants

Contaminant retention on geosorbents is controlled by their physicochemical properties, their structural pattern as well as the properties of the contaminants themselves. The properties of these adsorbents control their capacity to retain release contaminants in the subsurface environment.

Contaminants may be adsorbed on the solid phase or on suspended particles in the liquid phase. Environmental factors, such as temperature, pH, and water content in the subsurface prior to contamination, also affect the nature of contaminant adsorption. Other physical processes of retention include precipitation, deposition, and trapping. Under natural conditions, pollutants often consist of more than a single contaminant, comprising a mixture of organic and inorganic toxic compounds. Each of these compounds can react differently with the existing minerals and chemicals in the subsurface.

5.1 Surface Properties of Adsorbents

Clay minerals, oxides, and humic substances are the major natural subsurface adsorbents of contaminants. Under natural conditions, when humic substances are present, humate–mineral complexes are formed with surface properties different from those of their constituents. Natural clays may serve also as a basic material for engineering novel organo-clay products with an increased adsorption capacity, which can be used for various reclamation purposes.

Clay minerals are characterized by a high surface charge and a very small particle size. A detailed presentation of two types of layered silicate clay (kaolinite and smectite) is given in Chap. 1.

Clay minerals have a permanent negative charge due to isomorphous substitutions or vacancies in their structure. This charge can vary from zero to >200 $\mathrm{cmol_c/kg}$ (centimoles/kg) and must be balanced by cations (counter-ions) at or near the mineral surface (Table 5.1), which greatly affect the interfacial properties. Low counter-ion charge, low electrolyte concentration, or high dielectric constant of the solvent lead to an increase in interparticle electrostatic repulsion

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Table 5.1 Chemical composition and charge characteristics of selected layer silicates (McBride 1994)

Mineral	Chemical structure	Structure	Charge per half unit cell		Structural charge ($cmol_c/kg$)
			Tetrahedral	Octahedral	
Montmorillonite	$Ca_{0.165}Si_4(Al_{1.67}Mg_{0.33})O_{10}(OH)_2$	2:1 dioctahedral	0	−0.33	92
Beidelite	$Ca_{0.25}(Si_{3.5}Al_{0.5})Al_2O_{10}(OH)_2$	2:1 dioctahedral	−0.5	0	135
Talc	$Si_4Mg_3O_{10}(OH)_2$	2:1 trioctahedral	0	0	0
Vermiculite	$Mg_{0.31}(Si_{3.15}Al_{0.85})(Mg_{2.69}Fe^{3+}_{0.23}Fe^{2+}_{0.08})O_{10}(OH)_{10}$	2:1 trioctahedral	−0.85	0.23	157
Kaolinite	$Si_2Al_2O_5(OH)_4$	1:1 dioctahedral	0	0	0
Serpentine	$Si_2Mg_3O_5(OH)_4$	1:1 trioctahedral	0	0	0

forces, which in turn stabilize colloidal suspensions. An opposite situation supports interparticle association in negatively charged colloids and induces flocculation. These behaviors validate the diffuse double-layer model, which assumes that the layer-silicate surface can be treated as a structurally featureless plane with an evenly distributed negative charge (van Olphen 1967).

Oxides and hydroxides of Al, Fe, Mn, and Si may exist in the subsurface mainly as a mixture (known also as a *solid solution*) rather than as pure mineral phases. They are considered amphoteric materials, characterized by no permanent surface charge. Their cation and anion exchange capacities reflect adsorption of potential-determining ions such as H^+ and OH^-. Different surfaces have a diverse affinity for H^+ and OH^- ions and thus exhibit various points of zero charge (PZC). Details of various models for variable charge minerals may be found in the extensive review of McBride (1989).

Humic substances, including both humic and fulvic acids, are the main subsurface organic components capable of adsorbing contaminants. The functional groups on humic materials control the cation exchange capacity (CEC) and the complexation of metals. In the case of humic substances, for example, the CEC generally is calculated to be at least one electric charge (i.e., ionized group) per square nanometer (Oades 1989) although in some cases it may range from 0.3 to 1.3 (Greenland and Mott 1978). Because humic substances are polydisperse and characterized by diverse chemistry, it is difficult to obtain a well-defined understanding of their capacity for ion exchange and metal complexation.

Organo-mineral association in the subsurface is a natural process controlled by a range of bonding mechanisms, and therefore, it is practically impossible to separate one from other. The resulting organo-mineral complex has surface properties different from the original components. For example, hydrophilic clay surfaces may become hydrophobic.

5.2 Quantifying Adsorption

Quantifying adsorption of contaminants from gaseous or liquid phases onto the solid phase should be considered valid only when an equilibrium state has been achieved, under controlled environmental conditions. Determination of contaminant adsorption on surfaces, that is, interpretation of adsorption isotherms and the resulting coefficients, helps to quantify and predict the extent of adsorption. The accuracy of the measurements is important in relation to the heterogeneity of geosorbents at a particular site. The spatial variability of the solid phase is not confined only to field conditions; variability is present at all scales, and its effects are apparent even in well-controlled laboratory-scale experiments.

5.2.1 Adsorption–Desorption Coefficients

Adsorption–desorption coefficients are determined by various experimental techniques related to the status of a contaminant (solute or gas) under static or continuous conditions. Solute adsorption–desorption is determined mainly by batch or column equilibration procedures. A comprehensive description of various experimental techniques for determining the kinetics of soil chemical processes, including adsorption–desorption, may be found in the book by Sparks (1989) and in many papers (e.g., Nielsen and Biggar 1961; Bowman 1979; Boyd and King 1984; Peterson et al. 1988; Podoll et al. 1989; Abdul et al. 1990; Brusseau et al. 1990; Hermosin and Carnejo 1992; Farrell and Reinhard 1994; Schrap et al. 1994; Petersen et al. 1995).

Application of analytical techniques from molecular geochemistry can be used to study reactions at the molecular level. Such studies can elucidate the partitioning and interactions of contaminant species in aqueous, solid, and gas phases. While spectroscopic methods provide information on chemical reactions on the contaminant–solid interface, other techniques may provide additional spatial information at an atomic level. In an extensive review on molecular geochemistry, O’Day (1999) summarizes common analytical methods (Table 5.2) and discusses their benefits in understanding contaminant–solid interactions at the molecular level.

5.2.2 Adsorption Isotherms

The sorption process generally is studied by plotting the equilibrium concentration of a compound on the adsorbent, as a function of equilibrium concentration in the gas or solution at a given temperature. Adsorption isotherms are graphs obtained

Table 5.2 Summary of selected analytical methods for molecular environmental geochemistry

Analytical method	Type of energy	
	Source	Signal
Absorption, emission, and relaxation spectroscopies, IR and FTIR	Infrared radiation	Transmitted infrared radiation
Synchrotron X-ray absorption spectroscopy (XAS), X-ray absorption near-edge spectroscopy, extended X-ray absorption fine structure	Synchrotron X rays	Transmitted or fluorescent X rays; electron yield
Synchrotron microanalysis, X-ray diffraction	Synchrotron X rays	Fluorescent X rays
EELS (also called PEELS)	Electrons	Electrons
XPS and Auger spectroscopy	X rays	Electrons
Resonance spectroscopies		
NMR	Radio waves (+ magnetic field)	Radio waves
ESR (also called EPR)	Microwaves (+ magnetic field)	Microwaves
Scattering and ablation		
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X rays (synchrotron or laboratory)	Scattered X rays
SIMS	Charged ion beam	Atomic mass
LA-ICP-MS	Laser	Atomic mass
Microscopies		
STM	Tunneling electrons	Electronic perturbations
AFM (also called SFM)	Electronic force	Force perturbation
HR-TEM and STEM	Electrons	Transmitted or secondary electrons
SEM/EM with EDS or WDS chemical analysis	Electrons	Secondary, or backscattered electrons

AAS Atomic absorption spectroscopy, *AFM* atomic force microscopy (also known as SFM), *CT* computerized tomography, *EDS* energy-dispersive spectrometry. *EELS* electron energy loss spectroscopy, *EM* electron microscopy, *EPR* electron paramagnetic resonance (also known as ESR), *ESR* electron spin resonance (also known as EPR), *EXAFS* extended X-ray absorption fine structure, *FTIR* Fourier transform infrared, *HR-TEM* high-resolution transmission electron microscopy, *ICP-AES* inductively coupled plasma atomic emission spectrometry, *ICP-MS* inductively coupled plasma mass spectrometry. Reproduced by permission of American Geophysical Union. O'Day (1999). Copyright 1999 American Geophysical Union

by plotting measured adsorption data against the concentration value of the adsorbate. Several mechanisms may be involved in the retention of contaminants on adsorbents, and therefore, several adsorption isotherms with different shapes may exist. Giles et al. (1960) related the shape of the adsorption isotherms to the adsorption mechanism for a solute–solvent adsorbent system as follows:

- The *S-curve* isotherm exhibits an initial slope that increases with the concentration of a substance in the solution. This suggests that the relative affinity of

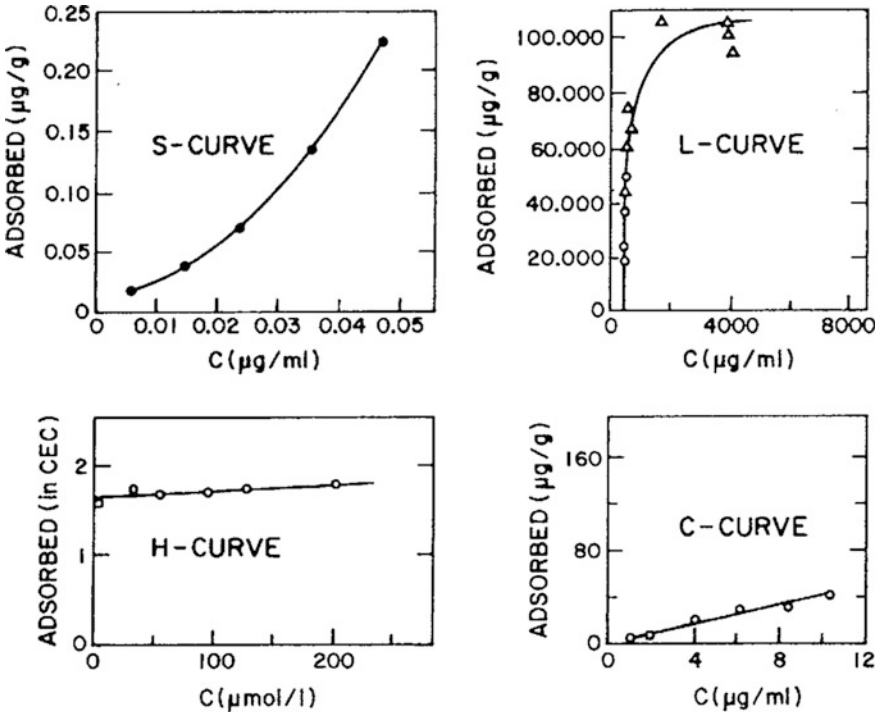

Fig. 5.1 Examples of adsorption isotherms. *S-type* aldrin on oven-dry kaolinite from aqueous solution. *L-type* parathion on oven-dry attapulgite from hexane solution. *H-type* methylene blue at pH = 6 on montmorillonite from aqueous solution. *C-type* parathion on clay soil from hexane solution (Yaron et al. 1996)

the adsorbent for the solute at low concentration is less than the affinity of the solid surface for the solvent.

