9

ANION AND MOLECULAR RETENTION

Soil particles remove anions and molecules from the soil solution, and release others to the soil solution, in varying degrees. The mechanisms of retention and release are electrostatic and chemical bonding. The mechanism of ion retention is actually exchange but the H^+, OH^-, and other ions released are usually unnoticed. These retention mechanisms are combinations of adsorption, absorption, precipitation, and solid solution mixing; distinguishing between the mechanisms is difficult. Soil–anion interaction varies from slight repulsion to weak to very strong attraction and retention (Table 9.1).

Differences in retention between the groups is illustrated by Fig. 9.1. A soil naturally high in chloride and borate was leached successively with 40 pore volumes of water. (A pore volume of water is that amount which fills all the voids between the soil particles.) The Cl^- concentration in the effluent was 1100 mM initially and decreased rapidly to almost zero after 5 pore volumes of water had passed through the soil. The $H_3BO_3/H_2BO_3^-$ concentration was about 15 mM initially and decreased much more slowly than Cl^-.

The leaching was stopped for 30 days and then was continued for 10 more pore volumes of water. The initial chloride concentration, the "rebound," was 0.5 mM

Table 9.1. Anion and molecular interaction with soils

Repelled to Weakly Retained	Moderately Retained	Strongly Retained
NO_3^-, SO_4^{2-}, SeO_4^{2-} HCO_3^-, CO_3^{2-}, ClO_4^- Cl^-, Br^-, I^-	H_3BO_3, $H_2BO_3^-$, F^- CrO_4^{2-}	$H_2PO_4^-$, HPO_4^{2-}, H_2S, HS^- $H_2AsO_4^-$, $HAsO_4^{2-}$, MoO_4^{2-}

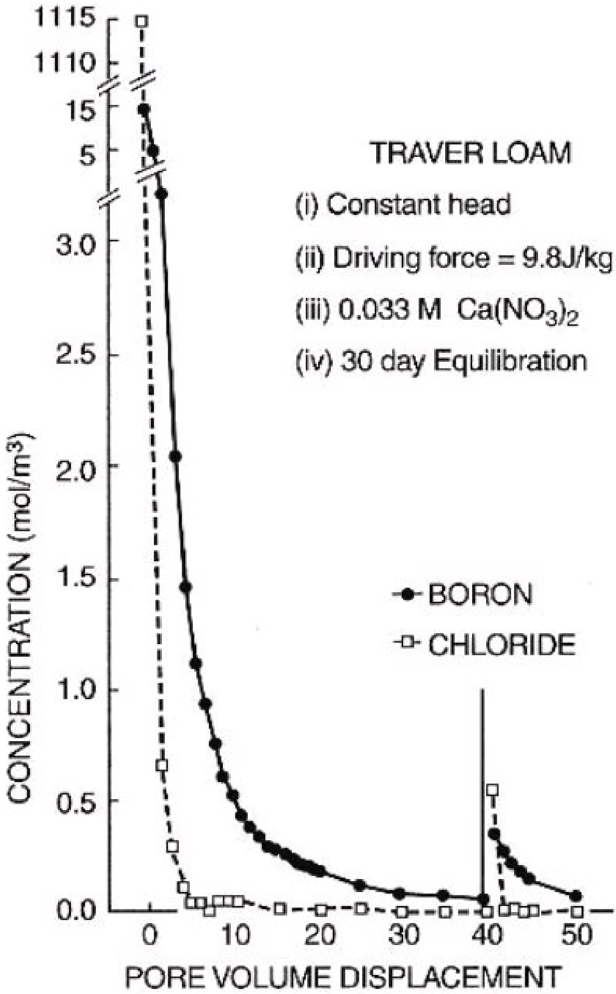

FIGURE 9.1. Boron and Cl^- concentrations in successive pore volume displacements (PVD) of the Traver loam soil. The solid vertical line at PVD = 40 indicates an intervening 30-day, saturated storage period. F. J. Peryea, F. T. Dingham and J. D. Rhoades. 1985. *Soil Sci. Soc. Am. J.* **49**:840.

and the borate concentration was 0.3 mM. The shape of the chloride and borate curves were the same as the first leaching sequence: Cl^- decreased rapidly again and borate decreased more slowly. The relative amount of borate that was released to the leaching solution during the 30-day incubation period was much greater than that of chloride.

Chloride was not retained by the soils. The chloride increase in the second leaching sequence was due to Cl^- diffusion from pores that were stagnant during the first leaching sequence. The borate increase, on the other hand, was due to a redistribution of available borate during the 30-day interval. Diffusion would account for only a tiny fraction of the second borate peak because the aqueous borate concentration was so much less than the aqueous chloride concentration. The second borate peak was due to slow release of borate ions from retention sites in the soil, a redistribution of borate to reestablish the "equilibrium" between strongly adsorbed and weakly adsorbed borate that was disturbed when the first leaching sequence depleted the weakly held fraction. The strongly adsorbed sites may have been deeper in the soil's weathered surface layer.

Strongly retained ions such as phosphate are released to the soil solution in the same way as borate but at lower concentrations and at slower rates. Weakly retained ions, in contrast, reach an equilibrium or steady-state concentration between the soil surface and the soil solution very quickly. When added to soil suspensions in the laboratory, phosphate in the soil solution decreases rapidly at first and continues to decrease over periods of weeks in the laboratory and weeks to months in the field. The laboratory reaction goes faster because the mixing and contact between soil particles and the soil solution is more complete.

Weak anion attraction and repulsion (anion exchange) in soils is primarily electrostatic and is similar to cation exchange. Anion exchange is rapid and reversible and the anion attraction is weak; chemical bonding is slower and stronger. Soils in Europe and North America are predominantly weakly to moderately weathered soils of neutral pH and have appreciable organic matter. In these soils the cation exchange capacity CEC greatly exceeds the anion exchange capacity (AEC). This preoccupation with cation exchange goes back to the initial studies by Thompson and Way in England in 1850. Soil chemistry has reflected this geographical bias. Anion exchange is important in Australia, New Zealand, and South Africa, where some soils are strongly weathered and have low organic matter contents and low pH; it occurs in European and North American soils, too.

In strongly weathered soils of low pH and low soil organic matter, and in soils derived from volcanic parent material, the AEC can equal or exceed the CEC (Table 9.2). The predominance of AEC or CEC can change from one stratum to the next in the same soil as the pH and composition of the soil strata change. Many of these high-AEC soils are coincidentally in the Southern Hemisphere, but anion exchange is also significant in acidic and highly weathered soils of the southeastern United States, in European forest soils, and in Japan.

One reason for the lesser interest in anion exchange may be that sulfate is the only macro-essential ion for plants that is retained to a significant extent as an exchangeable anion. Cation exchange, in contrast, covers four major cations: Ca, Mg, K, and Na. Each category in Table 9.1 covers a range of retention. Among the "weakly retained" anions, sulfate and probably selenate are retained the strongest by soils, because of their divalent charge. Nitrate, chloride, and perchlorate are retained the weakest. Nitrate and chloride are indeed considered to be repelled, rather than retained, in predominantly negatively charged soils because their retention is so weak. As in cation exchange, anion retention depends on the size and charge of the hydrated ion and on the ability of the ion to covalently bond with the soil surface.

The soil's retention of water-soluble cations and anions depends largely on colloid and ion charge. The aluminosilicate layer–lattice minerals tend to dominate the clay fraction of temperate and arid region soils. These minerals are predominantly negatively charged, so their physical adsorption of cations exceeds their adsorption of anions. Many anions of interest, however, are weakly soluble because they form strong chemical bonds with the cations in soil clays. These bonds can overcome the electrostatic repulsion of the negative charge and lead to strong soil retention.

Anion retention received little attention in North America until research on toxic wastes and on anionic pesticides demonstrated the importance of anion retention.

