

Note: This is a reference cited in AP 42, *Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the reference number, the AP42 chapter and section. The file name "ref02_c01s02.pdf" would mean the reference is from AP42 chapter 1 section 2. The reference may be from a previous version of the section and no longer cited. The primary source should always be checked.

AP42 Section:	9.2.1
Background Ch	2
Reference:	21
Title:	S. L. Tisdale et al., <i>Soil Fertility and Fertilizers</i>, MacMillan Publishing Company, New York, 1975.

FOURTH EDITION

Soil Fertility and Fertilizers

Samuel L. Tisdale

President (Retired), The Sulphur Institute
Formerly Professor of Soils
North Carolina State University

Werner L. Nelson

Senior Vice President, Potash & Phosphate Institute
Formerly Professor of Agronomy
North Carolina State University

James D. Beaton

Northwest Director, Potash & Phosphate Institute
Formerly Instructor of Soils
University of British Columbia

Macmillan Publishing Company NEW YORK

Collier Macmillan Publishers LONDON

Chapter 4

Basic Soil-Plant Relationships

THE purpose of this chapter is to review briefly the phenomenon of ion exchange in soils and to consider some of the suggested mechanisms for the movement of ions in the soil solution and into the cells of the absorbing roots.

Ion Exchange in Soils

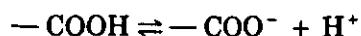
Ion exchange is a reversible process by which one type of cation or anion held on the solid phase is exchanged with another kind of cation or anion in the liquid phase. If two solid phases are in contact, exchange of ions may also take place between their surfaces. Of the two phenomena, cation and anion exchange, the first is generally considered to be more important, since the anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity. This property of cation exchange is one of the major distinguishing features between soils and other plant-rooting media.

Cation Exchange

Soils are composed of the three forms of matter: solids, liquids, and gases. The solid phase is made up of organic and inorganic materials. The organic fraction consists of the residues of plants and animals in all stages of decomposition, and the stable part is usually termed humus.

The inorganic fraction of soil solids is composed of primary and secondary minerals with different particle sizes. The soil fractions that are seats of ion exchange are the organic and the mineral components with effective particle diameters of less than 20 μm . This includes a portion of the silt and all of the clay fraction ($< 2 \mu\text{m}$) as well as colloidal organic matter.

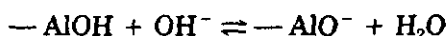
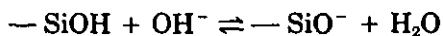
Because cations are positively charged, they are attracted to surfaces that are negatively charged. In the organic fraction these arise from the dissociation of H^+ from certain functional groups, particularly from carboxylic ($-\text{COOH}$) and phenolic ($-\text{C}_6\text{H}_4\text{OH}$) groups. Many carboxylic groups will dissociate at pH values below 7, leaving a negative charge at the site of the functional group, as shown in the following equation.



It is estimated that 85 to 90% of the negative charge of humus is due to these two functional groups alone. Two other groups, enol ($-\text{COH} = \text{CH}$) and imide ($=\text{NH}$), also contribute to the negative charge of organic matter.

Negative charges in the inorganic clay fraction generally arise from two sources. The first is isomorphous substitution in layer silicate minerals such as smectite, and the second is caused by the deprotonation of both (1) hydroxyl $-\text{OH}$ groups attached to the silicon atoms at the broken edges of the tetrahedral planes, and (2) exposed AlOH groups in layer silicates. The charge resulting from isomorphous substitution arises from the replacement of a silicon or aluminum atom by an atom of similar geometry but of lower charge (e.g., Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}). This produces a net negative charge which is fairly uniformly distributed over the plate-shaped clay particles. Isomorphous substitution occurs mainly during crystallization of layer silicate minerals, and once the charge is created it is largely unaffected by future changes in the environment. The charge resulting from isomorphous substitution is responsible for the permanent charge of soils.

With increasing pH, negative charges form at the edge of clay plates by reactions such as the following:



Layer silicate clay minerals in soils are of three general classes: 2:1, 2:1:1, and 1:1. The 2:1 clays are composed of layers, each of which consists of two silica sheets between which is a sheet of alumina. Examples of the 2:1 clays are smectites (montmorillonite), illite, and vermiculite. Muscovite and biotite are examples of 2:1 primary minerals which are often abundant in silt and sand fractions.

Chlorites are examples of 2:1:1 layer silicates commonly found in soils. This clay mineral consists of an interlayer hydroxide sheet in addition to the 2:1 structure referred to above.

The 1:1 clays are composed of a series of layers each of which contains one silica sheet and one alumina sheet. Kaolinite and halloysite are two of the most important clay minerals in this group.

Isomorphous substitution is the principal source of negative charge for the 2:1 and 2:1:1 groups of clay minerals but is of minor consequence for the 1:1 group of clays. Deprotonation or dissociation of H^+ from OH groups at the broken edges of clay particles is the prime source of negative charge in the 1:1 clay minerals. High pH values favor this deprotonation of exposed hydroxyl groups.

The oxides and hydrous oxides that are abundant in highly weathered soils have pH-dependent charges. These materials occur as coatings and interlayers of crystalline clay minerals. On exposure to moisture their surfaces become hydroxylated. Charges develop on these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- ions. The total charge of soil particles usually varies with the pH at which the charge is measured. The positive charge developed at low pH and the excess negative charge formed at high pH are termed pH-dependent charge. Only about 5 to 10% of the negative charge on 2:1 clays is pH dependent, while 50% or more of the charge developed on 1:1 clay minerals can be pH dependent.

The negative charge that develops on organic and mineral colloids is neutralized by cations attracted to the surfaces of these colloids. The quantity of cations expressed in milliequivalents per 100 g of oven-dry soil is termed the cation exchange capacity (CEC) of the soil. It is one of the important chemical properties of soils and is usually closely related to soil fertility. A thorough understanding of cation exchange is necessary to an understanding of soil fertility and acidity. Therefore, the following brief review is given of the way in which this quantity is determined.

Procedures dilution illustrate:

Cation exchange for another in numerous cations aluminum, iron, molybdenum, etc. Capacity, dependent on the rule, ions will be held. Also, the greater the amount held.

A conventional neutral 1 N ammonium ion ammonium-saturating KCl, the potassium chloride suspension were previously used. The amount of exchangeable cations is a measure of the soil's capacity.

To illustrate, 1.0 N NH_4Ac (ammonium acetate) is shaken over a soil and the soil is then adsorbed with KCl. The soil in the filtrate of course, retained = 3, as 0.018 g in 20 g of soil.

The CEC of soil and organic matter will have also, soils with more than soils with less. Generally, 1:1 mineral colloids; 2:1:1 chlorite to 300 meq per 100 g.

Effect of determining the United States estimated by extracting CEC at the soil's high CEC value to the so-called Coleman, K exchangeable buffered salt, exchange capacity extract only the soil. The exchange To measure the NH_4Ac to determine Another sample

Procedures differ for measuring CEC of soils, but the following simplified description illustrates the basic features.

Cation exchange, as pointed out previously, means the exchange of one cation for another in a solution phase. Soil colloids have adsorbed to their exchange sites numerous cations, including calcium, magnesium, potassium, sodium, ammonium, aluminum, iron, and hydrogen. These ions are held with varying degrees of tenacity, depending on their charges and their hydrated and unhydrated radii. As a rule, ions with a valence of 2 or 3 are held more tightly than monovalent cations. Also, the greater the degree to which the ion is hydrated, the less tightly it will be held.

A conventional method of CEC measurement is to extract a soil sample with neutral 1 N ammonium acetate. All of the exchangeable cations are replaced by ammonium ions and the CEC becomes saturated with ammonium. If this ammonium-saturated soil is extracted with a solution of a different salt, say 1.0 N KCl, the potassium ions will replace the ammonium ions. If the soil-potassium chloride suspension is filtered, the filtrate will contain the ammonium ions that were previously adsorbed by the soil. The quantity of ammonium ions in the leachate is a measure of the CEC of the soil in question and can easily be determined.