- The *L-curve* isotherm is characterized by an initial slope that does not increase with the concentration of the substance in the solution. This behavior corresponds to high relative affinity of the adsorbent at low concentration and a decrease in the free adsorbing surface.
- The *H-curve* isotherm is characterized by a linear increase that remains independent of the solute concentration in the solution (i.e., constant partitioning of the solute between the solvent and the adsorbing surface). This behavior indicates a high affinity of the solid phase for the solvent.
- The *C-curve* isotherm is similar to the *H*-curve, being characterized by a linear increase, but also passing through the origin. This behavior may be due to a proportional increase in the adsorbing surface as well as to surface accessibility.

Based on their molecular properties as well as the properties of the solvent, each inorganic or organic contaminant exhibits an adsorption isotherm that corresponds to one of the isotherm classifications just described. Figure 5.1 illustrates these isotherms for different organic contaminants, adsorbed from either water or hexane solution on kaolinite, attapulgite, montmorillonite, and a red Mediterranean soil (Yaron et al. 1996). These isotherms may be used to deduce the adsorption mechanism.

Weber and Miller (1989) summarized published data of 230 adsorption isotherms in which organic compounds were adsorbed from aqueous solutions onto various soils. They found the following distribution of behaviors using the classification defined by Giles et al. (1960): $S = 16\ \%$, $L = 64\ \%$, $H = 12\ \%$, $C = 8\ \%$. Based on this result, it can be concluded that the adsorbing material is the most important controlling factor in defining the pattern of the adsorption isotherm. This fact is confirmed by the work of Weber et al. (1992) for the herbicide fluoridone, which exhibited the *S*-type sorption isotherm on soil with low organic matter and high montmorillonite content, and the *L*-type sorption isotherm on a soil with moderate organic matter content and mixed mineralogy.

In addition to these characterizations of adsorption curves, mathematical descriptions of adsorption isotherms, based on physical models, often are used to study solid interactions with contaminants. The main adsorption isotherms include those of Langmuir, Freundlich, and Brunauer–Emmet–Teller (BET); they are depicted in Fig. 5.2.

The *Langmuir equation* (Eq. 5.1), derived originally to describe the adsorption of gases on solids, assumes that the adsorbed entity is attached to the surface at specific, homogeneous, localized sites, forming a monolayer. It is also assumed that the heat of adsorption is constant over the entire monolayer, that there is no lateral interaction between adsorbed species, that equilibrium is reached, and that the energy of adsorption is independent of temperature:

$$\frac{x}{m} = \frac{KCb}{1 + KC} = \frac{Kb}{\frac{1}{C} + K}, \tag{5.1}$$

where x is the amount of adsorbed chemical, m is the mass of adsorbent, C is the equilibrium concentration, K is a constant related to the bonding strength, and b is the maximum amount of adsorbate that can be adsorbed.

The best way to determine the parameter values is to plot the distribution coefficient (K_d), which is the ratio between the amount adsorbed per unit mass of adsorbent (x/m) and the concentration in solution (C):

$$K_d = \frac{x/m}{C}. \tag{5.2}$$

Multiplying Eq. (5.1) by $1/C + K$ and substituting into Eq. (5.2) gives a linear equation for K_d, expressed as

$$K_d = Kb - K\frac{x}{m}. \tag{5.3}$$

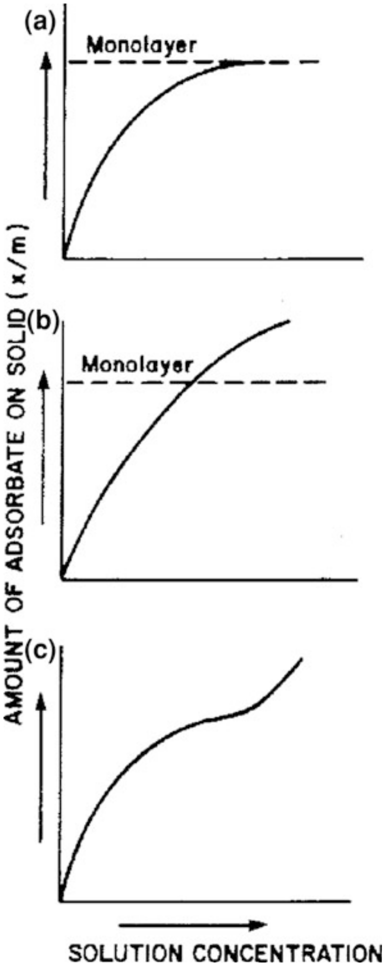

Fig. 5.2 Typical adsorption isotherms described by **a** Langmuir, **b** Freundlich, and **c** BET equations (Yaron et al. 1996)

If a straight line is obtained when K_d is plotted against x/m at low concentrations, the Langmuir equation is applicable. However, due to the restrictive assumptions, Langmuir isotherms usually are of minor importance in heterogeneous media such as the subsurface environment. Corrections therefore have been introduced to the Langmuir equation to overcome the problems of heterogeneous sites, coupled adsorption–desorption reactions, and adsorption of inorganic and organic trace elements on geosorbents.

The *Freundlich equation* was derived empirically, based on the logarithmic decrease in adsorption energy with increasing coverage of the adsorbent surface. Freundlich found that adsorption data for many dilute solutions could be fit by the expression

$$\frac{x}{m} = KC^{1/n}, \tag{5.4}$$

where K and n are empirical constants, and the other terms are as defined previously. The value of $1/n$ represents a joint measure of both the relative magnitude and diversity of energies associated with a particular sorption process (Karickhoff 1981; Weber et al. 1992). The linear form of the Freundlich equation is

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K. \tag{5.5}$$

The Freundlich equation can also be derived theoretically by assuming that the decrease in energy of adsorption with increasing surface coverage is due to the surface heterogeneity (Fripiat et al. 1971).

The main limitation of the Freundlich equation is that it does not predict a maximum adsorption capacity, because linear adsorption generally occurs at very low solute concentration and low loading of the sorbent. However, in spite of this limitation, the Freundlich equation is used widely for describing contaminant adsorption on geosorbents.

Composite linear isotherms express the natural conditions of heterogeneity specific to geosorbents (Lafleur 1979; McCarty et al. 1981; Karickhoff 1984). The relative equation expressing composite conditions of geosorbents may be of the type

$$q = \sum_{i=1}^{m} x_i q_i = \left(\sum_{i=1}^{m} x_i K_{di} \right) C = K_d C, \tag{5.6}$$

where q is the total solute mass sorbed per unit mass of bulk solid at equilibrium, x_i is the mass fraction of geosorbent constituting the reaction region or component i, q_i is the sorbed-phase concentration at equilibrium expressed per unit mass of that region or component, K_{di} is the partition coefficient for a reaction expressed per unit mass of component i, and K_d is the mass-averaged partition coefficient.

When one or more of the component elements of sorption is governed by a nonlinear relationship between the solution and the sorbed phase, the composite isotherm deviates from linearity. In these cases, modifications to the Freundlich isotherm have been developed (e.g., Lambert 1967; Weber et al. 1992) to express these conditions.

Overlapping patterns of some Langmuir-type sorption processes, which can occur at different sites of a complex sorbent (such as a geosorbent) and show different interaction energies, may be quantified by a Freundlich-type isotherm. A meaningful thermodynamic interpretation of this equation has been developed by Wauchope and Koskinen (1983), using a fugacity approach, with a proposed standard state for a sorbed organic contaminant (herbicide). This interpretation was based on the assumption that the organic fraction of the geosorbent forms a homogeneous solid comprising many components, which is known as a *solid solution*. The fugacity approach for the interpretation of environmental behavior of a chemical contaminant is described in detail by Mackay and Paterson (1981).

The *BET equation* describes the phenomenon of multilayer adsorption, which is characteristic of physical or van der Waals interactions. In the case of gas adsorption, for example, multilayer adsorption merges directly into capillary condensation when the vapor pressure approaches its saturation value and often proceeds with no apparent limit. The BET equation has the form

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C_h} + \frac{(C_h - 1)P}{V_m C_h P_0} \tag{5.7}$$

where P is the equilibrium pressure at which a volume V of gas is adsorbed, P_0 is the saturation pressure of the gas, V_m is the volume of gas corresponding to an adsorbed monomolecular layer, and C_h is a constant related to the heat of adsorption of the gas on the solid in question. If a plot of $P/(P_0 - P)$ against P/P_0 results in a straight line, the effective surface area of the solid can be calculated after V_m has been determined, either from the slope of the line $(C_h - 1)/V_m C_h$ or from the intercept $1/V_m C_h$.

It is interesting to note the effect of laboratory-scale variability on the nonlinear sorption behavior of contaminants in a porous medium, composed of various particles that are characterized individually by randomly distributed sorptive capacities and selectivity coefficients. A discrepancy is observed between the results obtained for an individual particle and for an ensemble of particles. As the variability in underlying sorptive properties increases, the Langmuir isotherm ceases to describe the behavior of the aggregates of individual particles, under either static or dynamic conditions. Assessment of the pollution hazard from parameters obtained in the laboratory therefore should consider the variability among the individual particles making up the analyzed geosorbent sample. Schwarzenbach et al. (2003) introduced the concept of “the complex nature of the distribution coefficient,” showing that this parameter may lump together many chemical species. The solute–geosorbent exchange should describe an appropriate equilibrium expression that incorporates properties of the various geosorbent components. The resulting K_d parameter is weighted by the availability of sorbent properties in the total solid phase of the sample measured. Despite this limitation, the distribution coefficient gives an effective representation of the solute–geosorbent relationship with regard to contaminant adsorption–desorption behavior.

In conclusion, the different shapes of isotherms describing equilibrium distributions of a contaminant, between geosorbents and aqueous or gaseous phases, depend on the sorption mechanism involved and the associated sorption energy. At low contaminant concentration, all models reduce to essentially linear correlation. At higher contaminant concentration, when sorption isotherms deviate from linearity, an appropriate isotherm model should be used to describe the retention process.

5.3 Kinetics of Adsorption

Adsorption kinetics involve a time-dependent process that describes the rate of adsorption of chemical contaminants on the solid phase. The "standard" chemical meaning of *kinetics* usually covers the study of the rate of reactions and molecular processes when transport is not a limiting factor; however, this definition is not applicable to subsurface conditions. In the "real" subsurface environment, many kinetic processes are a blend of chemical- and transport-controlled kinetics.