Table 9.2. Charge characteristics of various soil orders

			Charge $cmol_c\ kg^{-1}$	
Soil Order	Horizon	pH_{Salt}	Negative	Positive
Oxisol (Morais et al., 1976)	A	3.0	3.9	3.2
	A	7.8	11.6	1.4
	B	3.0	2.5	5.1
	B	8.2	5.3	2.0
Ultisol (Morais et al., 1976)	A	3.0	1.0	1.1
	A	8.5	5.0	0.8
	B	3.0	2.5	2.4
	B	8.5	3.8	1.7
Alfisol (Morais et al., 1976)	A	2.9	3.8	2.0
	A	8.5	14.0	−1.6
	B	2.9	2.4	5.5
	B	8.5	9.5	1.9
Andisol (Sumner et al., 1993)	A	4.6	3.8	2.6
	B	5.1	1.9	4.2
Oxisol (Sumner, 1963b)	B	3.5	2.3	5.1
	B	8.2	8.0	1.0

M. E. Sumner. 1998. *Future Prospects for Soil Chemistry*, Soil Science Society of America, Madison WI. Special Publication Number 55.

Strongly weathered soils contain Al and Fe(III) hydroxyoxides whose negative charge is low and whose positive charge can be relatively high, especially at low pH. When acidic, these "*variable charge*" soils can retain more anions than cations. The amorphous weathering products of volcanic soils of Japan also exhibit variable charge.

Molecular retention nowadays mostly refers to the widespread interest in the retention of organic pesticide molecules by soils. These molecules are mostly electrically neutral overall but have functional groups (PO_4^{3-}, Cl^-, NO_2^-, etc.) that interact with organic and inorganic soil solids. Positively and negatively charged molecules behave somewhat like simple cations or anions.

The soil's retention of uncharged molecules is largely independent of colloidal charge. For these substances, the soil is an inorganic matrix whose retention is based on the molecule's tendency to distribute between the gaseous, aqueous, and solid organic and inorganic soil phases. For organic molecules, this tendency depends on relative volatility, molecular weight, chemical composition, physical structure, solubility in the soil solution, the soil's organic matter content, and to some extent the soil's surface area. If the molecule also contains functional groups of inorganic nature, such as R—CO, R—COOH, R—CHO, $R—PO_4$, and $R—NH_2$, soil retention increases. The R—Cl unit of chlorinated hydrocarbons generally adds little to retention except by increasing the molecule's mass and nonvolatility.

The absorption of acid-forming gases (SO_2, NO, NO_2, HF, HCl) from the air increases with the molecule's water solubility and reactivity and increases with the soil's pH and base status. Weak bases such as NH_3 are retained more strongly by acid soils.

Soluble silica is ubiquitous in soil solutions, commonly at concentrations of about 10^{-4} M, or 2–5 mg Si L^{-1}, and is present as $SiOH_4$ rather than as an anion. It is less accurately described as silicic acid H_4SiO_4 because it is a very weak acid, $pK \sim 10^{-10}$. Soluble silica already saturates the soil sorption sites so little is removed from solutions flowing through soil. Indeed, the course of soil weathering is the slow release of soluble silica to the soil solution. The chemistry of silica is dominated by very slow reaction rates and by the presence of many forms of silica and aluminosilicate minerals of varying aqueous solubility. The solubility of quartz (SiO_2), chalcedony, chert, and other forms of SiO_2 is about 3 mg Si L^{-1}. Amorphous and hydrated opal $SiO_2 \cdot H_2O$ is soluble to the extent of 100 mg L^{-1}. The range of equilibrium aluminosilicate solubility is broader, but equilibrium and silicate solubility are rather incompatible terms. Particle size is at least as important a determinant of the soluble silica concentration in the soil solution.

The anions of concern to agriculture include Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, OH^-, and F^-. In addition, some micronutrients ($H_2BO_3^-$, MoO_4^{2-}, and $HAsO_4^{2-}$) and heavy metals (CrO_4^{2-}) exist as anions in soils, as do some pesticides, such as the dissociated phenoxyacetic acids (2,4,5-T and 2,4-D). Molecular species of interest include NH_3, undissociated weak acids such as H_3BO_3 and H_4SiO_4, and the undissociated forms of many pesticides (DDT, 2,4,5-T, ant 2,4-D.) The study of anionic and molecular retention by soils has been the subject of increasing research in recent years.

The approach in this chapter is to describe various retention mechanisms and to cite examples of their involvement in the retention of specific anionic and molecular species. Several of the mechanisms are general and apply to many of the species listed above. Adsorption isotherms are also discussed because of their widespread use to describe anion and molecular retention by soils.

9.1 ANION EXCHANGE

Anions are attracted by positively charged sites on surfaces and repelled by negative charges. Layer silicates in the clay fraction of soils are mostly negatively charged so that anions tend to be slightly repelled electrostatically. Soils, however, contain solids, including the layer silicates, that also develop positive charges (often simultaneously though in different locations). An anion approaching soil solids may thus be simultaneously repelled by negatively charged aluminosilicate surfaces and attracted to positive charges on clay edges, hydrous oxides, and allophane.

If a dilute, neutral solution of KCl is added to dry montmorillonite, the equilibrium Cl^- concentration in the bulk soil solution will be greater than the Cl^- concentration in the solution originally added to the clay. This phenomenon is observed whenever a salt solution is added to a dry colloid having no adsorbing capacity for the anion at the prevailing pH. The process is called *anion repulsion*, or less accurately *negative adsorption*, and is due to anion repulsion from the diffuse double layer (DDL) surrounding charged colloid surfaces. An alternative explanation for the increased Cl^- concentration in the bulk solution is hydration of the montmorillonite with H_2O, leaving less water for the salt.

Factors affecting anion repulsion include (1) anion charge and concentration, (2) species of exchangeable cation, (3) pH, (4) presence of other anions, and (5) nature and charge of the colloid surface. Ions commonly exhibiting net anion repulsion include Cl^-, NO_3^-, and SO_4^{2-}. Anion repulsion, as moles repelled per unit area of solid surface, increases with anion charge (valence). If the negative charge of a soil colloid surface remains constant and if no other reactions take place, anions of higher charge are repelled more than anions of lower charge. Mattson found that anion repulsion in a Na-montmorillonite suspension increased in the order: $Cl^- \approx NO_3^- < SO_4^{2-} < Fe(CN)_6^{4-}$. In soils that are dominated by Ca or other polyvalent cations, chemical reactions with the cations often change this purely electrostatic order. Increasing the anion concentration also increases the number of anions repelled, although the volume of the DDL from which the anions are excluded, the *exclusion volume*, decreases.

Anything that affects the DDL also affects anion repulsion. Thus, the Cl^- exclusion volume of layer silicate suspensions increases in the order $Ba^{2+} < Ca^{2+} < K^+ < Na^+$. The multiply charged and more tightly adsorbed cations better neutralize the negative charge and produce a more condensed double layer, so that a smaller number of anions is excluded and the exclusion volume is less. Lowering the pH decreases the soil's net negative charge and increases the positive charge, so anion repulsion decreases with soil pH.

Anion repulsion also decreases when anions can be adsorbed by positively charged sites on soil colloids. Pretreatment of the colloids with highly charged and tightly adsorbed anions such as phosphate can mask the positive charges. These adsorbed anions present a negative surface to anions added later. Anion repulsion is then greater than in the absence of the tightly adsorbed anions.

The greater the negative charge of the soil solids, the greater the anion repulsion. Montmorillonitic soils thus exhibit greater anion repulsion than do kaolinitic soils at all pH values, and especially at low pH, where kaolinite can develop a positive charge. Anion repulsion can have important consequences during solute transport through soils. When anions are excluded from some of the volume of water surrounding soil particles, the anions can travel through the soil as a concentration bulge at the water front. The anions thus appear to travel faster through the soil than the water carrying them.