To illustrate, suppose that 20 g of oven-dry soil was extracted with 200 ml of 1.0 N NH_4Ac (ammonium acetate). The extraction is accomplished by intermittent shaking over a period of 30 minutes. The soil-ammonium acetate solution is filtered and the soil is washed with alcohol to remove the excess solution. The soil containing the adsorbed ammonium ions is next extracted with 200 ml of a solution of 1.0 N KCl. The soil-potassium chloride solution is filtered and the ammonium contained in the filtrate is determined. Suppose that 0.054 g of NH_4^+ were found. This was, of course, retained by the 20 g of soil extracted (0.054 g is 3 meq—i.e., $0.054/0.018 = 3$, as 0.018 g is the milliequivalent weight of 1 meq). Because 3 meq were present in 20 g of soil, the CEC of the soil is 15 meq/100 g.

The CEC of a soil will obviously be affected by the nature and amount of mineral and organic colloid present. As a rule, soils with large amounts of clay and organic matter will have higher exchange capacities than sandy soils low in organic matter. Also, soils with predominately 2:1 colloids will have higher exchange capacities than soils with predominately 1:1 mineral colloids.

Generally, 1:1 mineral colloids have CEC values of 1 to 10 meq per 100 g; 2:1 mineral colloids such as montmorillonite and vermiculite, 80 to 150 meq per 100 g; 2:1:1 chlorites and 2:1 micas, 20 to 40 meq per 100 g; and organic colloids, 100 to 300 meq per 100 g.

Effective CEC. The use of neutral ammonium acetate displacement for determining the CEC of soils has been and is still used by many laboratories in the United States. However, some workers believe that CEC can better be estimated by extraction with an unbuffered salt which would give a measure of the CEC at the soils normal pH. Use of neutral N ammonium acetate will result in a high CEC value if the soil is acid simply because of the adsorption of NH_4^+ ions to the so-called pH-dependent exchange sites.

Coleman, Kamprath, Thomas, and other workers in North Carolina defined exchangeable cations in acid soils as those cations extracted with a neutral unbuffered salt, with the sum of these cations being termed the effective cation exchange capacity. Such an unbuffered salt solution (1.0 N KCl in this case) will extract only the cations held at active exchange sites at the particular pH of the soil. The exchangeable acidity thus extracted is due to aluminum and hydrogen. To measure the effective CEC, one sample of soil is extracted with neutral normal NH_4Ac to determine the exchangeable basic cations, such as K, Ca, Mg, and Na. Another sample of the same soil is extracted with 1.0 N KCl to determine the

exchangeable aluminum and hydrogen. The sum of the milliequivalents of calcium, magnesium, potassium, and sodium, plus aluminum and hydrogen, is the effective CEC.

Base Saturation. One of the important properties of a soil is its degree of base saturation, which generally reflects the extent of leaching and weathering of the soil. It is defined as the percentage of total CEC occupied by such basic cations as calcium, magnesium, sodium, and potassium. To illustrate how this quantity is calculated, suppose that in the example given the following ion quantities were found in the ammonium acetate extract from the leaching of the 20 g of soil:

Ca	0.02 g
Mg	0.006 g
Na	0.0115 g
K	0.0195 g

The milliequivalent weights of calcium, magnesium, sodium, and potassium are, respectively, 0.02, 0.012, 0.023, and 0.039. The milliequivalents of each of these ions present is

Ca	= 0.02/0.02	= 1 meq
Mg	= 0.006/0.012	= 0.5 meq
Na	= 0.0115/0.023	= 0.5 meq
K	= 0.0195/0.039	= 0.5 meq

Total 2.5 meq per 20 g of soil

(2.5 meq of bases per 20 g of soil is 12.5 meq per 100 g of soil). The total CEC of this soil was 15 meq per 100 g, so the percentage of base saturation is $(12.5/15) \times 100$, or 83.3.

As a general rule, the degree of base saturation of normal uncultivated soils is higher for arid than for humid region soils. Although not always true, especially in humid regions, the degree of base saturation of soils formed from limestones or basic igneous rocks is greater than that of soils formed from sandstones or acid igneous rocks. Base saturation is related to soil pH and to the level of soil fertility. For a soil of any given organic and mineral composition, the pH and fertility level increase with an increase in the degree of base saturation.

The ease with which cations are absorbed by plants is related to the degree of base saturation. For any given soil the availability of the nutrient cations such as calcium, magnesium, and potassium to plants increases with the degree of base saturation. For example, a soil with a base saturation of 80% would provide cations to growing plants far more easily than the same soil with a base saturation of only 40%. The relation between percent base saturation and cation availability is modified by the nature of the soil colloid. As a rule, soils with large amounts of organic or 1:1 colloids can supply nutrient cations to plants at a much lower degree of base saturation than soils high in 2:1 colloids.

As will be seen in the following section, the CEC, hence the percentage of base saturation, can be rather arbitrary figures unless the method by which they are measured is clearly defined. As a general rule, however, the statements made concerning base saturation and plant availability of cations are true.

Nature of Charge and CEC. The foregoing discussion of cation exchange and degree of base saturation was deliberately oversimplified to set forth clearly the fundamental reaction in this basic soil phenomenon. Actually, studies have shown that the cation exchange capacity of a soil is not a fixed quantity but is dependent on the pH and concentration of the extracting solution used for its

determination. exchange is ca clay minerals, oxides, and org capacity of so the acid range the alkaline r by the ionizat hydrous Al an soil organic m

When the C the value obta a highly buffe preceding sect growth, fertili with the buffe neutral N am the unbuffered determination used in many value obtained and according method for me

An.

It has been kn retained in for and alkaline s that are quite Chapter 6. Mo can be extract aluminum wit water.

These findin exchange prop chlorides and and sulfates.

Contrary to decrease in soil clays and those with predomina

The mechan than the simp tions. Anions some of which Specific adsorp possible.

The positive of anions origin exposing OH g with OH grou from hydrous mechanism for and subtropics

determination. The total negative charge on soil colloids which gives rise to cation exchange is caused by isomorphous substitution of ions in the lattice structure of clay minerals, the ionization of hydroxyl groups from hydrated iron and aluminum oxides, and organic matter. Numerous studies have shown that the cation exchange capacity of soils is a continuous function of pH, with this value being lowest in the acid range, pH 3 to 4, and increasing continuously as the pH increases up to the alkaline range, pH 8 to 9. This increase in CEC with increasing pH is caused by the ionization of the OH groups at the edges of the clay lattice and on the hydrous Al and Fe oxides and from the carboxyl and phenolic groups present in soil organic matter.

When the CEC of a soil is determined using an unbuffered neutral salt solution, the value obtained will be lower than would be the case if it were measured using a highly buffered solution at a pH of 7, 8, or 9. The effective CEC discussed in the preceding section therefore is probably a more meaningful value as far as plant growth, fertilizer additions, and liming are concerned than the CEC determined with the buffered solutions at high pH values. The CEC values found by using neutral *N* ammonium acetate are somewhere between the values found by using the unbuffered salt solution and barium chloride-triethanolamine. For routine CEC determinations, the ammonium acetate method is rapid and convenient and is still used in many laboratories in the United States. If one keeps in mind that the value obtained will be greater than that obtained using the unbuffered salt solution and accordingly makes the necessary allowances, it is a perfectly satisfactory method for measuring this important soil property.

Anion Exchange

It has been known for a long time that phosphates do not leach from soils but are retained in forms that may be removed only by extraction with various salt, acid, and alkaline solutions. A fraction of the phosphorus appears to be held in forms that are quite insoluble. The topic of phosphate retention is covered more fully in Chapter 6. More recently it has been found that much larger amounts of sulfate can be extracted from soils high in 1:1 clays and the hydrous oxides of iron and aluminum with a solution of potassium phosphate than can be extracted with water.