Understanding the kinetics of contaminant adsorption on the subsurface solid phase requires knowledge of both the *differential rate law*, explaining the reaction system, and the *apparent rate law*, which includes both chemical kinetics and transport-controlled processes. By studying the rates of chemical processes in the subsurface, we can predict the time necessary to reach equilibrium or quasi-state equilibrium and understand the reaction mechanism. The interested reader can find detailed explanations of subsurface kinetic processes in Sparks (1989) and Pignatello (1989).

The *mechanistic rate law* is not applicable to processes in the subsurface, if we assume only that chemically controlled kinetics occur and neglect the transport kinetics. Instead, *apparent rate laws*, which comprise both chemical- and transport-controlled processes, are the proper tool to describe reaction kinetics on subsurface soil constituents. Apparent rate laws indicate that diffusion and other microscopic transport phenomena, as well as the structure of the subsurface and the flow rate, affect the kinetic behavior.

Based on these rate laws, various equations have been developed to describe kinetics of soil chemical processes. As a function of the adsorbent and adsorbate properties, the equations describe mainly first-order, second-order, or zero-order reactions. For example, Sparks and Jardine (1984) studied the kinetics of potassium adsorption on kaolinite, montmorillonite (a smectite mineral), and vermiculite (Fig. 5.3), finding that a single-order reaction describes the data for kaolinite and smectite, while two first-order reactions describe adsorption on vermiculite.

The *Elovich equation* was developed to determine the kinetics of heterogeneous chemisorption of gases on solid surfaces. This equation assumes a heterogeneous distribution of adsorption energies, where the energy of activation (E) increases linearly with surface coverage (Rao et al. 1989). A simplified Elovich equation used to study the rate of soil chemical processes is given by

$$q = \frac{1}{Y}\ln(XY) + \frac{1}{Y}\ln(t + t_0), \tag{5.8}$$

where q is the amount sorbed at time t, X and Y are constants, and t_0 is an integration constant. An application of Eq. (5.8) for the case of PO_4 sorption on soils is shown in Fig. 5.4. In this particular case, a linear relationship is observed. Chien and Clayton (1980) found that the Elovich equation was best based on the highest values of the simple correlation coefficient. Polysopoulos et al. (1986),

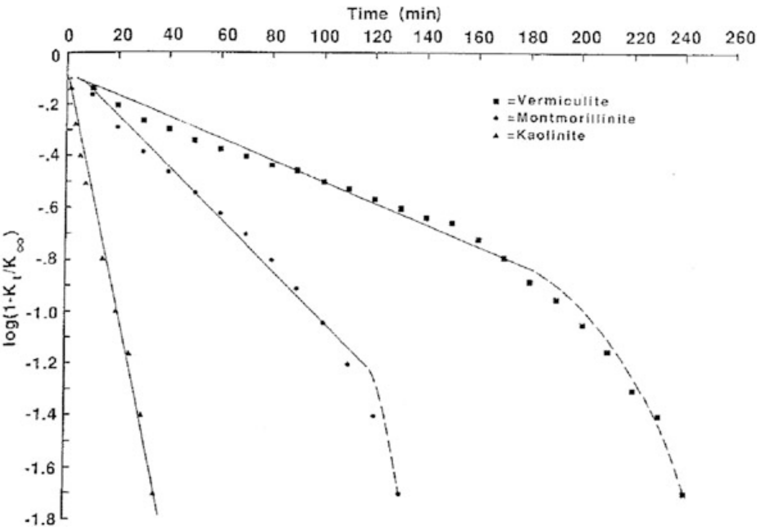

Fig. 5.3 First-order plots of potassium adsorption on clay, where K_t is the quantity of potassium adsorbed at time t, and K_∞ is the quantity of potassium adsorbed at equilibrium (Sparks and Jardine 1984)

however, show that the pre- and post-Elovichian sections, in many cases, are not observed, which leads to the incorrect conclusion that the entire rate process may be explained by one single kinetic law.

Sparks (1989) discusses the application of various kinetic equations to earth materials based on the analysis of a large number of reported studies. Even though different equations describe rate data satisfactorily, Sparks (1989) uses linear regression analysis to show that no single equation best describes every study.

According to the Arrhenius law, the rate of reaction is correlated linearly to the increase in temperature, with the rate constant k given by

$$k = Ae^{-E/RT}, \tag{5.9}$$

where A is a frequency factor, E is the energy of activation, R is the universal gas constant, and T is the absolute temperature. A low activation energy usually indicates a diffusion-controlled process, while higher activation energy indicates chemical-reaction-controlled processes (Sparks and Huang 1985; Sparks 1986). Data on the effect of temperature on the rate of potassium release from potassium-bearing minerals were presented by Huang et al. (1968) and are reproduced in Table 5.3. Huang et al. (1968) showed that a 10 K rise in temperature during the reaction period resulted in a twofold to threefold increase in the rate constant.

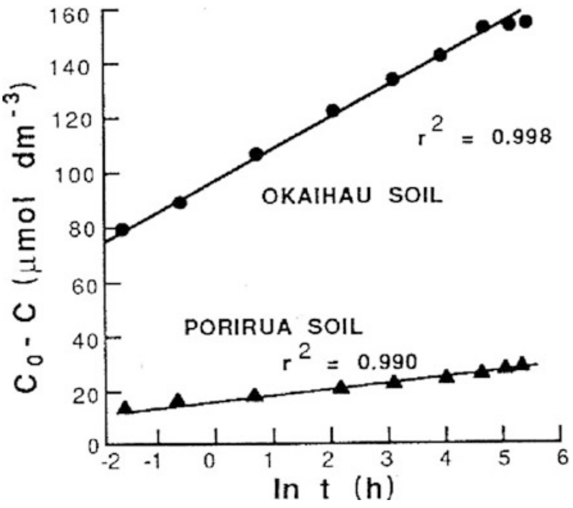

Fig. 5.4 Plot of Elovich equation for phosphate (PO_4) sorption on two soils, where C_0 is the initial concentration added at time zero, and C is the concentration in the soil solution at time t (Chien and Clayton 1980)

Table 5.3 Apparent rate constants for the release of potassium from potassium minerals, as a function of temperature (Huang et al. 1968)

Mineral	Temperature	
	301 K	311 K
Biotite	1.46×10^{-2}	3.09×10^{-4}
Phlogopite	9.01×10^{-4}	2.44×10^{-4}
Muscovite	1.39×10^{-4}	4.15×10^{-4}
Microcline	7.67×10^{-5}	2.63×10^{-4}

5.4 Adsorption of Ionic Contaminants

Chapter 2 mentioned that the adsorption of charged ionic compounds on the solid phase is a result of a combination of chemical binding forces and electric fields at the interface. Here, we extend the discussion on this topic, focusing mainly on aspects relevant to behavior of ionic contaminants in the subsurface environment.

Electrical neutrality on the solid surface requires that an equal amount of positive and negative charge accumulates in the liquid phase near the surface. If the surface is negatively charged, positively charged cations are electrostatically attracted to the surface. Simultaneously the cations are drawn back toward the equilibrating solution; as a result, a diffuse layer is formed and the concentration of cations increases toward the surface. On the other hand, ions of the same sign (anions) are repelled by the surface with diffusion forces acting in an opposite direction. The overall pattern is known as a *diffuse double layer* (DDL). The existence of a DDL was developed theoretically by Gouy and Chapman about 100 years ago and is an integral part of *electric double layer theory*.

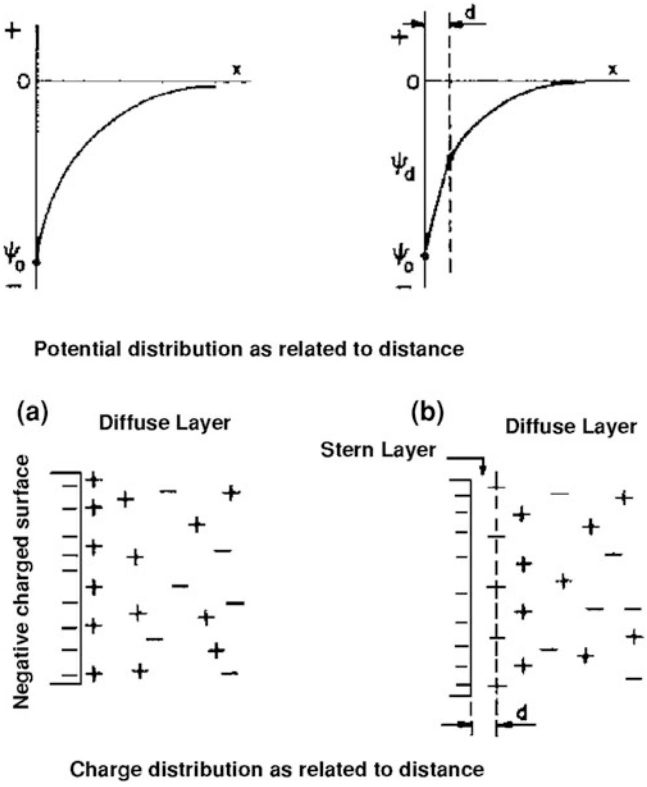

Fig. 5.5 Distribution of electrical charges and potentials in a double layer according to **a** Gouy–Chapman model and **b** Stern model, where ψ_0 and ψ_d are surface and Stern potentials, respectively, and d is the thickness of the Stern layer

The Gouy–Chapman model assumes (1) the exchangeable cations exist as point charges, (2) colloid surfaces are planar and infinite in extent, and (3) surface charge is distributed uniformly over the entire colloid surface. Even though this assumption does not correspond to the subsurface environment, it works well for the clay colloid component of the subsurface, a fact that may be explained by mutual cancelation of other interferences. Stern (1924) and Grahame (1947) refined the Gouy–Chapman model by recognizing that counter-ions are unlikely to approach the surface more closely than the ionic radii of the anions and the hydrated radii of the cations.

The Gouy–Chapman model assumes that the charge is spread uniformly over the surface, with the overall charge allocation in solution consisting of a non-uniform distribution of point charges. The solvent is treated as a continuous medium influencing the double layer only through its dielectric constant, which is assumed independent of its position in the double layer. Moreover, it is assumed that ions and surfaces are involved only in electrostatic interactions. The derivation is for a flat surface, infinite in size. The double-layer theory applies equally well to rounded or spherical surfaces (Overbeek 1952). The model of Stern (1924) assumes that the region near the surface consists of a layer of ions known as the *Stern layer* and a diffuse ion layer. A schematic representation illustrating the fundamental differences between the Gouy–Chapman and Stern models is presented in Fig. 5.5.