Anions approaching positively charged sites on layer silicate or hydrous oxide minerals are attracted electrostatically in the same manner as cations are attracted to negatively charged soil colloids. The effects of ion concentration, valence, and complementary ion on the distribution of exchangeable anions are similar to the effects described for cations (Chapter 8). Electrostatically retained anions are said to be *nonspecifically adsorbed*. Figure 9.2a illustrates the nonspecific adsorption of Cl^-. The dotted line shows electrostatic attraction of a positively charged mineral

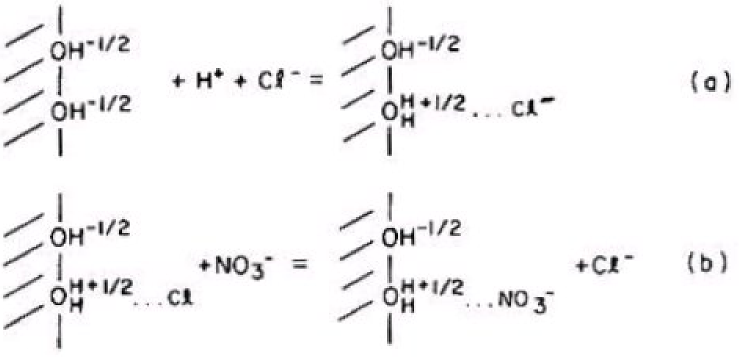

FIGURE 9.2. Nonspecific anion reactions at a solid/solution interface: (a) adsorption, (b) anion exchange. (After F. J. Hingston, R. J. Atkinson, A. M. Posner, and J. P. Quirk. 1967. *Nature* **215**:1459–1461.)

surface site for the anion. The positive charge in this case is the result of surface protonation, which increases with soil acidity. Figure 9.2b shows the exchange of one nonspecifically adsorbed anion (NO_3^-) for another (Cl^-). Exchange equations similar to those developed for cation exchange describe such reactions because nonspecifically adsorbed anions are in the solution adjacent to the solid surface and are readily exchangeable.

The Cl^-, NO_3^-, and SO_4^{2-} anions are considered to be nonspecifically adsorbed. Table 9.1 shows typical data for Cl^- and SO_4^{2-} adsorption by soils. The capacity of soils to adsorb anions increases with increasing acidity and is much greater for the kaolinitic soil, which has significant pH-dependent charge. At all pH values, the divalent SO_4^{2-} ion is adsorbed to a greater extent than the monovalent Cl^- ion, as would be expected on the basis of electrostatic attraction forces alone.

For the montmorillonitic soil, where pH-dependent charge and thus positive charge are of minor importance, Cl^- is adsorbed only slightly at low pH and not at all in the slightly acid to neutral pH range. Such data are typical of nonspecifically adsorbed anions. Even for kaolinite, and for soils containing considerable pH-dependent charge, anion adsorption is negligible at $pH > 7$. The generally negative charge of $pH > 7$ soils repels nonspecifically adsorbed anions.

Chloride, nitrate, and sulfate are common and important anions in most soils and have been studied extensively. Chloride, in particular, is often used as an indicator of NO_3^- mobility in soils, since Cl^- is not subject to the complicating biological reactions characteristic of NO_3^- . In most other respects, Cl^- behaves similarly to NO_3^-.

9.2 STRONG ANION RETENTION

Anions strongly retained by soils include PO_4^{3-}, AsO_4^{3-}, MoO_4^{2-}, CrO_4^{2-}, and F^-. These anions are essential microelements for plants and animals and are present in trace concentrations in the solutions of native soils. Because the amounts and tenacity of soil retention of these ions is so much greater than Cl, NO_3, and others, this retention has been misnamed as *specific adsorption*. These anions are simply water insoluble in the presence of the typical cations and colloids in soils. The state of these anions in the soil solution is a matter of great economic and environmental concern. Phosphate deficiency of agricultural crops is an ongoing global problem. A newer aspect is that these anions are being added to soils in fertilizers, agricultural wastes, fly ash from coal combustion, and municipal and industrial wastes. Initially, the additions increase the soil solution concentrations and plant availabilities of these anions. Since concentrations may reach levels that are appreciably greater than native levels, land disposal of such wastes has created public fear.

Some concerns about the safety of waste disposal on soils may be exaggerated. Within days to several weeks, the plant availability and movement of many ions decrease sharply and are nearly indistinguishable from the native concentrations, if the wastes are well mixed with the soil. The native concentrations of all ions vary widely from soil to soil yet their concentrations in plants and groundwater are low. If the wastes are distributed widely and the soil is given some time to react with the wastes, the probability of contaminated food or water is very low. Concentrating wastes in "hazardous waste landfills" where we try to isolate wastes from the environment is well intentioned, but prevents soil mixing and may be, in the long run, a counterproductive method of dealing with wastes.

The agricultural contribution to lake and stream contamination probably comes mostly from surface runoff of fertilized fields and from feed lots rather than from actual drainage water. Mixing, dilution, and time can mitigate soil contamination problems.

Anion removal from the soil solution is fast initially, but slows thereafter as the ions diffuse into the weathered and porous aqueous–solid phase on the surfaces of soil particles, increasing the diffusion pathlength. The diffusion also slows because the aqueous concentration, the driving force of the diffusion, is much less. Diffusion continues longer in the field than in the laboratory because the diffusion pathlengths from phosphate fertilizer granules to soil particles are much longer, and the water films on particle surfaces are thin. Phosphate retention in stirred suspensions in the laboratory reaches a steady state after several days. Phosphate from fertilizer granules in the field can release phosphate to plants for weeks before the phosphate is strongly adsorbed by the soil.

A hydrous oxide system is *amphoteric*; that is, its surface charge varies from negative to neutral to positive, depending on the pH of the aqueous solution. An electrostatic approach explains the exchange properties of hydrous oxides for chloride, sulfate, and other water-soluble anions. These surfaces can also interact chemically and strongly with weakly water-soluble anions. This gives Fe oxide- and Al oxide-dominated soils a much greater adsorption capacity for these anions than that predicted from electroneutrality alone, that is, greater than the quantity of adsorbed anions required to neutralize the surface positive charge. Indeed, iron oxides and other oxides scavenge (remove) arsenate, phosphate, molybdate, and other anions from solution with high efficiency.

Oxygen ions on a hydrous oxide surface can be replaced by oxyacid anions, such as phosphate, and by fluoride, which can enter into sixfold coordination with Al or Fe ions. This is known as *ligand exchange*, or *anion penetration*, for it takes place

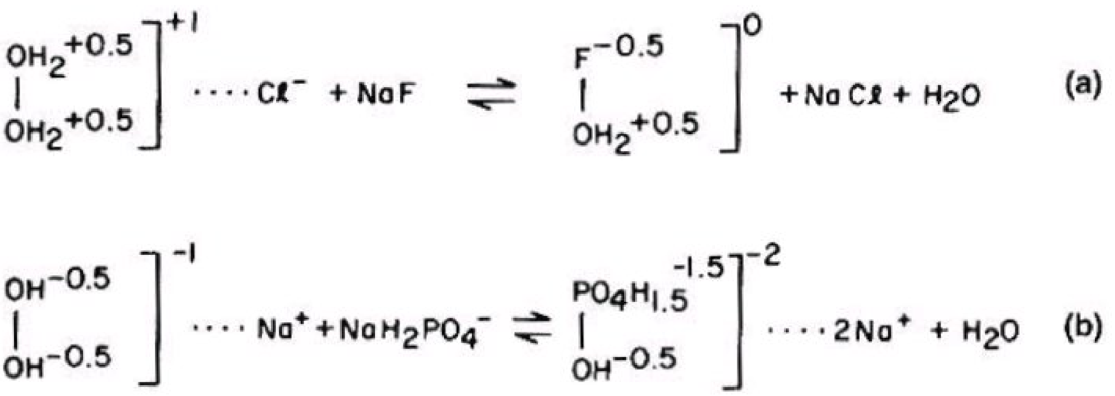

FIGURE 9.3. Specific anion reactions at a solid/solution surface: (a) Neutralization of positive charge, and (b) ionization of a proton of an adsorbed acid anion. (After F. J. Hingston, R. J. Atkinson, A. M. Posner, and J. P. Quirk. 1963. *Trans. 9th Int. Cong. Soil Sci.* 1:669–677.)