These findings have led to the realization that soils do indeed possess anion exchange properties, and subsequent studies have shown that anions such as chlorides and nitrates may be adsorbed, although not to the extent of phosphates and sulfates.

Contrary to cation exchange, the capacity for retaining anions increases with a decrease in soil pH. Further, anion exchange is much greater in soils high in 1:1 clays and those containing hydrous oxides of iron and aluminum than it is in soils with predominately 2:1 clays.

The mechanisms responsible for anion retention in soils are much more complex than the simple electrostatic attractions involved in most cation exchange reactions. Anions may be retained by soil particles through a number of reactions, some of which are simply electrostatic and are described as being nonspecific. Specific adsorption or chemisorption reactions of a nonelectrostatic nature are also possible.

The positive charge sites responsible for electrostatic adsorption and exchange of anions originate in the broken bonds, primarily in the alumina octahedral sheet, exposing OH groups on the edges of clay minerals. Anion exchange may also occur with OH groups on the hydroxyl surface of kaolinite. Displacement of OH ions from hydrous iron and aluminium oxides is also considered to be an important mechanism for anion exchange, particularly in highly leached soils of the tropics and subtropics, and it is in such soils that anion exchange is greatest. Clay minerals

in the montmorillonite group of expansible layer silicates usually have anion exchange capacities of less than 5 meq per 100 g. On the other hand, kaolinites can have an anion exchange capacity as high as 43 meq per 100 g at an acidic equilibrium pH of 4.7.

The pH of most productive soils in the United States and Canada is usually too high for full development of anion exchange capacities. As a result, anions, with the exception of phosphate and to a lesser degree sulfate, will not be retained. There are some soils, however, in the southeastern United States and others formed under high rainfall conditions in Hawaii, Washington, Oregon and in the Canadian province of British Columbia, that have acid subsoils, high in iron and aluminum hydrous oxides, capable of adsorbing anions, especially sulfate. The retention of chlorides and nitrates by anion adsorption is generally not considered to be of any great practical significance in most agricultural soils in North America. A more extensive treatment of phosphate and sulfate retention in soils will be found in Chapters 6 and 8.

Contact Exchange

The discussion of ion exchange so far has dealt only with the exchange of ions between liquid and solid phases. It is believed by some that this exchange can take place between ions held on the surfaces of solid-phase particles and that it does not have to occur via the liquid phase. The extension of this theory leads to the conclusion that ions attached to the surface of root hairs (such as H^+ ions) may exchange with those held on the surface of clays and organic matter in soils because of the intimate contact that exists between roots and soil particles.

The mechanism that permits such an exchange could be described in this way. Clays and plant roots both have CEC properties. Ions are believed to be held at certain spots or sites on both roots and colloidal soil surfaces. The ions held by electrostatic or van der Waals forces at these sites tend to oscillate within a certain volume. When the oscillation volumes of two ions overlap, the ions exchange places. In this way a calcium ion on a clay surface could then presumably be absorbed by the root and utilized by the plant.

There is uncertainty about the importance of contact exchange in the nutrition of plants. It has been estimated that roots may grow to only about 3% of the available nutrients in soils. In addition, there is some question about soil and roots coming into close enough contact for the exchange of ions to occur. There is a strong possibility, however, that the root-soil gap is eliminated by the mucilaginous gel that can occur around root surfaces. This mucigel could serve as a contact complex since it is known to be penetrated by soil particles.

The presence of ectotrophic mycorrhiza, a symbiotic association between fungi and the roots of plants, enhances the uptake of several plant nutrients, particularly phosphorus. This beneficial effect of mycorrhiza is greatest when plants are growing in impoverished soils. The hyphal threads of mycorrhizal fungi act as an extension of plant root systems, resulting in greater exploitation of soil in the root zone. It is possible that contact exchange becomes more significant when mycorrhiza are active.

Root Cation Exchange Capacities

Soil colloids are not the only component of the soil-plant system to exhibit cation exchange properties. It has been observed that plant roots themselves may also possess this property. Capacities ranging from less than 10 to almost 100 meq per 100 g have been measured.

The exchange properties of roots appear to be attributable mainly to carboxyl groups ($-COOH$) present in pectic substances. Such sites may account for from

70 to 90% of the is considered to living portions of

Plants differ c Legumes and ot ities reported fo species with hi preferentially o These cation ex pastures on soil legume disappea potassium than

Mov

For ions to be surface. There the root surfac mentioned prev of ions by mas about the occur has estimated t to corn. The val was estimated supplied by int

Root

change as a me throughout the system develop faces retaining ions by the conta that can come in soil equal to the or less of the so

TABLE 4-1. Rela Ions Move from S

Nutrient
Nitrogen
Phosphorus
Potassium
Calcium
Magnesium
Sulfur
Copper
Zinc
Boron
Iron
Manganese
Molybdenum

Source: Barber and Madison, Wis.: Soil Sc

70 to 90% of the exchange properties of roots. Uptake of exchangeable ions by roots is considered to be a passive process that is distinct from intake into the interior, living portions of cells.

Plants differ considerably in the magnitude of their measured root CEC values. Legumes and other dicotyledons generally have values at least double the capacities reported for monocotyledons, including the grasses. Legumes and other plant species with high CEC values tend to absorb divalent cations such as calcium preferentially over monovalent cations, whereas the reverse occurs with grasses. These cation exchange properties of roots help to explain why, in grass-legume pastures on soils containing less than adequate K^+ , the grass survives but the legume disappears. The grasses are considered to be more effective absorbers of potassium than are the legumes.

Movement of Ions from Soils to Roots

For ions to be absorbed by plant roots, they must come in contact with the root surface. There are generally three ways in which nutrient ions in soil may reach the root surface: (1) root interception, with the possibility of contact exchange, mentioned previously; (2) diffusion of ions in the soil solution; and (3) movement of ions by mass movement with the soil solution. Making certain assumptions about the occurrence and behavior of ions in soil, Barber at Purdue University has estimated the relative importance of these mechanisms in providing nutrients to corn. The values he obtained are shown in Table 4-1. The contribution of diffusion was estimated by the difference between total nutrient needs and the amounts supplied by interception and mass flow.

Root Interception. The importance of root interception and contact exchange as a mechanism for ion absorption is enhanced by the growth of new roots throughout the soil mass and perhaps also by mycorrhizal infections. As the root system develops and exploits the soil more completely, soil solution and soil surfaces retaining adsorbed ions are exposed to the root mass and absorption of these ions by the contact exchange mechanism is accomplished. The quantity of nutrients that can come in direct contact with the plant roots is the amount in a volume of soil equal to the volume of roots. It can be assumed that roots usually occupy 1% or less of the soil. Because roots grow through soil pores which may have higher

TABLE 4-1. Relative Significance of the Principal Ways in Which Plant Nutrient Ions Move from Soil to the Roots of Corn

Nutrient	Amount of Nutrient Required for 150 bu/A of Corn (lb/A)	Percentage Supplied by		
		Root Interception	Mass Flow	Diffusion
Nitrogen	170	1	99	0
Phosphorus	35	3	6	94
Potassium	175	2	20	78
Calcium	35	171	429	0
Magnesium	40	38	250	0
Sulfur	20	5	95	0
Copper	0.1	10	400	0
Zinc	0.3	33	33	33
Boron	0.2	10	350	0
Iron	1.9	11	53	37
Manganese	0.3	33	133	0
Molybdenum	0.01	10	200	0

* Source: Barber and Olson, in L. B. Nelson et al., Eds., *Changing Patterns in Fertilizer Use*, p. 169. Madison, Wis.: Soil Science Society of America, 1968.

than average nutrient content, it is estimated that roots would contact a maximum of 3% of the available nutrients in the soil.