The surface charge is balanced by the charge in solution, which is distributed between the Stern layer at a distance d from the surface and a diffuse layer having an ionic Boltzmann-type distribution. The total charge σ is therefore due to the charge in the two layers:

$$\sigma = (\sigma_1 + \sigma_2), \tag{5.10}$$

where σ_1 is the Stern layer, and σ_2 is the diffuse layer charge.

A development of the DDL theory also considers the interactions between the two flat layers of the Gouy–Chapman model. The double-layer charge is affected only slightly when the distance between the two plates is large. Grahame (1947) suggests that specifically adsorbable anions may be adsorbed into the Stern layer when they lose their hydration water, whereas the hydrated cations are attracted only electrostatically to the surface. Bolt (1955) added the effects of ion size, dielectric saturation, polarization energy, and coulombic interactions of the ions, as well as short-range repulsion of ions into the Gouy–Chapman model. Note that the simple Gouy–Chapman model gives fairly reliable results for colloids with a constant charge density not exceeding 0.2–0.3 C/m^2.

The Gouy–Chapman model provides an invaluable answer to a number of processes occurring in the subsurface system, by explaining the exchange capacity concept for the range of surface charge densities normally encountered in clays (Bolt et al. 1991). In general, double-layer theory explains the processes occurring in the contaminant-subsurface system when the pollutants have a charge opposite to that of the surface. By studying molecular dynamics simulations of the electrical double layer on smectite surfaces contacting concentrated mixed electrolyte (Na–CaCl$_2$) solutions, Bourg and Sposito (2011) defined three ion adsorption planes: 0, β, and d with different qualifications. The locations of β- and d-planes are independent of ionic strength or ion type, and “indifferent electrolyte” ions can occupy all three planes.

CEC and *selectivity* are among the most important processes that control the fate of charged (ionic) contaminants in the subsurface. These processes involve the cationic concentration in solution and the cation dimensions, as well as the configuration of exchange sites on the interface. The Gapon relation approaches the process as an exchange of equivalents of electric charges, where the solute concentration is measured in terms of activity and the adsorption on an equivalent basis.

Negatively charged surfaces having the same exchange properties do not necessarily interact in the same manner with different cations having the same

Table 5.4 Adsorption of heavy metals on goethite as a function of pH

Metal	pH							
	4.7	5.2	5.5	5.9	6.4	7.2	7.5	8.0
Cu	17	55	75	90				
Pb		43	56	75				
Zn				13	22	68		
Cd					23	44	53	
Co						39	54	78

Data expressed as percent of initial amount of metallic cation solution. Reprinted from Quirk and Posner (1975). Copyright 1975 with permission of Elsevier

valence. This is caused by the differential sizes and polarizability of the cations, by the structural properties of the adsorbent surfaces, and by the differences in the surface charge distribution. For example, ammonium ions (NH_4^+) are sorbed preferably over anhydrous H^+ or Na^+ in 1:2 clay minerals, because they may form NH-oxygen links in the hexagonal holes of Si-O sheets, and they may also link to adjacent oxygen planes in the interlayer space by an OH–N–HO bond. Selectivity of the divalent alkaline earth cations is less pronounced. Trivalent cations, such as Al^{3+}, coordinated octahedrally to water molecules, link more strongly than hydrated Ca^{2+} ions.

Cation selectivity on organic matter is related mainly to the disposition of the acidic groups in the adsorbent. Multivalent cations adsorb preferentially over monovalent cations, and transition metals adsorb preferentially over strong basic metals. Organo-mineral complexes exhibit a CEC smaller than the sum of the CECs of the components. This phenomenon is reflected in the pattern of cation selectivity (Greenland and Hayes 1981). Two aspects should be considered in the cation exchange process: the number of exchange sites occupied by the cation investigated and the selectivity of the cation relative to the concentration of the exchanging cation.

Heavy metal cations participate in exchange reactions with negatively charged surfaces of clay minerals, with Coulombic and specific adsorption being the processes involved in the exchange. Metal cationic adsorption is affected by pH. At low pH values (<5.5), some heavy metals do not compete with alkali metals (e.g., Ca^{2+}) for the mineral adsorption site. At higher pH values, heavy metal adsorption increases greatly; an example of heavy metal adsorption on goethite as a function of pH is given in Table 5.4.

Cationic organic contaminants often compete with mineral ions for the same adsorption site. At low pH, organic cationic molecules are adsorbed more strongly on earth materials than on mineral ions of a similar valence. At moderate pH values, however, mineral ions are favored over organic cations. In general, the charge density of the adsorbing surface is a determining factor in adsorption of cationic organic molecules, but their adsorption also is affected by the molecular configuration (Mortland 1970). Organic molecules may be adsorbed by clays via a cationic adsorption mechanism, but this process depends on the acidity of the medium.

Early work by Boyd et al. (1947), performed on zeolites, showed that the ion exchange process is diffusion controlled and the reaction rate is limited by mass transfer phenomena that are either film-diffusion (FD) or particle-diffusion (PD) dependent. Under natural conditions, the charge compensation cations are held on a representative subsurface solid phase as follows: within crystals in interlayer positions (mica and smectites), in structural holes (feldspars), or on surfaces in cleavages and faults of the crystals and on external surfaces of clays, clay minerals, and organic matter.

Cations held on external surfaces are immediately accessible to (subsurface) water. Once removed from the solid phase, they move to a region of reduced concentration. This movement is controlled by diffusion, and the diffusion coefficient (D) can be calculated using the equation described by Nye and Tinker (1977):

$$D = D_e \theta f \frac{dC_{\text{solution}}}{dC_{\text{ss}}} \tag{5.11}$$

where D_e is the diffusion coefficient in water, θ is the water content in the subsurface solid phase, f is the “impedance” factor related to the tortuosity, C_{ss} is the cation concentration in the subsurface (solid and water phases) expressed as mass/volume, and C_{solution} is the cation concentration in solution.

Cations held on the external surfaces of clays exhibit relatively rapid diffusion but are subject to an additional limitation. Because the arrival rate of ingoing cations at the exchange site is much slower than the release rate of the outgoing cations, the rate-determining step is the influx of exchanging cations to negatively charged sites. Sparks (1986) defined the following concurrent processes that take place during Na^+ and K^+ exchange in vermiculite: (1) diffusion of Na^+ with Cl^- through the solution film that surrounds the particle (FD), (2) diffusion of Na^+ ions through a hydrated interlayer space and chemical reaction leading to exchange of Na^+ in the particle (PD), (3) chemical reaction leading to exchange of Na^+ by K^+ ions on the particle surface (CR), (4) diffusion of displaced K^+ ions through the hydrated interlayer space of the particle (PD), and (5) diffusion of displaced K^+ ions with Cl^- through the solution film away from the particle (FD).

To enable a chemical reaction, the exchange ions must be transported to the active sites of the particles. The film of water adhering to and surrounding the particle, as well as the hydrated interlayer space within the particle, are zones of low contaminant concentration that are being depleted constantly by ion adsorption to the sites. The decrease in concentration of contaminant ions in these interfacial zones is then compensated for by ion diffusion from the bulk solution. Ion exchange occurs when a driving force, such as a chemical potential gradient, is maintained between solid and solution or when access to sites is kept free by the use of a hydrated and less preferred cation for exchange.

The properties of organic and inorganic constituents in the subsurface solid phase, as well as the properties of the contaminants (e.g., ion charge and radius), define the time span of ion exchange, which may range from a few seconds to days (Yaron et al. 1996). The slowly exchangeable cations are situated on exchange sites in interlayer spaces of the minerals (e.g., smectites) or in cages and channels of organic matter, and exchange and move into solution by diffusive flux.

In general, when a charged solid surface faces an ion of similar charge in an aqueous suspension, the ion is repelled from the surface by Coulomb forces. The Coulomb repulsion produces a region in the aqueous solution that is relatively depleted of the anion and an equivalent region far from the surface that is relatively enriched.

Anionic negative adsorption may occur in the subsurface when negatively charged clay minerals repel anions from the mineral surface. If, for example, a dilute neutral solution of KCl is added to dry clay, the Cl^- equilibrium concentration in the bulk solution will be greater than the Cl^- concentration in the solution originally added to the clay. Anionic negative adsorption is affected by the anion charge, concentration, pH, the presence of other anions, and the nature and charge of the surface. Negative adsorption may decrease as the subsurface pH decreases and when anions can be adsorbed by positively charged surfaces. The larger negative charge of the surface results in a greater anion negative adsorption. Acidic organic contaminants in their anionic form are expected to be repelled by negatively charged clay surfaces.

5.5 Adsorption of Nonionic Contaminants

The sorption of a nonpolar organic contaminant on a solid phase is derived by enthalpy- and entropy-related forces. Hassett and Banwart (1989) suggested that sorption occurs when the free energy of the reaction is negative due to enthalpy or entropy. The enthalpy is primarily a function of the changes in the bonding between the adsorbing surface and the sorbate (solute) and between the solvent (water) and the solute. The entropy is related to the increase or decrease in the order of the system on sorption.

The forces that control adsorption of nonionic contaminants on the solid phase were summarized by Yaron et al. (1996) in terms of enthalpy and entropy adsorption forces. These are discussed next.

Enthalpy-Related Adsorption Forces

Hydrogen bonding refers to the electrostatic interaction between a hydrogen atom covalently bound to one electronegative atom (e.g., oxygen) and another electronegative atom or group of atoms in a neighboring molecule. The hydrogen atom may be regarded as a bridge between electronegative atoms; this bonding is conceived of as an induced dipole phenomenon. The H bond generally is considered as the asymmetrical distribution of the first electron of the H atom induced by various electronegative atoms.

Ligand exchange processes involve replacement of one or more ligands by the adsorbing species. In some instances, the ligand exchange process can be regarded as a condensation reaction (e.g., between a carboxyl group and a hydroxyl aluminum surface). Under some conditions, ligand exchange reactions are very likely to be involved when humic substances interact with a clay material.

The *protonation mechanism* includes Coulomb electrostatic forces resulting from charged surfaces. The development of surface acidity by the solid phase of the subsurface offers the possibility that solutes having proton-selective organic functional groups can be adsorbed through a protonation reaction.

The π *bonds* occur as a result of the overlapping of π orbitals when they are perpendicular to aromatic rings. This mechanism can be used to explain the bonding of alkenes, alkylenes, and aromatic compounds to subsurface organic matter.

London-van der Waals forces generally are multipole (dipole–dipole or dipole-induced dipole) interactions produced by a correlation between fluctuating induced multipole (principal dipole) moments in two nearly uncharged polar molecules. Even though the time-averaged, induced multipole in each molecule is zero, the correlation between the two induced moments does not average to zero. As a result, an attractive interaction between the two is produced at very small molecular distances.