within the crystal and renders the surfaces of oxides more negative. The negative charge arises when part of the liberated hydroxyl ions are neutralized by the formation of water (Fig. 9.3). Ligand exchange can occur on surfaces initially carrying a net negative, positive, or neutral charge. This contrasts with nonspecific anion adsorption, which occurs only when the surface carries a net positive charge. Ligand exchange may explain why weak-acid anions show maximum adsorption at pH values about equal to their pK values (Fig. 9.4). At pH $=$ pK, both the amounts of

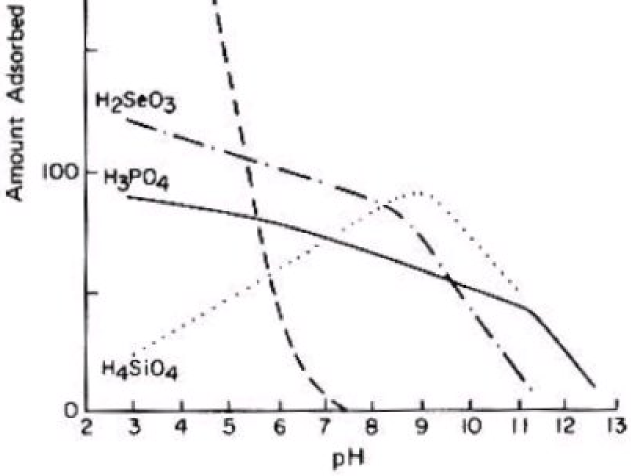

FIGURE 9.4. The adsorption of three oxyacids and fluoride on geothite as a function of pH. HF, pK = 3.45; H_2SeO_3, pK_2 = 8.35; H_3PO_4. pK_1 = 2.12, pK_2 = 7.21, pK_3 = 12.67; H_4SiO_4, pK_1 = 9.66. (After F. J. Hingston, R. J. Atkinson, A. M. Posner, and J. P. Quirk. 1968. *Trans. 9th Int. Cong. Soil Sci.* 1:669–677.)

anion (dissociated acid) available for ligand exchange and the amounts of undissociated acid capable of neutralizing liberated OH^- are greatest.

Fluoride ion is moderately adsorbed by soil minerals. Figure 9.4 shows fluoride adsorption by goethite (FeOOH). Fluoride adsorption conforms to the ligand exchange theory and is probably favored by the close similarity in size of F^- and OH^- ions. In acid soils at equal anion concentrations, F^- adsorption predominates over that of other common anions. This makes F^- an effective desorbing agent for previously adsorbed anions.

9.2.1 Phosphate Reactions in Soils

Phosphate is probably the most important example of specifically adsorbed anions. Many soils fix large quantities of phosphate by converting readily soluble phosphate to forms less available to plants. In terms of ligand exchange or anion penetration theory, phosphate adsorption on oxide surfaces can be explained by Fig. 9.5. Phosphate replaces singly coordinated ("A-type") OH groups and then reorganizes into a very stable binuclear bridge between cations.

In the laboratory, phosphate adsorption by layer silicates is rapid for a few hours and then continues more slowly for weeks. The initial rapid reaction can be envisioned as a combination of nonspecific adsorption and ligand exchange on mineral edges. The slower reaction probably consists of a complex combination of mineral dissolution and precipitation of added phosphate with exchangeable cations or cations within the lattices.

Low and Black showed that phosphate retention by kaolinite increased with time and phosphate concentration. Silica concentrations in the bulk solution increased simultaneously. The reaction was thought to be a two-stage reaction:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H^+ + 2H_2O = 2Al(OH)^{2+} + 2Si(OH)_4 \tag{9.1}$$

$$Al(OH)^{2+} + HPO_4^{2-} = \underset{\text{variscite}}{AlPO_4 \cdot H_2O} \tag{9.2}$$

with the Al phosphate precipitating on the surface or phosphate tetrahedra substituting for silicon tetrahedra. The more generally accepted explanation nowadays is the dissolution of Al^{3+} as kaolinite breaks down, followed by the precipitation of

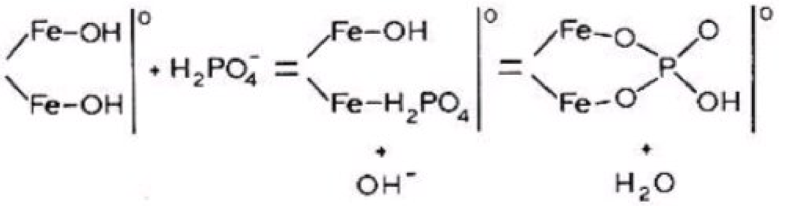

FIGURE 9.5. Representation of $H_2PO_4^-$ penetration into an iron oxide surface and subsequent formation of a stable binuclear bridge. (After J. C. Ryden, J. K. Syers, and F. R. Harris. 1973. *Adv. Agron.* **25**:1–45.)

Al phosphate. When hectorite (a 2:1 layer silicate in which Mg^{2+} is the dominant octahedral cation rather than Al^{3+}) is substituted for kaolinite, much less phosphate is retained. This points out the importance of Al to phosphate retention. In acid soils, phosphate retention is often closely related to the amounts of extractable Fe^{3+} and Al.

Phosphate forms weakly soluble Fe^{3+} and Al^{3+} compounds at low pH, more soluble Ca^{2+} and Mg^{2+} compounds at pH values near neutrality, and difficultly soluble Ca^{2+} compounds at higher pH. Lindsay and Moreno developed a solubility diagram for phosphate in a system containing variscite ($AlPO_4 \cdot H_2O$), strengite ($FePO_4 \cdot H_2O$), fluoroapatite ($Ca_{10}(PO_4)_6F_2$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), octocalcium phosphate ($Ca_4H(PO_4)_3$), and dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$). The solubility diagram (Fig. 9.6) describes equilibrium phosphate precipitation reactions at various pH values, but slow kinetics have prevented the quantitative application of solubility data to soils. In addition, assumptions have to be made about the activities and the solid phases that control the activities of Ca^{2+}, Fe^{3+}, and Al^{3+} in the soil solution. These assumptions limit the diagram to equilibrium, which can be approached but not reached in soils. Despite this shortcoming, Fig. 9.6 illustrates the changes in phosphate minerals as phosphate fertilizers slowly transform to less-soluble states in soils.

Figure 9.6 illustrates the relative stabilities of several phosphate compounds in soils of various pH values. Soil solution compositions can be plotted on the diagram by measuring soil pH and soluble phosphate concentrations. Data above a compound's isotherm represent supersaturation with respect to the solid, indicating that the compound will precipitate. Data below the isotherm indicate undersaturation of phosphate in the soil solution with respect to that compound, so that the solid, if

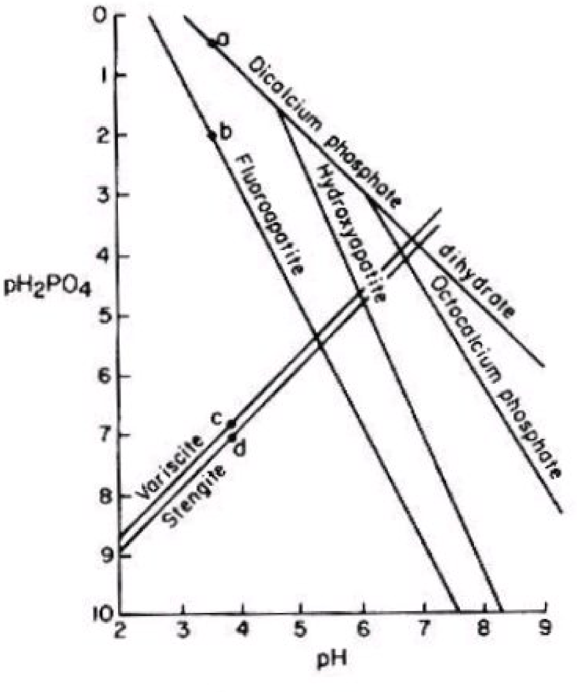

FIGURE 9.6. Solubility diagram for phosphorus compounds at 25° C and 5×10^{-3} M calcium. (After W. L. Lindsay and E. C. Moreno. 1960. *Soil Sci. Soc. Am. Proc.* **24**:177–182.)

present, would dissolve. Intersections of two isotherms represent solutions in equilibrium with both solids.