Mass Flow. Movement of ions in the soil solution to the surfaces of roots is an important factor in satisfying the nutrient requirement of plants. This movement is accomplished largely by mass flow and diffusion. Mass flow, a convective process, occurs when plant nutrient ions and other dissolved substances are transported in the flow of water to the root that results from transpirational water uptake by the plant. Some mass flow can also take place in response to evaporation and percolation of soil water.

Amounts of nutrients reaching roots by mass flow are determined by the rate of water flow or the water consumption of plants and the average nutrient concentrations in the soil water. The level of a particular nutrient around the root will fluctuate depending on the balance between the rate at which it reaches this zone by mass flow and the rate of uptake by the root. Mass flow supplies an overabundance of calcium and magnesium in many soils and most of the mobile nutrients, such as nitrogen and sulfur, if concentrations in the soil are sufficient (Table 4-1).

Diffusion. It is apparent in Table 4-1 that most of the phosphorus and potassium moves to the root by diffusion. Diffusion occurs when an ion moves from an area of high concentration to one of low concentration by random thermal motion. As plant roots absorb nutrients from the surrounding soil solution, a diffusion gradient is set up. Plant roots absorbing nutrients in this manner thus create a sink to which nutrients diffuse. A high plant requirement or a high root "absorbing power" results in a strong sink or a high diffusion gradient, favoring ion transport.

The three principal soil factors influencing the movement of nutrients into the root are the diffusion coefficient, concentration of the nutrient in the soil solution, and the buffering capacity of the solid phase of the soil for the nutrient in the soil solution phase. Of these factors, the diffusion coefficient is the most important since it controls how far nutrients can diffuse to the root. For a given spacing of roots in soil, it determines the fraction of the nutrients in the soil that can reach the root during a specific period of plant growth.

Using the general equation from Fick's law of diffusion it can be shown that the effective diffusion coefficient, D_e , for the diffusion of an ion in soil, is influenced by three principal factors: volumetric water percentage, θ ; tortuosity factor, f , which expresses the irregular and indirect pathway of diffusion in the pores of the soil; and the buffering capacity, b . The relationship of these parameters to the diffusion coefficient is

$$D_e = D_w \theta f \frac{1}{b} \quad (1)$$

where D_w is the diffusion coefficient for the particular nutrient in water. From equation (1) it can be predicted that diffusion can be increased by high soil moisture contents or volumetric water percentage. Raising θ also reduces tortuosity, which in turn increases diffusion. High soil moisture levels thus have a substantial influence on diffusion.

Buffering capacity usually decreases as nutrient levels in the soil are raised. Reduction in buffering capacity is associated with a rise in the rate of diffusion. Fertilization of part of the soil or localized placement is a practical means of increasing the effective diffusion coefficient.

Although not indicated in the foregoing equation, the effective diffusion coefficient varies directly with the square of the temperature (absolute), thus making it very sensitive to soil temperature. Movement of nutrient ions by diffusion is

slow under most of the root surface conditions, typical phosphorus, 0.1 roots in the top need to diffuse absorption by t

Under some root surface be This results in a gradient, and surface and bac but as roots do be a buildup of when the plan levels of one of the uptake of c

The importa with ions for a supply the liqu influenced by t these colloids a is also import: ease of replace by plant uptake Mehlich in No beidellite clay calcium-satura observed simil.

Com nature of ions is defined as th surface of a col exchanged, the retention stren cations increas

An appreciat where ammoni This exchange exchange comp more sodium th for sodium, the held trivalent capacity and completely.

The usual e dominated soi sodium is rele cations are he exchangeable divalent catio semia of rum changeable po in absorption

slow under most soil conditions and occurs over very short distances in the vicinity of the root surface. Although values vary greatly with soils and soil moisture conditions, typical average distances for diffusion to the root are nitrogen, 1 cm; phosphorus, 0.02 cm; and potassium, 0.2 cm. The mean distance between corn roots in the top 15 cm of soil is about 0.7 cm, indicating that some nutrients would need to diffuse half this distance, or 0.35 cm, before they would be in position for absorption by the plant root.

Under some conditions the concentration of certain ions may build up at the root surface because the root is unable to absorb them at a sufficiently rapid rate. This results in a phenomenon known as "back diffusion," in which the concentration gradient, and hence the movement of certain ions, will be away from the root surface and back toward the soil solution. Normally such a condition will not occur, but as roots do not absorb all nutrient ions at the same rate, there may on occasion be a buildup of those ions that are less rapidly absorbed, particularly during periods when the plant is absorbing moisture rapidly. It should be noted that elevated levels of one or more nutrients in the rhizosphere can have important effects on the uptake of other nutrients.

The importance of both diffusion and mass flow in supplying the root surface with ions for absorption depends on the ability of the solid phase of the soil to supply the liquid phase with these ions. Solution concentrations of ions will be influenced by the nature of the colloidal fraction of the soil and the degree to which these colloids are saturated with basic cations. The nature of the adsorbed cations is also important. Results of several studies have shown, for example, that the ease of replacement of calcium from colloids, either by dilute hydrochloric acid or by plant uptake, varies in this order: peat > kaolinite > illite > montmorillonite. Mehlich in North Carolina, for example, showed that an 80% calcium-saturated beidellite clay (a 2:1 clay) gave the same percentage release of this ion as a 35% calcium-saturated kaolinite or a 25% calcium-saturated peat. Other workers have observed similar relationships.

Complementary Ion Effect. There is another phenomenon affecting the nature of ions in the soil solution. It is known as the complementary ion effect and is defined as the influence of one adsorbed ion on the release of another from the surface of a colloid. When only a portion of the cations held by soil colloids is being exchanged, the release of a given cation from exchangeable form is easier as the retention strength or the strength of bonding of the complementary exchangeable cations increases.

An appreciation of the complementary ion effect can be gained from an example where ammonium in the soil solution is exchanging with calcium on soil colloids. This exchange will take place more readily when the complementary cation on the exchange complex is aluminum rather than sodium. Ammonium will replace much more sodium than it will aluminum. By ammonium becoming involved in exchange for sodium, there is less of it available for replacement of calcium. The more strongly held trivalent aluminum tends to satisfy a greater part of the cation exchange capacity and permits the exchange of ammonium for calcium to proceed more completely.

The usual ease of cation replacement in montmorillonite- and organic matter-dominated soil systems follows the order $\text{Na} > \text{K} = \text{NH}_4 > \text{Mg} > \text{Ca} > \text{Al}$, where sodium is released most easily and aluminum least readily. Since the divalent cations are held more tightly than monovalent cations, excessively high levels of exchangeable ions such as ammonium or potassium can induce deficiencies of divalent cations such as calcium and magnesium. The occurrence of hypomagnesemia of ruminants is sometimes caused by the presence of high levels of exchangeable potassium, aluminum, and/or ammonium and the resultant depression in absorption of magnesium by plants. Ruminants consuming large amounts of

low-magnesium forage may develop the nutritional disorder known as grass tetany or hypomagnesemia.

Fertilizer Additions. Application of fertilizers to soils helps, at least temporarily, to maintain a high concentration of nutrient ions in the soil solution. Addition of nutrients such as phosphorus and potassium with restricted mobility in the soil because of their reactions with soil components will produce enriched soil pockets which can persist for long periods. As plant roots absorb ions, the presence of added fertilizer will increase the likelihood of a favorable diffusion gradient, thereby enhancing ion movement to root surfaces. Fertilizer applications can also have a positive influence on nutrient uptake by raising the concentrations of nutrient ions carried to the root in the transpirational flow of water.

Fertilization helps to offset soil conditions that retard the movement of nutrient ions to roots. Some of the principal soil factors influencing ion transport are reviewed in the next section.