The van der Waals forces also include dispersion forces that arise from correlations between the movement of electrons in one molecule and those of neighboring molecules. Under such conditions, even a molecule with no permanent dipole moment forms an instantaneous dipole as a result of fluctuations in the arrangements of its electron cloud. This instantaneous dipole polarizes the charge of another molecule to give a second-induced dipole, resulting in a mutual dipole–dipole attraction. All molecules are subject to attraction by dispersion forces whether or not more specific interactions between ions or dipoles occur. Although the momentary dipoles and induced dipoles constantly change positions, the net result is a weak attraction. When many groups of atoms in a polymeric structure interact simultaneously, the van der Waals components are additive.

Chemisorption denotes the situation in which an actual chemical bond is formed between the molecules and the surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged, forming new compounds that better satisfy the valences of the surface atoms. The enthalpy of chemisorption is much greater than that of physical adsorption. The basis of much catalytic activity at surfaces is that chemisorption may organize molecules into forms that can readily undergo reactions. It often is difficult to distinguish between chemisorption and physical sorption, because a chemisorbed layer may have a physically sorbed layer deposited above it.

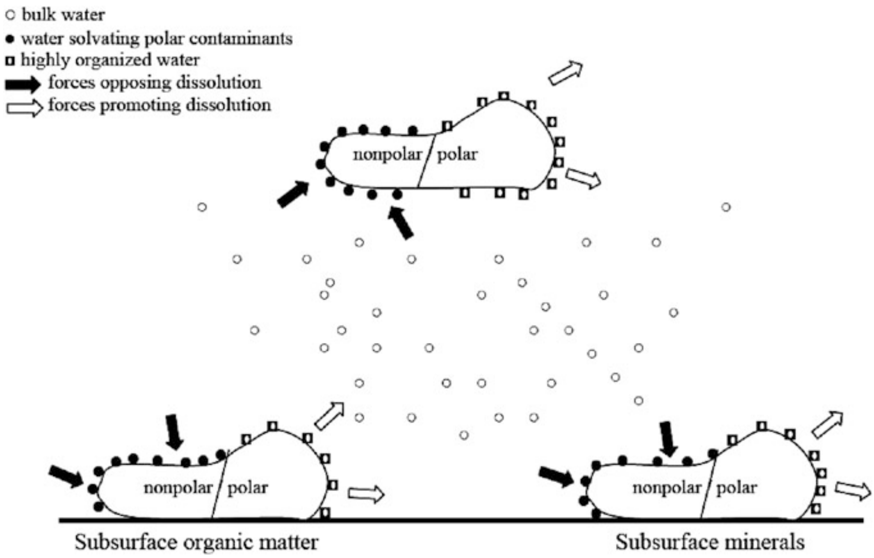

Fig. 5.6 Forces affecting sorption of nonpolar organic contaminants

Entropy-Related Adsorption Force

Entropy-related adsorption, denoted *hydrophobic sorption* (or *solvophobic interaction*), is the partitioning of nonpolar organics out of the polar aqueous phase onto hydrophobic surfaces. Figure 5.6 shows a schematic model of forces that contribute to the sorption of hydrophobic organics, relevant to the subsurface environment.

A major feature of hydrophobic sorption is the weak interaction between the solute and the solvent. The primary force in hydrophobic sorption appears to be the large entropy change resulting from the removal of a solute from solution. The entropy change is due largely to the destruction of the cavity occupied by the solute in the solvent and the destruction of the structured water shell surrounding the solvated organic. Hydrophobic interfaces may be found mainly on organic matter and on organically coated minerals.

Hydrophobic sorption, being an entropy-driven process, provides the major contribution to sorption of hydrophobic contaminants on subsurface solid phases. When a hydrophobic organic compound is adsorbed on a solid phase, the partitioning of the compound and its adsorption by the surface directly from the water phase should be considered. These processes occur in partially saturated and saturated subsurface regimes, where water is likely to be the wetting phase. In such cases, the wetting phase completely or partially coats the solid-phase surface, thus increasing the retention capacity because the wetting phase serves as an additional sink.

Rao et al. (1989) suggested that at least four mechanisms of adsorption should be considered for hydrophobic organic compounds. The first mechanism involves the sorption of the neutral molecular species from the aqueous phase, which is similar to hydrophobic sorption. The second mechanism of interest comprises the specific interactions of a dissociated (ionic) species with various functional groups on the sorbent surface. Several models developed for predicting the ion exchange of inorganic ions may be used for predicting this type of sorption. A third sorption mechanism, molecular ion pairing, involves transfer of organic ions from the aqueous phase to the organic surface phase. A fourth mechanism covers transfer of organic ions from the aqueous phase to the organic surface, while the counter-ions remain in the electric double layer of the aqueous phase. The relative contribution of each of these mechanisms depends on (1) the extent of compound dissociation as a function of the acid dissociation constant, pK_a, and solution pH; (2) the ionic charge status of the solid interface as a function of the pH and of the point of zero charge; and (3) the ionic strength and composition of the water phase.

Often, contaminants reach the subsurface as complex mixtures, and therefore, an understanding of the adsorption process under these more complicated conditions is required. Under a waste disposal site, where organic or organo-metal complexes are involved, for example, sorption may involve multiphase (water and organic) solvent interactions. To deal with this combination of parameters, one can use the theoretical approach of Rao et al. (1985). This approach is based on the predominance of solvophobic interactions for predicting sorption of hydrophobic organic chemicals from mixed solvents. With increasing volume fractions of a completely miscible organic solvent in a binary mixed solvent, the hydrophobic organic solvent sorption coefficient decreases exponentially because the solubility and sorption coefficient are inversely related.

Further in-depth discussions of nonionic pollutant adsorption on subsurface components can be found in the classical review of Mortland (1970) or in the reviews of Calvet (1989), Hassett and Banwart (1989), Hayes and Mingelgrin (1991), Delle Site (2001), as well as in a number of books (such as those by Theng 1974; Greenland and Hayes 1981; Saltzman and Yaron 1986; Yaron et al. 1996; and Schwarzenbach et al. 2003).

5.6 Other Factors Affecting Adsorption

Independent of the molecular properties of contaminants, the subsurface solid-phase constituents are a major factor that control the adsorption process. Both the mineral and organic components of the solid phases interact differentially with ionic and nonionic pollutants, and in all cases, environmental factors, such as temperature, subsurface water content, and chemistry, affect the mechanism, extent, and rate of contaminant adsorption.

The structural properties of the subsurface clay fraction are a controlling factor in defining the rate and extent of the ion exchange process. In the case of kaolinite, for example, the tetrahedral layers of adjacent clay sheets are held tightly by H bonds and only planar external surface sites are available for exchange. In contrast, under adequate hydration conditions, smectites are able to swell, allowing a rapid passage of ions into the interlayer space. Vermiculite is characterized by a more structured interlayer space because the region between layers of silicate is selective for certain types of cations like K^+ and NH_4^+ (Sparks and Huang 1985). Cation exchange also is affected by the particle size of the mineral fraction. For example, it was reported (Kennedy and Brown 1965) that, of the total Ca–Na content of a sand layer, 90 % is composed of particles of 0.12–0.20 mm and only 10 % contains a 0.20–0.50 mm sand fraction. Similar behavior was observed on silt materials where the exchange rates (Ba–K) on medium and coarse silt diminish with increasing particle size.

The organic fraction composition may influence the exchange capacity. A key contribution to the exchange capacity of humus is given by the carboxyl and phenolic hydroxyl functional groups. Under appropriate pH conditions, uranic acids in polysaccharides or carboxy-terminal structures in peptides can contribute to the negative charge and CEC of the soil organic matter. The basic amino acids lysine, arginine, and histidine are positively charged at $pH = 6$; the amino terminal groups in peptides and polypeptides can be expected to be the principal contributors to positive charges in subsurface organic materials, in an appropriate pH environment (Talibuden 1981). Based on a study of pH dependence of organic contaminant sorption on soil organic matter, Bronner and Goss (2011) suggest that protonation/deprotonation of carboxylic groups in humic matter has no significant influence on the sorption process.

The CEC of the organo-mineral complexes is less than the sum of each of the separate organic and mineral components. The CEC decrease may be explained by changes occurring in the humus configuration following coating of the mineral surface. A significant elucidation of the relative contributions of mineral and organic colloids to the adsorption of organic contaminants was made through studies with separated fractions and well-defined model materials (Gaillardon et al. 1977; Kang and Xing 2005; Celis et al. 1996). A different approach was to study and compare adsorption before and after organic matter removal (Saltzman et al. 1972) to assess the relative importance of soil minerals in parathion uptake. Although the removal of organic matter from soil by oxidation with hydrogen peroxide (a commonly used, strong oxidation agent) could affect the properties of an adsorbent, the results obtained may provide qualitative information about its role and properties in the contaminant retention process. The reported results showed that parathion has a greater affinity for organic adsorptive surfaces than for mineral ones. The important finding from this approach suggests that adsorption is dependent on the type of association between organic and mineral colloids, which determines the nature and the magnitude of the adsorptive surfaces. Although the importance of organic matter has been well established, the properties of organic colloids relevant to the adsorption of contaminants remain to be characterized thoroughly. The available information suggests that these properties could be related to the ratio among humic acid, fulvic acid, and humin, as well as the presence of active groups (e.g., carboxyl, hydroxyl, carbonyl, methoxy), high CEC, and surface area.

The main properties affecting adsorptive capacity of clay are considered to be the available surface and the CEC, as well as the nature of the saturating cation, the hydration status, and the surface acidity. Although amorphous oxides and hydroxides of iron, aluminum, and silica can adsorb organic molecules, only limited information exists in this direction. It is known, however, that Al and Fe hydroxides can adsorb organic contaminants, and therefore, their presence leads to an increase in the adsorption capacity of montmorillonite (Terce and Calvet 1977). For example, after removing Al and Fe oxides from soil particles, the adsorptive capacity of soils for atrazine (an organic herbicide) decreased significantly and the adsorption kinetics were affected (Huang et al. 1984).

The adsorption of contaminants on geosorbents also is affected by climatic conditions reflected in the subsurface temperature and moisture status. Calvet (1984) showed how the soil moisture content may affect adsorption of contaminants originating from agricultural practices. The moisture content determines the accessibility of the adsorption sites, and water affects the surface properties of the adsorbent. The competition for adsorption sites between water and, say, insecticides may explain this behavior. Preferential adsorption of the more polar water molecules by soil hinders insecticide adsorption at high moisture content; reduced competition is found at low moisture content, leading to an increase in adsorption. A negative relationship between pesticide adsorption and soil moisture content has been known for a long time (e.g., Ashton and Sheets 1959; Yaron and Saltzman 1978).

It is important to examine the effect of moisture content on the surface properties of clays and organic matter in relation to the adsorption of organic contaminants. In general, it is accepted that water molecules are attracted to clay surfaces mainly by the exchangeable cations, forming hydration shells. Adsorbed water provides adsorption sites for organic contaminants. An important feature of water associated with clay surfaces is its increased dissociation, giving the surface a slightly acidic character. A negative relationship usually exists between the surface acidity of clays and their water content.