Consider a soil of pH 4 to which soluble phosphate fertilizer is added, resulting in a phosphate potential, or pH_2PO_4 (= negative logarithm of the $H_2PO_4^-$ activity), of 0.5. This is point *a*, which falls on the dicalcium phosphate dihydrate isotherm and is at equilibrium with that solid phase. Point *a* is above the isotherms for fluoroapatite, variscite, and strengite, indicating supersaturation of the aqueous solution with respect to these compounds. Fluoroapatite might tend to precipitate first, reducing phosphate levels in solution (and increasing the value of pH_2PO_4). Assuming constant soil pH, pH_2PO_4 will tend to increase to the equilibrium line of fluoroapatite ($pH_2PO_4 = 2.0$, point *b*). When pH_2PO_4 is greater than 0.5, the soil solution is undersaturated with respect to dicalcium phosphate dihydrate and it will dissolve, increasing the phosphate in solution once more. The phosphate concentration can be any value between *a* and *b*, depending on the rate of $CaHPO_4$ dissolution versus that of $Ca_5F(PO_4)_3$ precipitation. This precipitation–dissolution reaction will continue until all of the dicalcium phosphate dihydrate dissolves. The soil solution is then represented by point *b*, in equilibrium with fluoroapatite. The least soluble (most stable) compounds indicated on the diagram at acid pH are variscite and strengite. The soil solution at point *b* is highly supersaturated with respect to both of these compounds. As a result they should begin to precipitate immediately. The diagram predicts that both dicalcium phosphate dihydrate and fluoroapatite will eventually disappear to form variscite and/or strengite (points *c* and *d*). Either transformation results in a substantial reduction in soluble phosphate concentrations compared to those of the initially fertilized soil (point *a*). Large quantities of phosphate should thus be fixed as insoluble Fe^{3+} and Al phosphates in acid soils.

The diagram also indicates that phosphate should precipitate in basic soils as one of several Ca phosphates, the least soluble of which are hydroxy- and fluoroapatite. Variscite and strengite are too soluble to exist under basic conditions, and they should not form in basic soils. Both variscite and strengite, in fact, would be good phosphate fertilizers in alkaline soils because of their solubility in basic soils, if they were applied as finely ground materials. Calcium phosphate ore ("rock phosphate," mostly hydroxy- and fluoroapatite) is similarly effective in acid soils. Rock phosphate is treated with sulfuric acid to make "superphosphate," nominally $CaHPO_4$; treatment with phosphoric acid yields "triple superphosphate," nominally $Ca(H_2PO_4)_2$. Both superphosphate and triple superphosphate are more soluble than rock phosphate and make phosphate more immediately available when added to soils at any pH.

Figure 9.6 explains the observations that (1) phosphate is fixed in large amounts as iron and aluminum phosphates in acid soils, where Fe^{3+} and Al^{3+} activities are high; (2) calcium fixes phosphate similarly in basic soils, where Ca^{2+} activity is high; and (3) maximum amounts of phosphate are available at slightly acid to neutral pH where the solubilities of Fe, Al, and Ca phosphates are highest simultaneously.

For most soils, the various mechanisms responsible for phosphate retention are nearly impossible to separate. Phosphate is retained by a multistage process, probably involving several of the mechanisms described above as well as other unknown reactions. Even carefully designed experiments are often confounded by reactions other than those intended to be studied. Precipitation is especially difficult to eliminate as a mechanism; all of the specific adsorption mechanisms can be viewed as modified precipitation reactions.

The mechanisms of phosphate retention by soil organic matter are not known, but are believed to be important in maintaining plant-adequate levels of phosphate in the soil solution. Inositol hexaphosphate and possibly other organic phosphate compounds apparently are retained in soils by precipitation reactions. Many common, water-soluble, organic phosphate compounds become nonextractable to water at almost the same rate as, and to the same extent as, dissolved inorganic phosphates. Thus, although organic phosphate is reported to leach from soils, a large proportion of it appears to move attached to particulate matter rather than as dissolved phosphate. Retention mechanisms for organic phosphate include (1) sorption through orthophosphate groups to Fe and Al oxides by mechanisms similar to those for inorganic phosphate, and (2) sorption by interaction of the organic portion of the phosphate ester with organic or inorganic soil components.

At current rates of fertilizer usage, we have about a 200-year supply of good-grade phosphate ore worldwide. The importance of phosphate fertilization to agriculture and the relatively short supply of phosphate ore have led to many, as yet unsuccessful, attempts to increase the low availability of the large amounts of phosphate present in almost all soils. These attempts include leaching the soil with silicate, which might replace phosphate that is strongly retained by Fe, Al, and aluminosilicates; creating polymeric phosphate fertilizers (pyro- and metaphosphates) instead of the normal ortho (monomeric) forms; and breeding plant varieties that can better utilize soil phosphate. To overcome the high cost of shipping phosphate per unit P and of spreading it on rugged terrain, New Zealanders went so far as to propose spreading elemental P from airplanes. White P, however, is a dangerous explosive and the safe, polymeric red and black P forms are too insoluble and unreactive in soils. Unlocking native phosphate would be an important step in achieving sustainable agriculture.

The "*breakthrough curves*" of Fig. 9.7 summarize the net effects of repulsion and specific adsorption on the relative adsorption of anions by soils. Solutions containing the anions at initial concentration C_0 were added to soil columns. The effluent concentration is C. The volume of water is expanded as pore volumes added to the

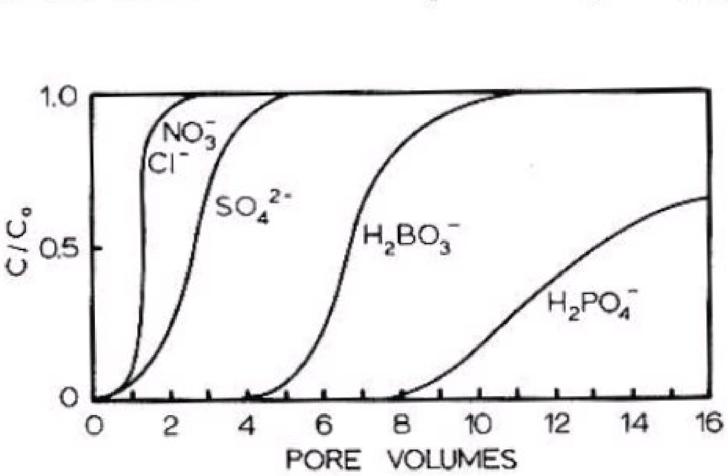

FIGURE 9.7. Representative breakthrough curves of anions weakly, moderately, and strongly retained by soils.

soil column. The Cl^- and NO_3^- solutions flowed through the soil columns almost as quickly as the water. The other anions were delayed because of soil adsorption. Sulfate and phosphate retention increased with iron and aluminum hydroxyoxide and allophone contents. The long-term capacity of most soils to adsorb phosphate is orders of magnitude greater than the amounts of phosphate added as fertilizer.

9.3 MOLECULAR RETENTION

A solute in water need not be initially charged to be retained by soils. Molecules in the soil solution can become charged and then be adsorbed as cations or anions. They may also remain nonionic and adsorb as a consequence of polarity that produces localized charge within the molecule.