Soil Factors Influencing Ion Transport. A number of soil factors, the most important of which are soil texture, moisture content, and temperature, modify delivery of ions to the plant root surface by diffusion and mass flow. The finer the texture of the soil, the less rapid will be the movement of soil moisture and the diffusion of ions through the water. Also, ions diffusing through soil moisture in clay soils are much more likely to be attracted to adsorption sites on the clay than in a sandy soil. The tortuosity parameter in the equation given earlier for the effective diffusion coefficient accounts for these effects of soil texture.

A reduction in soil moisture has a similar effect on both water movement and ion diffusion. As soil moisture is reduced (an increase in soil moisture tension), water movement slows down. Thus the movement of moisture to the root surface is slowed. Similarly, as the moisture content of the soil is lowered, the moisture films around the soil particles become thinner and the diffusion of ions through these films becomes more tortuous. Transport of nutrients to the root surface is probably most effective at a soil moisture content corresponding to field capacity.

Low temperatures will slow down the transport of ions by both diffusion and mass flow. As explained previously in this chapter, diffusion rates are proportional to temperature squared. The movement of nutrients ions by mass flow will be reduced at low temperatures because the transpirational demands of plants will be substantially less at low temperatures than under warmer conditions. In addition, the transport of ions in the flow of water evaporated at the soil surface will diminish at low soil temperatures.

Uptake of ions at the root surface, which is responsible for creating and maintaining diffusion gradients, is strongly influenced by temperature. Within the range of about 10 to 30°C, an increase of 10°C usually causes the rate of ion absorption to go up by a factor of 2 or more. The stream of water moving from the soil into the root is also very sensitive to temperature, since this water must move through endodermal cytoplasm and is therefore subject to factors such as temperature which influence metabolism.

Ion Absorption by Plants

Ion absorption by plants is a topic of great complexity and one that can be given only passing treatment in this book. The present consensus concerning the mechanics of ion absorption is that ions enter roots by exchange, by diffusion, and by the action of carriers or metabolic ion-binding compounds. These three mechanisms are associated with two components of the root system. One is termed *outer space*, or apparent free space, and the other is termed *inner space*. Absorption of ions into the outer space is believed to be governed by the processes of simple

TABLE 4-2. (

Diffusion and exch
Nonlinear with ti
short times
Ions stoichiometri
ions
Not highly selecti
Nonmetabolic
Ions in solution or

Source: Gauch,
the publisher, An

diffusion and e
abolic; that is,
of absorption. I
The characte
have been sum

Inner
erally accepted
gradient) appar
ponent, thus a
various carrier
bines with free
barriers not pe
carrier complex
the carrier is be

Two different
For some ions a
concentrations
into play. The p
the locale of the

As indicated in
process. Althoug
they do not com
last three eleme
Selenium will c
anions. Interest
do not compete

The nature of
that they are dir
of ion-binding p
triphosphate ma
to form or destr
ribonucleoprotei
binds the anions
nitrogen-contain
leases the ions d

The cell mitoc
has indicated th
work has been de
in the active tra
that the observ

TABLE 4-2. Characteristics of Ion Movement into Inner and Outer Cell Spaces

Outer	Inner
Diffusion and exchange adsorption	Ion-binding compounds or carriers
Nonlinear with time, equilibrium approached in short times	Linear with time for periods up to several hours
Ions stoichiometrically exchangeable for other ions	Ions essentially nonexchangeable and dialyzable
Not highly selective	Specific with regard to site and entry
Nonmetabolic	Dependent on aerobic metabolism
Ions in solution or adsorbed in outer space	Ions in vacuoles and partly in cytoplasm

Source: Gauch, *Annu. Rev. Plant Physiol.*, 8:31 (1957). Reprinted with permission of the author and the publisher, Annual Reviews, Inc., Palo Alto, Calif.

diffusion and exchange adsorption. Absorption of ions into the inner space is metabolic; that is, an expenditure of energy by the root cell is required for this type of absorption. In contrast to absorption in the outer space, it is largely irreversible.

The characteristics of the modes of entry of ions into the two types of root space have been summarized in Table 4-2.

Inner Space. The concept of an ion-binding compound or carrier is generally accepted, and active accumulation (accumulation against a concentration gradient) apparently involves a combination of the ions with a protoplasmic component, thus accounting for the selectivity of ions in this type of absorption. The various carrier theories all envision a metabolically produced substance that combines with free ions. This carrier-ion complex can then cross membranes and other barriers not permeable to free ions. After the transfer is accomplished, the ion-carrier complex is broken, the ion is released into the inner space of the cell, and the carrier is believed in some cases to be restored.

Two different mechanisms are involved in transport of ions into the inner space. For some ions a "mechanism 1" operates at very low concentrations, while at high concentrations above about 1 mM a "mechanism 2" with different properties comes into play. The plasmalemma, or external cytoplasmic membrane, is implicated as the locale of these dual mechanisms.

As indicated in Table 4-2, transfer into the inner space of cells is a highly selective process. Although potassium, rubidium, and cesium compete for the same carrier, they do not compete with elements such as calcium, strontium, and barium. The last three elements do, however, compete among themselves for another carrier. Selenium will compete with sulfate but not with phosphate or with monovalent anions. Interestingly, $H_2PO_4^-$ and HPO_4^{2-} apparently have separate carriers and do not compete with one another for entry into the inner space.

The nature of the ion-binding compounds is not known exactly, but it is likely that they are directly connected with proteins or are themselves proteins. A number of ion-binding polypeptides have been found. It has been suggested that adenosine triphosphate may react with specific metabolic intermediates in the Krebs cycle to form or destroy ion carriers. Another hypothesis suggests that the carriers are ribonucleoproteins in which nucleic acid binds the cations and the protein moiety binds the anions. Still other workers suggest that the carriers are phosphorylated nitrogen-containing intermediates in protein synthesis and that the carrier releases the ions on incorporation into the protein at the site of synthesis.

The cell mitochondria have also been suggested as ion carriers, and some work has indicated that cations and anions accumulate in these bodies. Considerable work has been done in Sweden which indicates that the cytochromes are implicated in the active transport of ions. It has been pointed out by other workers, however, that the observed high correlation between cytochrome activity and ion uptake

does not constitute proof that ion transport is achieved by the operation of the cytochrome system.

Outer Space. A considerable fraction of the total volume of the root is accessible for the passive absorption of ions. The "outer" or "apparent free space," where the diffusion and exchange of ions occurs, is located in the walls of the epidermal and cortical cells of the root and in the film of moisture lining the intercellular spaces. Walls of the cells of the cortex are apparently the principal locale of the outer space. This extracellular space is outside the outermost membrane, the plasmalemma, which is a barrier to diffusion and exchange of ions.

Extracellular spaces exist in the mesophyll cells of leaves where ions are able to diffuse and exchange. Most of the nutrient ions reach the "outer" space of leaves via the xylem, from the roots. Mineral ions in rain, irrigation water, and in foliar applications penetrate leaves through the stomata and cuticle to reach the interior of leaves, where they become available for absorption by mesophyll cells.

The possible relation between outer space and translocation of ions to the tops of plants is of considerable interest. Some workers maintain that ions actively accumulated by roots are not exchangeable, hence are not free to move to the tops of plants. The ions in the outer space, however, apparently are transported quite freely to plant tops. Other workers have observed that the movement of ions from roots to shoots is determined by the rates of water absorption and transpiration, suggesting that mass flow may be important in the movement of ions. They also observed that the relative contributions of the active and passive components to the total accumulation of ions in shoots depended both on water absorption and the concentration of the medium. The passive component is more important at high than at low solute concentrations.

Because active absorption is believed to result in fixation in the tissue of the ions so absorbed, the concepts of free space and passive absorption are useful in explaining the movement of salts through root systems. Many workers believe that the cells of roots and plant tops may accumulate ions from the transpiration stream, for obviously any ions that enter the roots and are carried upward by mass flow come in contact with many adsorption sites on numerous actively accumulating cells. This, in turn, would lead to a considerable gradient in the concentration of ions in the transpiration stream and may support the observation that ions from dilute external solutions do not appear to reach plant tops through passive absorption.