Adsorption usually increases as the temperature decreases, while desorption is favored by temperature increases. The temperature may indirectly affect adsorption by its effect on organic–water interactions. The complex relationship among adsorbent, adsorbate, and solvent as affected by temperature was described by Mills and Biggar (1969) for the case of an organic insecticide. The adsorption of lindane (1,2,3,4,5,6-hexachlorocyclohexane) and its beta-isomer by a peat (high organic content), a clay soil, a Ca-bentonite, and silica gel decreased as the temperature of the system increased. The authors suggested that this adsorption–temperature relationship reflects not only the influence of energy on the adsorption process but also the change in solubility of the adsorbate. They considered that the change in activity in solution with temperature is related to the change in reduced concentration, which is the ratio between the actual concentration of the solute at a given temperature and its solubility at the same temperature. Adsorption isotherms obtained by using the reduced concentration, in contrast to normal adsorption isotherms, showed an increase in adsorption with increasing temperature. This finding suggests that the heat involved in the adsorption process mainly affects solute solubility. Similar results emphasizing the significant influence of temperature on adsorption through its solubility effect were reported by Yamane and Green (1972) for atrazine and by Yaron and Saltzman (1978) for parathion.

Strong, sometimes irreversible retention of organic contaminants on hydrated humic substances can be explained by penetration and trapping in the internal structure. Burchill et al. (1981) showed that hydrated exchangeable cations and some dissociated functional groups, as well as water held by various polar groups of the humic substances, provide adsorption sites for organic contaminants. At low moisture content, the hydrophobic portions of the organic matter structure may bind hydrophobic nonionic organic contaminants. Pignatello (2012) showed that in some soils, it is possible that there are (qualitatively) many different kinds of natural organic matter (NOM) microdomains, which form microstructures that play an important role in selectivity, kinetics and reversibility of organic contaminant sorption. The physical microstructure of the NOM responds to changes in environmental conditions, such as concentration of sorbing chemicals, temperature, and moisture content, thus developing a dynamic system that evolves with time. Pignatello (2012) considers that NOM apparently has a “memory” of its exposure history to environmental stresses, which “challenges the historical paradigm of NOM as a passive sorbent with immutable structure.”

5.7 Nonadsorptive Retention of Contaminants

Nonadsorptive (physical) retention of chemicals in the subsurface has received less attention, despite the fact that significant quantities of contaminants can be retained by processes other than purely adsorptive ones.

5.7.1 Contaminant Precipitation

Contaminant precipitation involves accumulation of a substance to form a new bulk solid phase. Sposito (1984) noted that both adsorption and precipitation imply a loss of material from the aqueous phase, but adsorption is inherently two-dimensional (occurring on the solid-phase surface), while precipitation is inherently three-dimensional (occurring within pores and along solid-phase boundaries). The chemical bonds that develop due to formation of the solid phase in both cases can be very similar. Moreover, mixtures of precipitates can result in heterogeneous solids with one component restricted to a thin outer layer, because of poor diffusion. Precipitate formation takes place when solubility limits are reached and occurs on a microscale between and within aggregates that constitute the subsurface solid phase. In the presence of lamellar charged particles with

Table 5.5 Values of pK_a for major heavy metal contaminants (de Boodt 1991)

Heavy metal	pK_a
Cd^{2+}	8.7
Co^{2+}	8.9
Cr^{2+}	6.5
Cu^{2+}	6.7
Mn^{2+}	10.6
Ni^{2+}	8.9
Pb^{2+}	7.3
Zn^{2+}	7.6
Fe^{3+}	3.0

impurities, precipitation of cationic pollutants, for example, might occur even at concentrations below saturation (with respect to the theoretical solubility coefficient of the solvent).

Considering that heavy and transition metals may reach subsurface water as hydrated cations at neutral pH, they may behave as acids, due to formation of a hydration shell surrounding the cation. The "acidity" of hydrated cations depends on the acid dissociation constant (pK_a) values. The lower the pK_a value of the metal, the lower the pH at which precipitates are formed. Values of pK_a for major heavy metals are presented in Table 5.5.

There is a relationship between the solubility of a metal in water, the amount of precipitates formed, and the pH. Formation of a solid precipitate is expressed according to the equation

$$A_aB_{b(\mathrm{solid})} \rightleftharpoons aA^{+\mathrm{b}}_{(\mathrm{aq})} + bB^{-\mathrm{a}}_{(\mathrm{aq})}, \tag{5.12}$$

where A is a metal and B is a ligand, which precipitate to form the solid $A_aB_{b(\mathrm{s})}$, and a and b are stoichiometric coefficients subject to the constraint of electroneutrality.

The ion activity product (IAP) is a measure of the activity of ions present in the solvent. By definition, the activity of a mineral phase (if present) is unity. Thus, the amount of precipitate does not affect the reaction between the solid and the solvent. When the IAP is much smaller than equilibrium values, there is no precipitation, and because the activity denominator generally is equal to 1, the IAP is given by

$$\mathrm{IAP} = [A^+]_{\mathrm{measured}}[B^-]_{\mathrm{measured}} \tag{5.13}$$

when equilibrium is reached, solubility product constants are used to describe saturated solutions of ionic compounds of relatively low solubility. When the ion concentration in solution reaches saturation, equilibrium between the solid and dissolved ions is established.

The equilibrium constant is given by the product of the concentration of ions present in a saturated solution of ionic compounds,

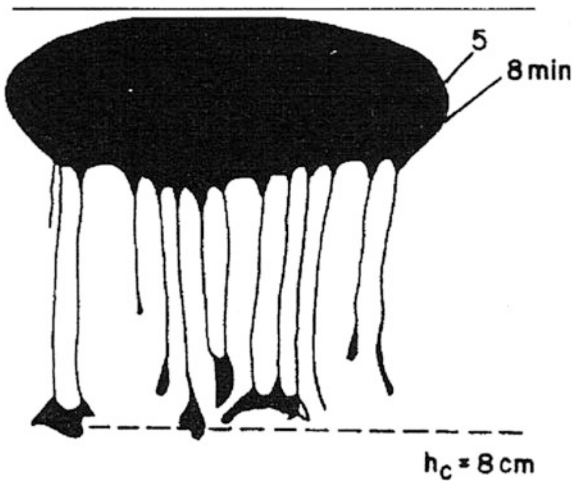

Fig. 5.7 Illustration of a water-immiscible liquid trapped in the vadose zone immediately after a spill. The *dashed line* represents the water table region (Schwille 1984)

$$K_{sp} = [A^{b+}][B^{a-}]^b, \tag{5.14}$$

where K_{sp} is the solubility product, or the equilibrium constant, between an ionic solid and its saturated solution. When IAP $< K_{sp}$, the solution is below saturation and minerals dissolve on contact with the solution. When IAP $> K_{sp}$, the solution is "supersaturated" and precipitation occurs.

The IAP can be larger than the corresponding solubility product constant for the solid if the active shell of the solid is of radius <1 μm. This behavior may be explained by the fact that the surface energy of these very small particles contributes to the Gibbs energy of the precipitate, increasing the activity relative to that in the standard state, where the interfacial energy component is negligible. Additional precipitate formation processes may occur in the presence of nucleating agents.

It should be noted that, in the natural subsurface solid phase, differentiation between adsorption and precipitation can be very difficult, because the new solid phase may precipitate homogeneously onto the surface of an existing solid phase. Weathering may provide host surfaces for the more stable phase into which they transform chemically.

5.7.2 Liquid Trapping

Trapping is an important form of nonsorptive retention of contaminants in the subsurface. Trapping may occur, for example, when spills of water-immiscible fluid compounds (e.g., petroleum products) leave residual ganglia or bulb configurations in the subsurface.

Water and immiscible fluids interact during transport through pore spaces, distributing themselves according to the properties of the liquids and of the solid and gas phases. Above the retention capacity, subsurface pore geometry permits the flow of nonwetting fluids, leaving behind clusters of water-immiscible liquids that are disconnected from the main body of organic liquid. These clusters are sometimes called *blobs* or *ganglia*, with the trapped immiscible fluid being referred to as the residual organic liquid saturation. Figure 5.7 illustrates the retention of such a liquid in a partially saturated porous medium. Thus, trapped immiscible liquid can remain in the vadose zone for an indefinite time, serving as a source of contamination that decreases in magnitude as a result of processes such as volatilization into the gas phase, dissolution in the leaching water, or chemically or biologically induced decomposition. The degree of porous medium saturation by an immiscible liquid can be expressed in terms of the utilization of pore space by the liquid and air phases (van Dam 1967; Schwille 1984) or as the organic liquid content in volume units.

If the organic liquid saturation is measured as the volume of organic liquid per unit void volume, measured over a representative volume of the porous medium, then S_o, the fraction of pore space occupied by the organic liquid is

$$S_o = V_{\text{organic liquid}} / V_{\text{voids}}, \tag{5.15}$$

where the subscript o indicates the organic liquid. The residual saturation at which the organic liquid becomes discontinuous and immobile is then

$$S_{or} = V_{\text{discontinuous organic liquid}} / V_{\text{voids}}, \tag{5.16}$$

where the subscript or indicates residual organic liquid. In the saturated zone, the water saturation (S_w) is given by $S_w = 1.0 - S_o$.

The extent of trapping is determined primarily by the physical properties of the vadose zone. If the organic liquids are characterized by a low vapor pressure and a low solubility in water, they remain trapped in the partially saturated zone. In this particular case, the porous medium behaves like an inert material and the behavior of the organic liquids depends only on their own properties, with no interaction between the liquid and the solid phases.

5.7.3 Particle Deposition and Trapping

Retention of suspended particles in porous media occurs by straining (trapping), physicochemical filtration (deposition), and detachment. Depending on the size of the suspended particle, a number of mechanisms may be responsible for physicochemical filtration: (1) *gravitational sedimentation*, where the gravitational forces acting on the particle cause it to settle onto a sediment grain (collector), (2) *interception*, where the particle size and trajectory are such that it encounters the collector grain while flowing past, and (3) *Brownian diffusion*, where the particle is brought into contact with a collector due to its Brownian motion (Yao et al. 1971; Elimelech et al. 1995). Geometric models (Sakthivadivel 1966, 1969) suggest that straining could have a significant influence when the ratio of the particle diameter to the median grain diameter of the porous medium is greater than 0.05. Similarly, a limiting ratio of 0.154 for predicting straining of particles in constrictions has been proposed (Herzig et al. 1970). However, recent experimental evidence suggests that straining could be important at much smaller particle to grain size ratios (Bradford et al. 2003). Mobilization (detachment) of deposited particles also is a key process governing colloid transport and fate. Mobilization can take place following drastic changes in pore water chemistry and when the hydrodynamic forces overcome the adhesive forces between particles and the medium grains (Amirtharajah and Raveendran 1993).