Molecules such as NH_3, amino acids, and protein can protonate (add H^+) in acid solutions and be adsorbed as cations on negatively charged soil solids:

$$B + H^+ = BH^+ \tag{9.3}$$

where B is a weakly basic molecule. The tendency of a molecule to protonate is characterized by its pK_a:

$$K_a = \frac{(H^+)(B)}{(BH^+)} \qquad pK_a = pH + \log\frac{(BH^+)}{(B)} \tag{9.4}$$

The greater the pK_a of a basic molecule, the greater is its tendency to protonate. Important molecules that protonate include the *s*-triazine and *s*-triazole herbicides and ammonia. Their pK_a values are given in Table 9.3.

When soil pH > pK, weak-acid anions are adsorbed by positively charged sites on Fe and Al oxides or layer silicate edges. The weak acids (high pK_a values) include

Table 9.3. pK_a values of some molecular species

Species	pK_a[a, b]	Reaction
s-Trazine (atrazine)	1.68	$BH^+ = B + H^+$
s-Trazole (amitrole)	4.17	$BH^+ = B + H^+$
2,4-D	2.80	$R—COOH = R—COO^- + H^+$
2,4,5-T	3.46	$R—COOH = R—COO^- + H^+$
H_2CO_3	6.37	$H_2CO_3 = HCO_3^- + H^+$
H_3BO_3	9.14	$H_3BO_3 = H_2BO_3^- + H^+$
NH_3	9.26	$NH_4^+ + OH^- = NH_3 + HOH$
H_4SiO_4	9.66	$H_4SiO_4 = H_3SiO_4^- + H^+$

[a] Organic pK_a reproduced from *Pesticides in Soil and Water*, 1974, p. 47.

[b] Inorganic pK_a reprinted with permission from *Handbook Chemistry and Physics*, 50th ed., 1969–1970. Copyright, The Chemical Rubber Co., CRC Press, Inc.

H_3BO_3 and H_4SiO_4 (or $Si(OH)_4$). These acids remain uncharged in most agricultural soils and do not form anionic or cationic bonds. Important weak acids that dissociate to form anionic bonds with soil include the phenoxyacetic acids (2,4-D and 2,4,5-T) and carbonic acid (H_2CO_3). Their pK_a values are also given in Table 9.2.

Molecules that do not protonate or deprotonate to become charged species can still be adsorbed on soil by hydrogen bonding and van der Waals attraction. The *hydrogen bond* is a dipole–dipole interaction in which H^+ bridges between two electronegative atoms. The hydrogen is held by a weak electrostatic bond to one electronegative atom and by a stronger covalent bond to the other. The functional groups of the soil's solid phase that are capable of hydrogen bonding include the O^{2-} on silicate surfaces, edge hydroxyls, and the carboxyl, hydroxyl, and amino groups of organic matter. Individual hydrogen bonds are relatively weak, but many polar molecules (particularly pesticides) have numerous sites capable of hydrogen bonding with soils, especially with soil organic matter. The summation of many hydrogen bonds results in strong retention of, for example, carbaryl and carbamate insecticides.

Many organic molecules, although uncharged and without apparent hydrogen bonding, are nonetheless strongly retained by soils. The intense interest in this phenomenon stems from possibility of movement of pesticides and other organic molecules in soils to groundwater. A less obvious phenomenon is the soil's adsorption of organic molecules from the atmosphere. Uncharged molecules have been adsorbed from the atmosphere and produced in the soil by organic decay since the earth was formed, yet the groundwater and atmosphere are remarkably free of them. This is partly due to the strong retention of organic molecules by soils, a second reason is the active degradation of organic substances by soil microorganisms.

Soil retention of uncharged molecules is often described as *van der Waals attraction*, which is a way of saying that the retention mechanism is unknown or poorly understood. In the 19th century, van der Waals modified the ideal gas law to account for the attraction between gas molecules, without knowing the nature of attraction. Charge-induced dipole interactions and dipole-induced dipole interactions are the forces thought to be involved. The van der Waals attractions are weak and short-ranged. They are additive, and each atom of the molecule and its adsorbent contribute to the total bond energy. Such forces operate in all adsorbent–adsorbate relationships but appear to be the principal forces of adsorption for nonpolar molecules such as DDT and N_2. The electrostatic forces of charged species overshadow van der Waals attractive forces.

Molecular retention involves no charges and therefore requires no strict 1–1 exchange between the soil and the soil solution. Ion retention requires exchange to maintain charge neutrality. The amount of molecular retention, however, is limited by the number of exposed sorption sites, or by the amount of sorbing surface and material, in the soil.

Percolating solutions containing organic molecules pass through an intricate network of soil pores. Organic molecules tend to be nonpolar and to prefer an environment less polar than that of the highly polar water. If some other less polar phase is present, such as soil surfaces and especially SOM surfaces, the organic molecules are in effect forced out of the aqueous phase onto organic-coated soil surfaces. The SOM also attracts organic molecules by providing a phase into which they can "dissolve" or form a solid solution. That action helps to purify contaminated water or gas flowing through the soil. The soil's adsorption capacity is small for organic molecules but is continually renewed by microbial decay of the adsorbed molecules.

The separation of organic molecules out of the soil solution onto the solid phase is called *partitioning*. The ratio of a molecule's concentrations in the water and SOM phases is a constant, the partition coefficient K_D:

$$K_D = \frac{\text{concentration}_{\text{I(soil)}}}{\text{concentration}_{\text{II(soil solution)}}} \tag{9.5}$$

and is a measure of the relative solubility of the molecule in both phases. For substances that are only slightly soluble in water, the values of K_D are very large. Dibenzothiophene ($(C_6H_5)_2C_4H_4S$) is weakly water soluble and its soil/water K_D value is 11 000. Passing dibenzothiophene-contaminated water through soil containing organic matter greatly depletes the water of this compound.

The extent to which an organic compound partitions out of water onto soil is determined by physical–chemical properties of both the soil and the compound. The soil's organic matter content is the single best characteristic for estimating the amount of soil adsorption of pesticides and other organic molecules. The partition, or sorption, coefficient of the organic molecule K_{OC} (equal to K_D/SOM) is rather independent of soil type. This suggests that SOM is the principal soil component responsible for pesticide sorption and that the role of SOM is similar in different soils.

The K_{OC} value is correlated to physical–chemical properties of the organic molecules. One such easily determined property is the partition coefficient K_{OW} of a molecule between octanol and water replicates fairly well the partitioning between soil and the soil solution. The correlation of K_{OW} to K_{OC} in soils is

$$\log K_{OC} = -0.99 \log K_{OW} - 0.34 \tag{9.6}$$

The K_{OC} is a first approximation of a pesticide's mobility in soil from readily available pesticide and soil properties.

Partitioning by this *hydrophobic adsorption* explains why soils retain organic molecules, but direct soil–organic interaction occurs also. Dry soils retain organic molecules more strongly and in greater amounts than do wet soils. Differences between organic molecules with respect to soil retention become more obvious when the competition with water for soil surfaces is absent. For a gas passing through a dry soil, the soil/gas partition coefficient of methane is about the same as that for dinitrogen (N_2) and helium. Methane flows as easily through soil as the unreactive N_2 and He molecules. The partition coefficient increases exponentially with molecular weight to about 10^5 for gaseous octane (Fig. 9.8). Unsaturated double bonds and aromatic ring structures increase retention slightly, and alcohol, aldehyde, and acid functional groups in the gas molecule increase its soil retention greatly. Presumably, nitrogen, phosphate, and sulfur functional groups also increase retention. Those dis-