Mass flow as a means of explaining ion transport is not without its flaws. Selectivity of ions in mass flow is most difficult to explain. An excellent example is found in sodium, which is virtually excluded from the tops of some plant species. Despite the incompleteness of the picture in regard to ion absorption by plants, the present concepts of outer and inner space and their relation to active and passive absorption of ions are useful in explaining many of the observed facts. As in many other incompletely understood biological phenomena, future research will undoubtedly unveil more and more that is presently hidden from view.

Little has been said to this point about the differences between plants in selectivity of nutrient uptake. Many aspects of absorption, transport, and utilization of mineral nutrients in plants are under genetic control. Considerable evidence has been assembled which shows that genotypes within a species may differ greatly in various features of mineral nutrition, including rates of absorption and translocation of specific elements, efficiency of metabolic utilization, tolerance to high concentrations of elements in the growth medium, and other factors. The differential tolerance of soybean varieties to iron stress is exhibited in Table 4-3. The Bragg cultivar was able to absorb sufficient iron to grow satisfactorily, whereas the Forrest cultivar developed severe deficiencies of this nutrient. In addition to genetically controlled differences in mechanisms of mineral nutrition, the mor-

TABLE 4-3.

Cultivar

North
Amsoy 71
Corsoy
Hodgson
Bonus
Williams
South
Forrest
Davis
Lee
Bragg
Tracy

* Soils from () crops.

Source: Brown

phology of root varieties are or more finely

Sur

1.

catic
revie

2.

revie
cuss

mine

3.

of a
wascomp
is me

4.

it is c
anionother
expla

5.

faces
scribroots
phen

6.

surfa
enhaions
the rture
wate

TABLE 4-3. Differential Response of Soybean Varieties to Iron Stress

Cultivar	Yield* (g dry weight)			Iron Concentration in Tops (ppm)		
	Quinlan	Tripp	Milloille	Quinlan	Tripp	Milloille
North						
Amsoy 71	1.17	2.83	1.50	32	55	38
Corsoy	1.16	2.68	2.22	33	39	43
Hodgson	1.55	3.03	1.96	43	40	43
Bonus	1.32	2.57	1.99	42	51	48
Williams	1.40	3.21	2.32	29	39	45
South						
Forrest	1.07	2.70	1.60	20	28	22
Davis	0.98	2.12	1.41	27	49	43
Lee	1.15	3.06	1.61	26	37	39
Bragg	1.46	2.87	1.87	39	49	45
Tracy	1.36	2.99	2.05	37	36	47

* Soils from Oklahoma, Kansas, and Utah, respectively, which have produced iron stress in other crops.

Source: Brown and Jones, *Agron. J.*, 69:401 (1977).

phology of roots can also significantly influence the uptake of nutrient ions. Some varieties are better able to exploit soil for nutrients and moisture because of larger or more finely branched root systems.

Summary

1. Ion exchange, which is defined as the reversible process by which cations and anions are exchanged between solid and liquid phases, was reviewed with emphasis on the phenomenon as it occurs in soils.

2. The determination of cation exchange capacity (CEC) in soils was reviewed, and the factors affecting this important property were discussed. The CEC of a soil is related to the nature and amounts of the mineral and organic colloids present. It increases as soil pH rises.

3. Base saturation, which is the degree to which the exchange capacity of a soil is saturated with basic cations (i.e., Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+}), was covered in relation to the nature of the charge on the exchange complex. The dependence of the CEC on the way in which this property is measured was discussed.

4. Anion exchange can take place in soils, but for all practical purposes it is confined to the phosphate and sulfate ions. Unlike cation exchange, anion exchange increases with a decrease in soil pH. The reason that other anions do not undergo adsorption in most agricultural soils was explained.

5. Contact exchange, which is the exchange of ions between the surfaces of two solids without movement through a liquid phase, was described. Its possible importance in soils was considered because plant roots themselves exhibit the property of cation exchange. The latter phenomenon was also discussed briefly.

6. Plant nutrient ions are brought into contact with the absorbing surfaces of roots by (a) root interception and contact exchange, which is enhanced by the growth of roots through the soil mass; (b) diffusion of ions in the soil solution; and (c) mass flow of soil water, which brings the nutrient ions into contact with the plant roots. Absorption of moisture by the roots is one of the principal causes of the mass flow of soil water.

7. Mass flow supplies large amounts of calcium and magnesium and a large proportion of the nitrogen and sulfur requirements of plants. Most of the phosphorus and potassium moves from the soil to the root surface by diffusion. Mass flow and diffusion are influenced by soil factors such as clay content, moisture levels, and temperature. Nutrient concentrations in the soil solution have an important effect on the transport of ions to root surfaces.

8. Fertilizer applications can improve the mass flow and diffusion of ions to the root by increasing nutrient concentrations in the soil solution. Diffusion is slowed by increasing clay content, low soil moisture, and low temperatures. The addition of phosphorus and potassium helps to offset these retarding effects by increasing the diffusion gradient.

9. Some of the suggested mechanisms by which ions are actually absorbed by plants were considered. Ions are absorbed by both active and passive mechanisms. Active absorption is thought to take place by metabolically produced carriers which transfer the ions across otherwise impassable barriers. Passive absorption is governed largely by exchange adsorption and diffusion phenomena. Actively absorbed ions are believed to be taken into what is termed the *inner space* in roots, whereas ions that are passively absorbed move into the *outer space* of roots. It was pointed out that much is still to be learned about the mechanics of ion absorption by roots.

Questions

1. Define ion exchange.
2. From what sources does the charge on soil colloids arise?
3. Why does anion adsorption appear to be of no importance in most agricultural soils?
4. Potassium acetate solution was used to determine the cation exchange capacity of a soil. Ten grams of oven-dry soil was extracted with 200 ml of 1.0 N KAc. It was found that 0.078 g of potassium was retained by the soil. What is its CEC?
5. Can one determine by the method described in Question 4 the percent base saturation of this soil? Why?
6. In the example listed on page 98, what assumption must be made if the percentage of base saturation measured is to be considered valid? Under what conditions would you assume that this assumption is valid?
7. Cation exchange in soils appears to increase as the pH _____
Anion exchange in soils appears to increase as the pH _____
8. A soil was found to have a CEC of 24 meq per 100 g. If the exchange capacity were saturated with sodium, to how many grams of sodium chloride would this be equivalent?
9. The CEC of a soil as measured using 1.0 N neutral ammonium acetate gives lower values than those obtained when a solution of BaCl_2 -triethanolamine buffered at pH 8.3 is used. Why?
10. What is the origin of the effective CEC in mineral soil colloids?
11. What is contact exchange?
12. A soil has a CEC of 25 meq per 100 g on an oven-dry basis. Suppose that this soil was 5% saturated with potassium and you wished to increase the saturation to 9%. Assuming that all of the added potassium would be adsorbed, how much 100% potassium chloride would have to be added to an acre furrow slice of this soil to raise