Deposition and trapping of contaminants on colloidal materials and other suspended particles may occur during their transport through the vadose zone and thus create an additional route for pollutant distribution in the subsurface. Below hazardous waste sites, for example, an unexpected transport process of cationic radionuclides (e.g., Pu, Am) or various heavy metals has been observed, which can be explained only by colloid-facilitated transport (McCarthy and Zachara 1989; Penrose et al. 1990; Ryan and Elimelech 1996). Laboratory experiments testing colloid-facilitated redistribution in the partially saturated zone confirmed that colloids can accelerate the transport of cationic and anionic metals (e.g., Vilks et al. 1993) or toxic organic chemicals (e.g., Vinten et al. 1983). Colloidal materials involved in the process of enhanced redistribution of contaminants in the subsurface include inorganic matter like clay minerals, oxides and carbonate particles, with sizes in the range of 10 nm to a few micrometers, as well as organic colloids like humic substances and microbial exudates.

Vinten et al. (1983) demonstrated that the vertical retention of contaminated suspended particles in soils is controlled by the soil porosity and the pore size distribution. Figure 5.8 illustrates the fate of a colloidal suspension in contaminated water during transport through soil. Three distinct steps in which contaminant mass transfer may occur can be defined: (1) contaminant adsorption on the porous matrix as the contaminant suspension passes through subsurface zones, (2) contaminant desorption from suspended solid phases, and (3) deposition of contaminated particles as the suspension passes through the soil.

The suspended solid particle size and the volume of effluent also must be considered in examining deposition in the subsurface. For example, under leaching of a waste disposal site or following irrigation with sewage effluent, the coarse fraction of suspended solids is retained in the upper layer, while the finer colloidal fraction is more mobile, and its transport is controlled by the porosity of the subsurface solid phase.

Particle deposition from aqueous suspensions onto stationary surfaces is a dynamic phenomenon characterized by a transient or time-dependent rate of deposition. The deposition of contaminated suspended particles is affected by the

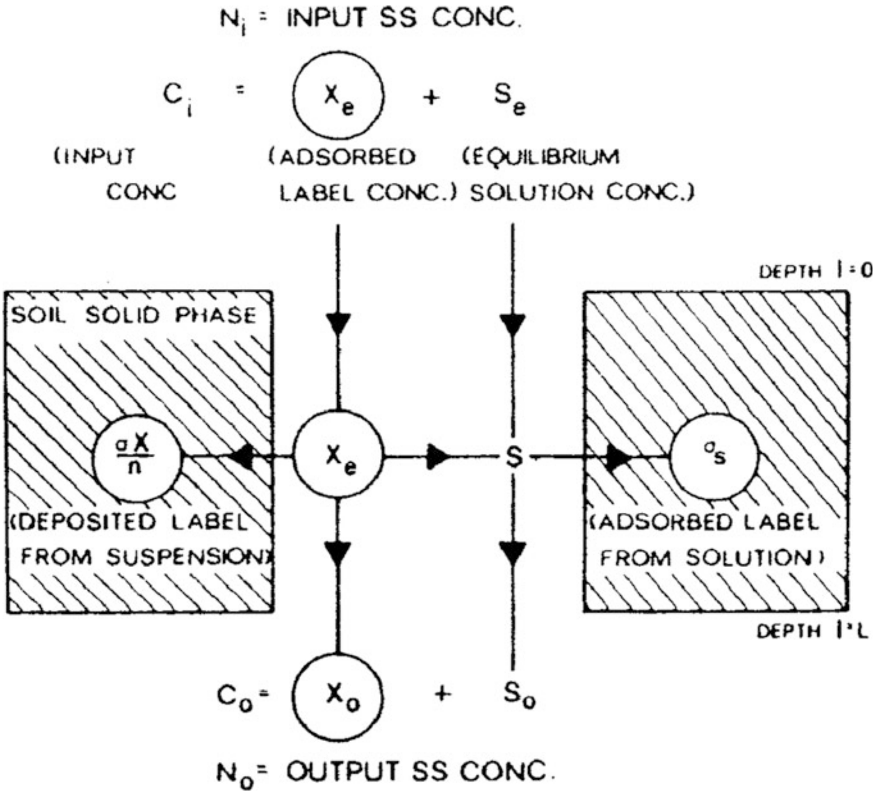

Fig. 5.8 Diagrammatic representation of transport of a labeled suspension through soil; *SS* denotes suspended solids (Vinten et al. 1983)

nature of the surrounding porous medium. A declining deposition rate is observed when particle–particle interactions are repulsive, so that the potential deposition zone becomes progressively occluded as particles accumulate; this leads to a blocking phenomenon.

Ryan and Elimelech (1996) note that conventional filtration theories are applicable only to the initial stage, when mineral grains are devoid of retained particles. As particles deposit onto mineral surface sites with charge characteristics favorable for deposition, the particle deposition rate progressively declines due to the blocking phenomenon. The heterogeneity of the subsurface makes application of deposition models very difficult, and therefore, they usually are relevant only for well-defined materials. Amitay-Rosen et al. (2005) used magnetic resonance imaging to demonstrate spatial and temporal deposition and trapping patterns of colloids in porous media.

5.8 Reversible and Irreversible Retention

Reversible and irreversible retention of contaminants on the subsurface solid phase is a major process in determining pollutant concentrations and controlling their redistribution from the land surface to groundwater. After being retained in the solid, contaminants may be released into the subsurface liquid phase, displaced as water-immiscible liquids, or transported into the subsurface gaseous phase or from the near surface into the atmosphere. The form and the rate of release are governed by the properties of both contaminant and solid phase, as well as by the subsurface environmental conditions. We consider here contaminants adsorbed on the solid phase.

Release through reversible retention can be assessed on the basis of physicochemical and biological processes. In the case of the former, release is caused by a change in the properties of the fluid surrounding the retaining solid phase. Lowering of the pollutant concentration in the liquid phase, for example, may cause a change in the established equilibrium, and as a consequence, enhanced transfer of the adsorbed compound to the liquid phase occurs. Also, contaminants that previously entered living organisms by an uptake process may subsequently be released. In many cases, the release isotherms do not coincide with the retention isotherms, indicating the phenomenon of hysteresis. This means that not all adsorbed molecules can be transferred back into the solution phase. In the subsurface, where a multicomponent solid phase is present, and where phenomena other than adsorption–desorption may occur, it is better to use the term *retention hysteresis* rather than *adsorption hysteresis*. Retention hysteresis may vary according to the nature of the contaminant and the solid phase, the site and sample history (e.g., wetting-dry cycles), and the experimental procedure used.

Genuine (true) and apparent hysteresis may be considered to explain contaminant release from the subsurface solid phase. Genuine hysteresis assumes that observed data are real and the equilibrium results can be explained on the basis of well-identified phenomena. Apparent hysteresis results from an experimental artifact due, for example, to a failure to reach retention or release equilibrium.

5.8.1 Genuine Hysteresis

Genuine hysteresis is considered when contaminant release results only from desorption. Experimental data can be interpreted in terms of genuine desorption only when the system is at equilibrium and released molecules are those adsorbed onto the solid-phase surface. Molecules brought back into the solution as result of dissolution, diffusion out of the solid matrix, or biotic/abiotic transformation cannot be considered desorbed molecules. In the subsurface, it is almost impossible to distinguish between desorbed molecules and molecules that were not subjected to adsorption and desorption.

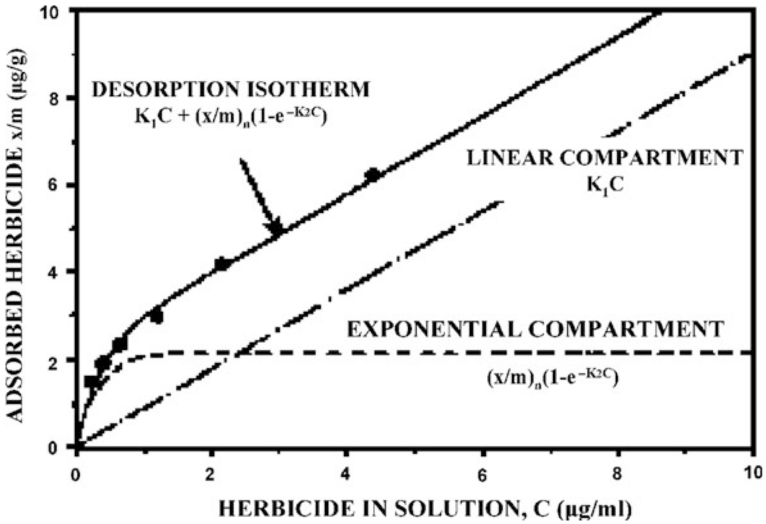

Fig. 5.9 Splitting of the desorption isotherm of dimefuron in the presence of 0.01 M $CaCl_2$ into two other isotherms, corresponding to the two-compartment (*linear*, *exponential*) model of desorption isotherms (Barriuso et al. 1992b)

Desorption isotherm may differ from adsorption isotherms for systems that are not at equilibrium, because the desorption rate is lower than the adsorption rate. Theoretical treatments by Ponec et al. (1974), for gas adsorption, and Giles et al. (1974), for solute adsorption, indicate that the activation energy for adsorption is zero or near zero. Under these conditions, these authors showed that the activation energy for desorption is greater than that for adsorption; consequently, the rate of desorption is lower than adsorption. This behavior pattern also is valid when adsorption is accompanied by dissociation of the adsorbed molecules (Ponec et al. 1974). Adsorbed molecules may be classified according to two categories: molecules retained through physical interactions and able to desorb and molecules that interact strongly with the solid matrix and therefore are released slowly or not at all (Barriuso et al. 1992a, b). Because different mechanisms are involved in the adsorption–desorption process, different types of desorption isotherms can be observed. In one case, desorption is described by a linear isotherm; in another case, the release is described by an exponential function for equilibrium concentrations in solution. Figure 5.9 gives an example of a combination of such correlations for the release of the herbicide dimefuron adsorbed on a clay loam soil.

Several other explanations have been put advanced to explain retention hysteresis, including (1) surface precipitation of metallic cations whose hydroxides, phosphates, or carbonates are sparingly soluble; (2) chemical reactions with solid surfaces, including organic surfaces, which form complexes with metallic cations; and (3) incorporation into the subsurface organic matter through chemical reactions and biochemical transformation. For the case described by Fig. 5.9 or explanations (1) and (2), the contaminant release always exhibits a hysteresis pattern. When dealing with chemical reactions and biochemical transformations (explanation 3), contaminant retention, in some situations, may reach total irreversibility.