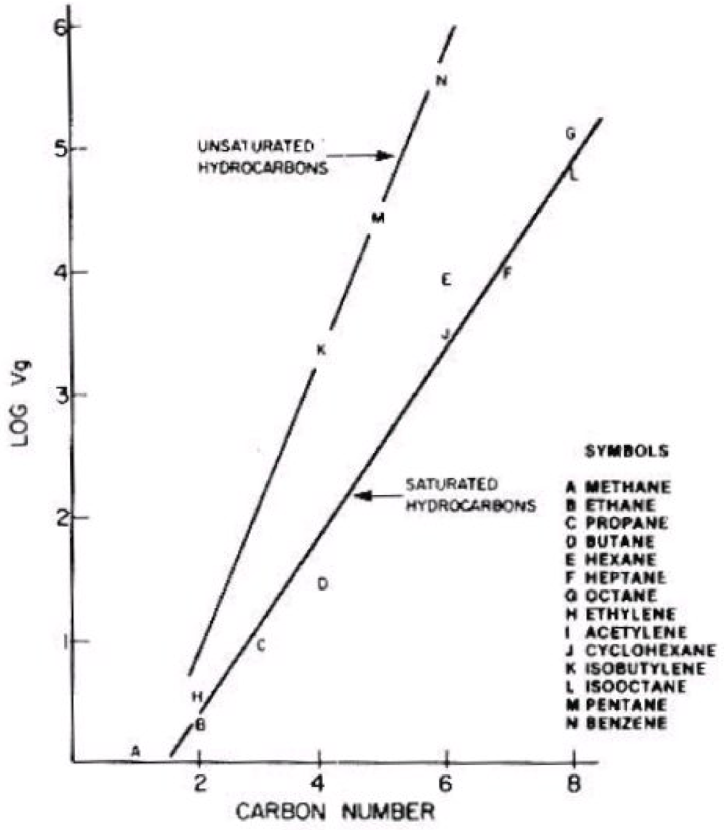

FIGURE 9.8. Retention of various hydrocarbons by a dry soil at 15° C. V_g, the retention volume, is closely related to the soil/gas partition coefficient K_D. (From H. L. Bohn et al. 1980. *J. Environ. Qual.* **4**:563.)

tinctions, however, are less obvious in the presence of water because it competes with the gases for adsorption sites. For more polar and water-soluble organic molecules, direct adsorption by inorganic soil surfaces and dissolution into the soil solution are also important.

The adsorption of a particular uncharged species can rarely be identified with only one mechanism, although the dominant mechanism can often be inferred. Thus, care should be taken in extrapolating data from, for example, a weakly basic herbicide to other weakly basic herbicides. The individual properties of the molecule, such as (1) chemical character, shape, and configuration, (2) acidity or basicity, (3) water solubility, (4) charge distribution, (5) polarity, (6) size, and (7) polarizability, all influence molecular adsorption by soil.

As with cations and anions, soil interaction with molecules happens only if the substance contacts soil particles. Surface spreading or burial is insufficient; the wastes must be mixed with the soil to react with it. The sensational Love Canal case, for example, involved the burial of organic liquids in 55-gallon (215-L) drums stacked in shallow trenches underground. Had the organic liquids been mixed and allowed to interact with the soil, the leakage and movement after the thin steel drums corroded might never have happened, and it certainly would have been less severe.

9.4 ADSORPTION ISOTHERMS

Adsorption isotherms describe solute adsorption by solids at constant temperature and pressure. An adsorption isotherm shows the amount of adsorbate sorbed as a function of its equilibrium concentration. A variety of isotherm shapes are possible, depending on the affinity of the adsorbent for the adsorbate (Fig. 9.9).

To generate adsorption data, a known amount of adsorbate in aqueous solution is mixed with a known amount of *adsorbent*. At equilibrium, the amount of adsorbate removed from solution is assumed to be adsorbed. Secondary reactions (such as precipitation) must be eliminated or corrected for. Precipitation is indicated in some cases by a rapid increase in apparent adsorption (disappearance from solution) with a small change in solution concentration. Three equations are commonly used to describe adsorption: the Langmuir, Freundlich, and Brunauer–Emmett–Teller (BET) equations.

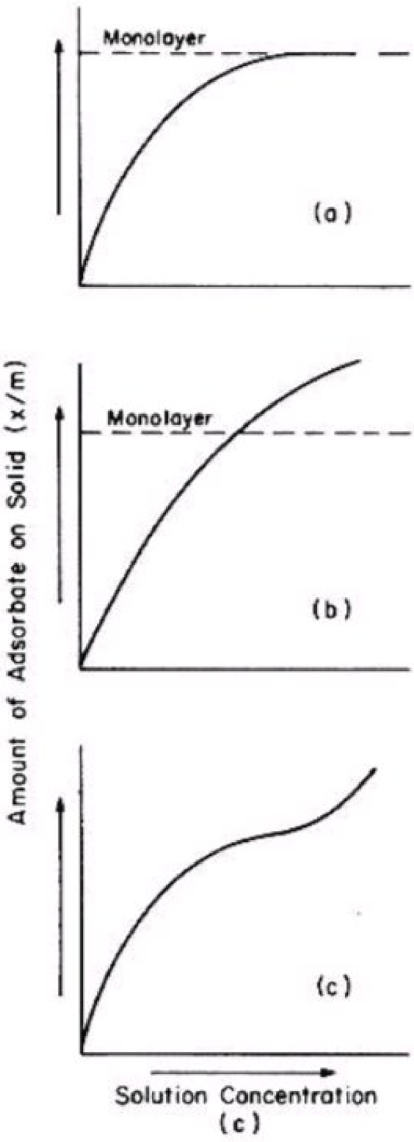

FIGURE 9.9. Typical adsorption isotherms described by the (a) Langmuir, (b) Freundlich, and (c) BET equations.

The Langmuir equation was initially derived for the adsorption of gases by solids. The derivation was based on three assumptions: (1) a constant energy of adsorption that is independent of the extent of surface coverage (i.e., a homogeneous surface); (2) adsorption on specific sites, with no interaction between adsorbate molecules; and (3) maximum adsorption equal to a complete monomolecular layer on all reactive adsorbent surfaces (Fig. 9.8a). A common form of the Langmuir equation is

$$\frac{x}{m} = \frac{KCb}{1 + KC} \tag{9.7}$$

where x/m is the weight of adsorbate per unit weight of adsorbent, K is a constant related to the binding strength, b is the maximum amount of adsorbate that can be adsorbed (i.e., a complete monomolecular layer), and C is the adsorbate concentration. Rearranging Eq. 9.7 yields the more convenient linear form

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{1}{b} \tag{9.8}$$

If adsorption conforms to the Langmuir model, plotting $C/(x/m)$ versus C yields a straight line with a slope $1/b$ and intercept $1/Kb$. The Langmuir constant K is the quotient of the slope $1/b$ and intercept $1/Kb$.

Equation 9.7 assumes constant free energy of adsorption on the surface, a situation that rarely occurs in nature. Instead, the energy of adsorption tends to decrease with increasing surface coverage. The interaction with already-adsorbed molecules increases with increasing surface coverage. The net effect is that the two phenomena tend to compensate for each other, yielding a relatively constant energy of adsorption. In systems where the energy of adsorption is not constant, the Langmuir equation may still describe adsorption over a portion of the adsorption range, since the variation in energy of adsorption over such a range can be small if only one type of bonding site or mechanism predominates.

A true adsorption maximum, however, is rarely observed. Precipitation reactions can exhibit Langmuir-type behavior. If only a limited quantity of a solute that precipitates is present, a Langmuir isotherm can result as the solute increases, that is, a "sorption maximum" occurs. This behavior is found at low solute concentrations, where no precipitation occurs until the solute's solubility product is reached.

An advantage of using the Langmuir equation for describing adsorption is that it defines an adsorption limit on a given array of sites that meet the Langmuir model's criteria. This limit has been used to estimate the adsorption capacity of soils for phosphate and various herbicides. Comparing such capacities can also suggest adsorption mechanisms. Unfortunately, the adsorption maxima usually do not occur, instead adsorption continues but at ever-decreasing amounts.