13

14

15

16

17

18

19

20

21

22

23

24

25

Sel

Adar

35

Asha

an

12

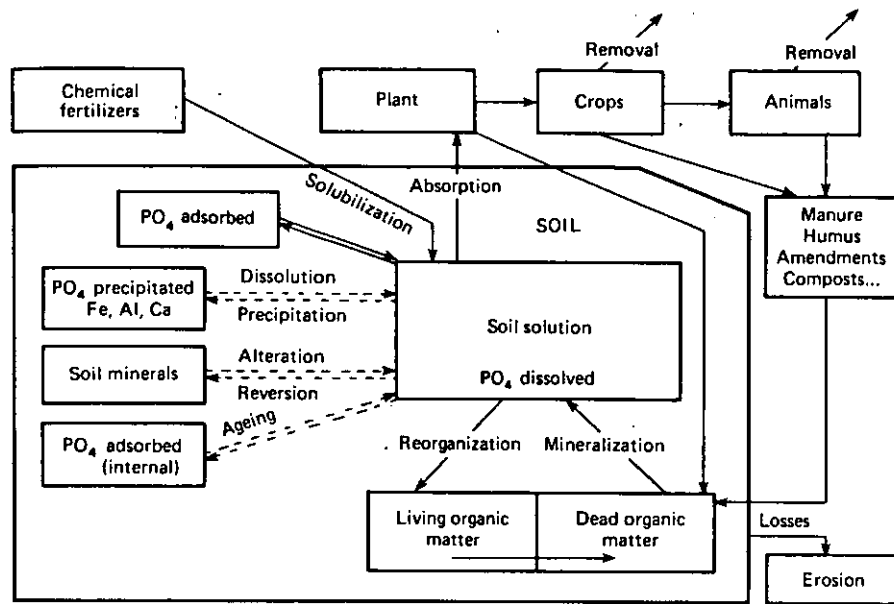


FIGURE 6-2. Phosphorus dynamics system in the soil. [Modified after Gachon, *Bull. Assoc. Fr. Etude Sol*, 4:17 (1969).]

very insoluble. Phosphates also react with clays to form generally insoluble clay-phosphate complexes.

The inorganic phosphorus content of soils is frequently higher than that of organic phosphorus. An exception to this rule would, of course, be the phosphorus contained in predominantly organic soils. In addition, the organic phosphorus content of mineral soils is usually higher in the surface horizon than it is in the

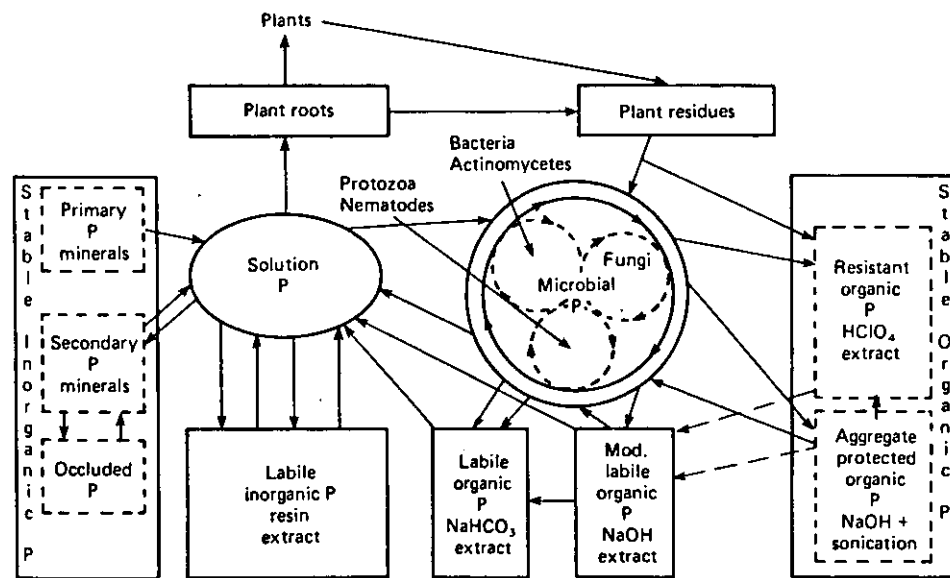


FIGURE 6-3. Schematic illustration of the measurable components of the phosphorus cycle in soils, showing the interchange of solution, organic, and microbial forms. [Chauhan et al., *Can. J. Soil Sci.*, 61:373 (1981).]



United States.
inted with per-

redicting the likelihood
d reflect contributions
plants. Two of these
e concentration of soil
ommonly used extrac-

detail in Chapter 12,
tion at this point that
those of the available
c growth.

interrelationships are
enerally as organic or
it occurs. The organic
ay or may not be as-
oils vary enormously,
content in the surface
range from 25 to 55%
accounting for upward
nplified picture of the
organic and microbial
S.

phosphorus occurs in
urine, and other ele-
sparingly soluble to

from region to region. Direct adsorption may be the most important way that SO_2 enters soils.

Because of the growing concern over air pollution, legislation may ultimately be enacted to require the cleaning and scrubbing of all waste gases. Many industrial companies are presently required to clean effluent gases, and it is likely that this practice will spread and, in turn, will reduce the amounts of sulfur brought down by the rain and absorbed from the atmosphere directly by plants and soil. While the emission of sulfur compounds into the atmosphere by industrial activity has received a lot of unfavorable publicity, the fact remains that 70% of the total content of sulfur compounds in the atmosphere is of nonmanmade origin. Volatile sulfur compounds are released in large quantities from volcanic activity, from tidal marshes, from decaying organic matter, and from other sources.

Forms and Behavior of Sulfur in Soils. Sulfur is present in the soil in many different forms, both organic and inorganic. It exists in multiple oxidation states ranging from +6 in H_2SO_4 and its derivatives (hexavalent or oxidized sulfur) to -2 in H_2S and its derivatives (divalent or reduced sulfur). Also, sulfur occurs in solid, liquid, or gaseous phases.

The inorganic forms are readily-soluble sulfate, adsorbed sulfate, insoluble sulfate coprecipitated with calcium carbonate, and reduced inorganic sulfur compounds. Since plants obtain sulfur primarily from soil as dissolved sulfate, easily soluble sulfate plus adsorbed sulfate represent the readily available fraction of soil sulfur which is utilized by plants.

Many surface soils contain most of their sulfur in organic combinations. Researchers agree that in excess of 90% of the total sulfur in most noncalcareous surface soils exists in organic forms.

The dynamic nature of sulfur in soils and the relationships between the variety of forms are shown schematically in Figure 8-1. There are similarities between

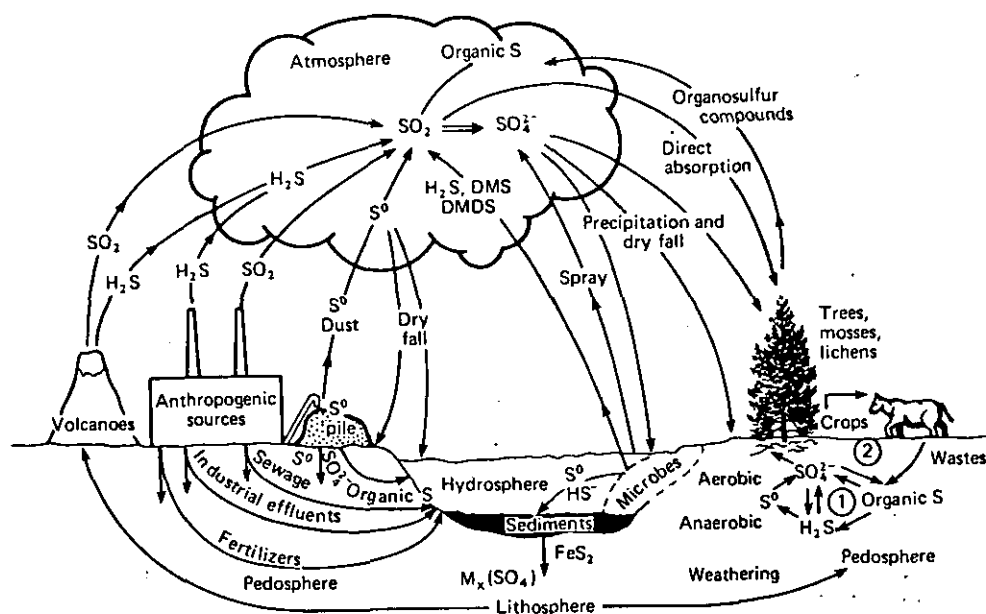


FIGURE 8-1. Simplified version of the overall sulfur cycle in nature. The encircled 1 refers to the microbiological cycle and the encircled 2 depicts a food cycle with higher animals. (Krouse and McCready, in P. A. Trudinger and D. J. Swaine, Eds., *Studies in Environmental Science*, Vol. 3: *Biogeochemical Cycling of Mineral-Forming Elements*. Amsterdam: Elsevier Scientific, 1979.)

the nitrogen and sulfur occurrence in soils is

Easily Soluble SO_4^{2-} ion. Concentrations have proved adequate to require higher concentrations.