5.8.2 Apparent Hysteresis

Apparent hysteresis occurs mainly when complete equilibrium is not reached. Diffusion into the solid matrix or into micropores of aggregates is considered a main cause of apparent hysteresis. In a transitory state, sorption occurs concurrently with desorption and the concentration of contaminant in the liquid phase is erroneously low because some fraction is associated with sorption.

Apparent hysteresis also may be caused by other phenomena. During the consecutive extractions and dilution steps used as a common technique in desorption studies, *weathering* of the sorbent may occur, resulting in a possible increase of contaminant sorption and decrease in its release. *Degradation* of the contaminant induced by physicochemical or biological factors, or a volatilization process leading to a decreased contaminant concentration in solution, are additional factors affecting a true hysteresis result.

The *moisture status* of the subsurface solid phase also may lead to an apparent hysteresis in the adsorption–desorption process. It is known that clay materials, mainly smectites, and humic substances can hydrate and swell or dehydrate and shrink. The physicochemical state of many molecules sorbed in wet conditions may be modified on drying, making the substances more difficult to desorb. The retention of sorbate molecules during drying or slow swelling of organic surfaces may be the reason for the decrease in their desorption. On rewetting, when molecules are sorbed at polar surface sites, they orient their hydrophobic part toward the solution phase, reducing considerably the access of water, and thus slowing down the swelling and desorption (Mingelgrin and Gerstl 1993).

Drying of the subsurface solid phase can cause an increase in the rate of desorption. If penetration of a sorbate toward inner surfaces does not reach its equilibrium by the time drying commences, a fraction of the sorbate may remain localized at more accessible outer surfaces in an amount greater than that corresponding to the equilibrium level. Under these conditions, the drying of the system may increase the rate of desorption during successive rewetting.

The *history of the surface* is an additional factor affecting the release of contaminants adsorbed on solid phases into the liquid or gaseous phase. For example, the effect of drying on contaminant desorption is influenced by the time allowed for its transport into the aqueous phase. In sorbing systems, like sediments that are permanently wet, the history of the system determines the fate of sorbed molecules (Pignatello 1989).

Release methodology may lead to incorrect desorption parameters, which in turn may be (erroneously) interpreted as hysteresis. For example, Hodges and

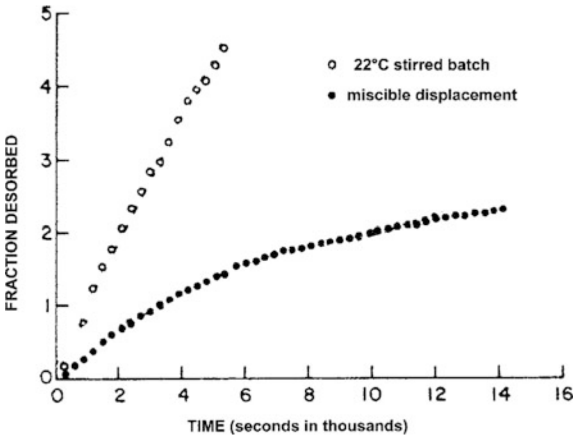

Fig. 5.10 Effect of measurement technique on sulfate desorption from soils (modified after Hodges and Johnson 1987)

Johnson (1987) used two experimental techniques (rapidly stirred batch and miscible displacement with slow flow rate) to study sulfate desorption and found that, in the stirred batch experiments, the desorption readings were less than those obtained by the miscible displacement technique (Fig. 5.10). Even within the miscible displacement technique, the time of leaching was found to have a major effect. The estimated (by extrapolation) time required for complete desorption was 10–20 times greater than for adsorption.

Bowman and Sans (1985) compared two methods (dilution and consecutive desorption) for measuring the desorption of selected synthetic organic pesticides from organo-clay systems. Note that dilution of suspensions may increase the accessibility of an adsorbing surface, so this method is not strictly comparable with the classical method. In all cases studied, only minimal hysteresis in the desorption isotherm was obtained using the dilution method, whereas almost all systems investigated with the consecutive desorption method exhibited considerably larger hysteresis. Rao and Davidson (1980) also suggested that, in the case of pesticides, the centrifugation–resuspension step is in some way responsible for the hysteresis effect, explained by the fact that partially irreversible compaction of the adsorbent during centrifugation greatly increases the time required for desorption.

5.8.3 Bound Residues

The term *bound residue* was adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1984. According to this definition and that of the European Commission (adopted in 1991), nonextractable residues in soil are chemical species, originating from pesticides, which are not extracted by methods that do not significantly change the chemical nature of the residue. Fuhr et al. (1998) expanded the meaning of *bound residues* to the “compounds in soil, plant

Table 5.6 Examples of bound pesticide residues in soils (Calderbank 1989)

Structural type	Bound residues (% of applied)	Parent detected
Herbicides		
Anilides and ureas	34–90	No
Bipyridyliums	10–90	Yes
Nitroanilines	7–85	No
Phenoxy	28	No
Phosphonate (glyphosphate)	12–95	Yes
Triazines	47–57	?
Insecticides		
Carbamates	32–70	Yes
Organochlorines	7–25	?
Organophosphates	18–80	Yes
Pyrethoids	3–23	No
Fungicides		
Chlorophenols	45–90	Yes?
Nitroaromatic (dinocap)	60–90	Yes?

or animals which persist in the matrix form of the parent substance or its metabolites after extraction." Gevao et al. (2000) include the proviso that bound residues do not include metabolites that are indistinguishable from naturally occurring compounds. Expanding this definition for the subsurface environment, we can state that *bound residues may comprise all toxic chemical species of anthropogenic origin (parent and metabolites) associated with the subsurface solid phase that cannot be separated by current extraction technology.*

Bound residues were first mentioned in the literature by Bailey and White (1964), in relation to pesticide extraction from soils. Over the years, many experiments have shown that the extraction of pesticides from soils is never complete, even when using solvents for which the molecules are highly soluble. Wanner et al. (2005) showed by analysis of ^{14}C-labeled molecules that the fungicide dithianon in soil exhibits bound residues of $\approx$63 % of the applied amount after 64 days. Calderbank (1989) showed that, for a large number of organic agrochemicals, up to 90 % of the applied radioactive-labeled substances become unextractable (Table 5.6). Calderbank (1989) examined a series of experimental data and noticed that different amounts of parent products become irreversibly retained as a function of their molecular structure (Table 5.6). Moreover, it was observed that the extractability decreases with aging, probably because the phenomena responsible for hysteresis become more efficient with increasing residence in soil.

The environmental significance of bound residues must be considered in relation to NOM (Barraclough et al. 2005). Contaminants entering the subsurface contain many functional groups similar to those of NOM and thus become involved in many of the same biological and chemical transformations. If, with aging, the bound residues become indistinguishable from subsurface organic matter, no environmental risk occurs. In contrast, however, if over time, the bound residues exhibit properties different than those of NOM, compounds having a toxic character become a contamination risk for the subsurface.

Bound residues of anthropogenic origin, found in the soil layer, may be compared with those of natural organic molecules released from plant and animal debris and utilized as a source of energy by microbial populations. Parent molecules and their metabolites may interact in the subsurface with the organic matter and then be desorbed and develop further by long-time contact. In this process, known as *aging*, molecules become more tightly bound or entrapped into organic matter or clay fractions of the solid phase. Barraclough et al. (2005) noted that the mass balance of xenobiotics in the subsurface exhibits the same variation as that seen with natural products, in terms of their partitioning between evolved CO_2 and their incorporation into the humic and fulvic substances. For example, more than 80 % of the labeled carbon from a number of xenobiotic compounds was still in the soil several years following their application (Burauel and Fuhr 2000). In a different case, 73 % of the carbon originating from a labeled phenanthrene was recovered as CO_2 after only 82 days (Richnow et al. 2000). Note that the data on carbon evolution may show the rate of incorporation of the labeled carbon from xenobiotics into the subsurface solid phase, but such studies alone do not give information on the bonding of parent compounds and their metabolites on molecular levels. The type of interaction, however, is an important factor determining both the likelihood and rate of release and the form in which the molecules are mobilized.

The mechanism of bound residue formation is better understood today due to the use of advanced extraction, analytic, and mainly spectroscopic techniques (e.g., electron spin resonance, ESR; nuclear magnetic resonance, NMR; Fourier transform infrared spectroscopy), methods that are applied without changing the chemical nature of the residues.

Physical entrapment following intraorganic matter diffusion (IOMD) or interparticle diffusion in clay minerals is another potential explanation for the formation of bound residues. Diffusion out of the solid phase may account partly for hysteresis, particularly for molecules that diffused into the organic aggregates. Entrapping in humic polymer aggregates, suggested by Kahn (1982) and further examined by Wershaw (1986) and Kan et al. (2000), is a possible explanation for hysteresis of substances compatible with the structure of humic substances. The rapid desorption phase is a result of an entrapped pool of readily desorbed material, and the slow phase is controlled by an entrapped or irreversible compartment inside the most hydrophobic part of humic aggregates.

To calculate the release through diffusion of an entrapped residue, Barraclough et al. (2005) considered the size of organic matter particles (effective radius 10^{-7} to 10^{-9} cm) and the effective diffusion coefficient of small organic molecules in a sorbing medium ($D \approx 10^{-9}$ cm^2/s). The time for 50 % of the material in a sphere to diffuse out is given by

$$t_{1/2} = 0.03r^2/D, \tag{5.17}$$

where r is the effective radius (cm) and $t_{1/2}$ is in seconds (Helfferich 1962).

For these entrapped contaminant "spheres," the diffusion is rapid, on the order of seconds rather than days. Kan et al. (2000) suggested a diffusion model for xenobiotics with a slow desorption phase, with a half-life of years rather than seconds, assuming that diffusion is hindered by the NOM matrix and occurs when the dimensions of diffusing molecules approach those of the pores. Under these conditions, hindrance from the wall becomes significant (Renkin 1954) and the drag factor F can be expressed as

$$F = 1 - 2.09\left(r_m/r_p\right) + 2.14\left(r_m/r_p\right)^3 - 0.95\left(r_m/r_p\right)^5 + \cdots, \tag{5.18}$$

where r_m and r_p are the radii of the molecule and the pore, respectively. To extend the diffusion half-life from seconds to years would require a drag factor of around 10^{-8}, in the case where no interaction occurs between the diffusing molecules and the entrapping matrix.

Another process leading to irreversible retention involves chemical binding of contaminant molecules to organic matter (Bollag and Loll 1983). Fulvic and humic acids are the compounds commonly involved in such binding. If binding on organic matter matrix involves physical entrapment, van der Waals forces, or charge transfer, significant release occurs only as a result of matrix-induced degradation by microorganisms or plant enzymes. The reactions involved appear to be the same as those responsible for humic substance formation. Phenol and aromatic amines may bind to organic matter by oxidative coupling, while substituted urea and triazines may not (Bollag et al. 1992). Binding of toxic organic molecules on an organic matter matrix can take place also during humic substance formation by polymerization processes.

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