If data fail to conform to the Langmuir equation, the Freundlich equation often fits the data successfully:

$$\frac{x}{m} = KC^{1/n} \tag{9.9}$$

where K and n are empirical constants and the other terms are defined above. The equation was originally empirical, without a theoretical foundation. It implies that the energy of adsorption decreases logarithmically as the fraction of covered surface increases, similar to the solid solution ideas. The Freundlich equation can be derived theoretically by assuming that the decrease in energy of adsorption with increasing surface coverage is due to surface heterogeneity. The degree of heterogeneity is unknown in most adsorption studies, and both the Langmuir and Freundlich equations are better thought of as empirical curve fitting of adsorption data, rather than describing the actual mechanism of adsorption.

The linear form of the Freundlich equation is

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K \tag{9.10}$$

The frequent good fit of adsorption data to the Freundlich equation is influenced by the insensitivity of log–log plots and by the flexibility afforded curve fitting by the two empirical constants K and n. This flexibility does not guarantee accuracy, however, if the data are extrapolated beyond the experimental range. The Freundlich equation has the further limitation that it does not predict a maximum adsorption capacity, however mythical the adsorption maximum may be. Despite its shortcomings, the Freundlich equation is a common adsorption equation and is included in several models for predicting pesticide behavior in soil.

APPENDIX 9.1 MULTISITE AND MULTILAYER ADSORPTION

A number of recent studies involving the adsorption of solutes from solution by mineral surfaces have resulted in data suggesting *multiple-site adsorption*. That is, several different arrays of sites are postulated, each of which fulfills the requirements of the Langmuir model. For example, Fig. 9.10 shows data for phosphate adsorption on

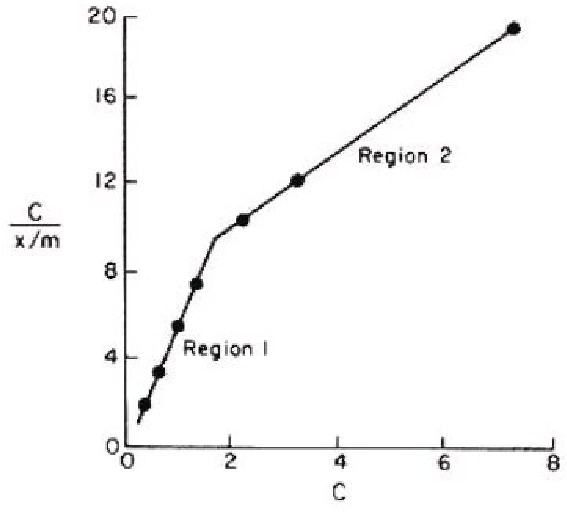

FIGURE 9.10. Phosphorus adsorption data plotted according to the Langmuir equation. (After J. K. Syers, M. G. Browman, G. W. Smillie, and R. B. Corey. 1973. *Soil Sci. Soc. Am. Proc.* **37**:358–363.)

soil plotted according to the traditional linear Langmuir form. The data suggest two sets of sites, each with its own binding strength and adsorption maximum. Alternatively, the data suggest two mechanisms of adsorption on similar sites. The adsorption curve is resolved by dividing the curve into several straight-line components. For Fig. 9.10, only two straight lines are needed. The form of the Langmuir equation for two-site adsorption is

$$\frac{x}{m} = b_1 - \frac{x/m_1}{K_1C} + b_2 - \frac{x/m_2}{K_2C} \tag{9.11}$$

where subscripts 1 and 2 refer to regions (or mechanisms) 1 and 2. The adsorption maximum for the soil is the sum b_1 plus b_2. This form of the Langmuir equation can be used to describe adsorption sites for species whose total adsorption appears to be the sum of both a high-energy and a low-energy component. Such a distribution of adsorption energies is reasonably well established for soil phosphate. To fit adsorption data more closely to the Langmuir model, even three- and four-site models have been invoked.

In addition to multisite adsorption, many gases and vapors adsorbed by solids do not produce a typical monolayer-type adsorption isotherm (Fig. 9.9a), but rather produce an isotherm indicating multilayer adsorption (Fig. 9.9c). An equation that treats multilayer adsorption is the BET equation, named after developers Brunauer, Emmett, and Teller. Multilayer adsorption is characteristic of physical or van der Waals attraction. It often proceeds with no apparent limit, since multilayer adsorption merges directly into capillary condensation as the vapor pressure of the adsorbate approaches its saturation value.

The BET equation has been used to determine the surface area of solids from gas adsorption data. The equation not only predicts the shape of the adsorption isotherm, but also gives the volume of gas V_m required to form a monolayer. The BET equation has the form

$$A = \frac{V_m}{V_0} N_a A_m \tag{9.12}$$

where A is the surface area of the adsorbent, V_m is the volume of gas adsorbed, V_0 is the molar volume of adsorbate gas (22.4 liters at 25° C), N_a is Avogadro's number, and A_m is the cross-sectional area of the adsorbate molecule. Surface area determinations are often based on N_2 adsorption by the solid at $-195°$ C. For N_2, $A_m = 16.2 \times 10^{-20}$ m^2. The linear form of the BET equation is

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{(C-1)P}{V_mCP_0} \tag{9.13}$$

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

The BET equation has been applied to ion adsorption from soil solutions, although the extended Langmuir equation (Eq. 9.11) would seem to apply as well. The BET equation has also been used to study the adsorption of pesticides having relatively high vapor pressures.

An alternative explanation of retention by adsorption is to consider the substance being held by solid-state mixing on the surfaces of soil particles (see Chapter 3). The advantage to the solid-state mixing concept is that the quantitative interpretation is based on the same thermodynamics as ions in aqueous solutions. It provides a plausible explanation of why the retention energy progressively decreases as the adsorbate concentration increases, why soils retain ions at different energies, and why soil particles retain substances much more strongly than their own pure minerals while releasing other ions as the soil weathers.

Retention by solid solution cannot be differentiated from adsorption on the basis of experiment. They are simply different explanations for the same phenomenon. The idea of adsorption sites can be reconciled by considering that those areas are where solid-state mixing, because of the solid's surface structure and composition, is most likely.

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QUESTIONS AND PROBLEMS

1. Distinguish between specific and nonspecific reactions of anions soils. Give examples of anions that tend to be specifically and nonspecifically reactive in soils.

2. What are the forces acting on an anion as it approaches a layer silicate? How will these forces vary from soil to soil? What is the dominant for acting on anions in most agricultural soils?

3. How do the following factors affect anion repulsion:
   - **(a)** Anion charge
   - **(b)** Anion concentration
   - **(c)** Exchangeable cation
   - **(d)** Soil pH
   - **(e)** Other anions

4. Are all anions adsorbed alike in soils? If not, explain the differences, giving examples of each reaction type.
5. What reactions are responsible for the fixation of phosphate in acid and basic soils?
6. How are molecular species such as N_2 and NH_3 retained by soils?
7. Certain mechanisms are active in the retention of all species (cationic, anionic, and molecular), while other mechanisms are active in the retention of only certain species. Explain, giving examples of species retained predominantly by each specific mechanism.
8. Refer to Fig. 9.5. Describe the sequence of events if a soil of pH 7.5 were fertilized to a pH_2PO_4 level of 2.
9. Given the data below, determine if the adsorption of 2,4,5-T conforms to the Langmuir or the Freundlich models and determine the appropriate adsorption parameters (K, n, b). You may need to restrict your attention to a limited concentration range.

Initial Solution Concentration (mg L^{-1})	Final Solution Concentration (mg L^{-1})	Volume of Solution (mL)	Weight of Soil (g)
5	3	10	5
10	6	10	5
25	15	10	5
50	30	10	5
100	70	10	5

10. Explain in your own words the peaks and inflection points of Fig. 9.3.
11. Maximum phosphate availability in soils tends to occur around pH 6 to 6.5. Explain why in terms of Fig. 9.5.
12. Based on Table 9.3, predict the relative mobility of (a) s-triazole, (b) H_3BO_3, and (c) 2,4-D in pH 4.5, 7.0, and 8.5 soils.