Sulfate ions reach or more of soluble SO_4^{2-} is supplied by mass

Except for soils in most soils are generally as inorganic SO_4^{2-} . In 10% or less. Readily between 1 to 10% of the most well-drained soil sulfur.

Concentrations of SO_4^{2-} in American soils. In some the amount of readily sulfur-deficient soils

Levels of readily available sulfur considerably within a maximum in subsurface. Accumulations of easily siferous horizons and ing are restricted.

Adsorbed Sulfur in soils, particularly those with minimum and iron. Many contain appreciable amounts of sulfur. These soils in the southeastern United States, Asia, and Africa. After such soils approach the sulfur released will be

This fraction is believed to be growing in highly weathered soils. release of organic sulfur SO_4^{2-} may not be as rapid over longer periods of time

Although crops can suffer from sulfur deficiency in the reach the retention zone are unlikely to have sufficient

The analyses reported SO_4^{2-} in various southern soils only an approximate method and significant occurrence of adsorbed sulfur in soils containing very little. These zones of high concentration from 6 to 30 in. below the

whereas NH_4^+ cannot. Urea, diammonium phosphate, ammonium carbonate, and ammonium hydroxide may cause more damage than materials such as monoammonium phosphate, ammonium sulfate, and ammonium nitrate. This was discussed in Chapter 5. Placement to the side and below the seed is an effective method of avoiding the problem.

Salt Index

Fertilizers increase the salt concentration of the soil solution. The salt index of a fertilizer is a measure of this phenomenon and is determined by placing the material under study in the soil and measuring the osmotic pressure of the soil solution. Osmotic pressure is expressed in atmospheres. Salt index is actually the ratio of the increase in osmotic pressure produced by the material in question to that produced by the same weight of sodium nitrate, based on a relative value of 100.

Fertilizer salts differ greatly in their effect on the concentration of the soil solution. Mixed fertilizers of the same grade may also vary widely in salt index, depending on the carriers from which they are formulated. It would be well to emphasize that the higher-analysis fertilizers will generally have a lower salt index per unit of plant nutrients than water-soluble, lower-analysis fertilizers because they are usually made up of higher-analysis materials. For example, to furnish 50 lb of nitrogen, 250 lb of ammonium sulfate would be required, whereas with urea 110 lb would be required. Hence the higher-analysis fertilizers have less of a tendency to produce salt injury than equal amounts of plant nutrients in the lower-analysis fertilizers.

The salt index per unit, 20 lb, of plant nutrient for several materials is shown in Table 13-5. Nitrogen and potassium salts have much higher salt indices and

TABLE 13-5. Salt Index per Unit of Plant Nutrients Supplied for Representative Materials

Material	Analysis *	Salt Index per Unit of Plant Nutrients
Nitrogen carriers		
Anhydrous ammonia	82.2	0.572
Ammonium nitrate	35.0	2.990
Ammonium sulfate	21.2	3.253
Monoammonium phosphate	12.2	2.453
Diammonium phosphate	21.2	1.614
Nitrogen solution 2A	40.6	1.930
Potassium nitrate	13.8	5.336
Sodium nitrate	16.5	6.060
Urea	46.6	1.618
Phosphorus carriers		
Superphosphate	20.0	0.390
Superphosphate	48.0	0.210
Monoammonium phosphate	51.7	0.485
Diammonium phosphate	53.8	0.637
Potassium carriers		
Manure salts	20.0	5.636
Potassium chloride	50.0	2.189
Potassium chloride	60.0	1.936
Potassium nitrate	46.6	1.580
Potassium sulfate	54.0	0.853
Potassium magnesium sulfate	21.9	1.971

* By analysis is meant the percentage of nitrogen in nitrogen carriers, of P_2O_5 in phosphorus carriers, and of K_2O in potassium carriers.

Source: Rader et al., *Soil Sci.*, 55:201. Copyright 1943 by The Williams & Wilkins Company.

TABLE 13-5-4.4-8.3 and

Ammoniating
Diammonium
Urea
Ammonium s
Treble superp
Superphospha
Muriate of pot
Conditioner
Filler

are much mo
close to or in
of a mixed fer
The comparis
in Table 13-6.
of plant nutri
of higher-ana

In consider
differences in
amounts per a
increasingly in

Gen
Ban

vantageous, ar
The early gro
leaf growth is
in the leaves, t
produced in the
near the very
healthy leaves
in corn are dif
any source is
barley is deter
remainder of th
is expressed.

Starter respo
temperatures t
slow mineraliza
matter; restrict
of phosphorus a
other nutrients
commonly refer

The advantag
Some of the fac

TABLE 13-6. Comparative Salt Index of 5-4.4-8.3 and 10-8.8-16.6

	5-4.4-8.3 (5-10-10)		10-8.8-16.6 (10-20-20)	
	Pounds	Salt Index	Pounds	Salt Index
Ammoniating solution	148	5.79	—	—
Diammonium phosphate	—	—	373	6.37
Urea	—	—	260	9.71
Ammonium sulfate	195	6.51	—	—
Treble superphosphate	—	—	417	2.10
Superphosphate	1000	3.90	—	—
Muriate of potash (41% K)	400	21.89	—	—
Muriate of potash (50% K)	—	—	667	38.72
Conditioner	100	—	110	—
Filler	157	—	180	—
	2000	38.09	2000	56.90

are much more detrimental to germination than phosphorus salts when placed close to or in contact with the seed. From this information the relative salt index of a mixed fertilizer can be calculated if the formulation of the fertilizer is known. The comparison between the 5-4.4-8.3 (5-10-10) and 10-8.8-16.6 (10-20-20) is shown in Table 13-6. In fertilizers of these formulations the salt index for equal quantities of plant nutrients is 38.09 and 28.45, respectively. This then is another advantage of higher-analysis fertilizers.

In considering the placement of fertilizers at planting it is important that the differences in salt effects among fertilizers be kept in mind. Obviously, if higher amounts per acre of higher-analysis fertilizers are to be used, the problem becomes increasingly important.

General Considerations

Band Applications. Early stimulation of the seedlings is usually advantageous, and it is desirable to have N-P-K near the plant roots.

The early growth of the plant top is essentially all leaves. In a crop such as corn leaf growth is completed in about 60 days. Since the photosynthesis is carried on in the leaves, the number of leaves produced in this period will influence the grain produced in the next 45 days. It is important to have a small amount of nutrients near the very young plants to promote early growth and the formation of large healthy leaves (Figure 13-14). Also, the various plant parts such as the ear bud in corn are differentiated very early in the growth cycle and lack of stress from any source is desirable. Alberta investigators report that the yield potential of barley is determined by the four-leaf stage. Environmental factors through the remainder of the growing season will determine the degree to which this potential is expressed.

Starter response to N-P-K is often independent of fertility level. Under cool temperatures the early available nutrient supplies may be inadequate because of slow mineralization of nitrogen, phosphorus, sulfur, and so on, from the soil organic matter; restricted release of plant nutrients from soil minerals; reduced diffusion of phosphorus and potassium; or limited absorption of phosphorus, potassium, and other nutrients by the plant. Localized applications of fertilizer at planting are commonly referred to as starter or planting fertilizers.

The advantage of early stimulation depends on the crop and seasonal conditions. Some of the factors that might be considered are the following.