

Chapter 7: Anion and molecular retention

I. Anions and molecules of importance in soils

Anions of major importance to agricultural soils and soil chemistry are: H_2PO_4^- , HPO_4^{2-} , SO_4^{2-} , HCO_3^- , NO_3^- , Cl^- , F^- and OH^- . Also, micronutrients such as boron and molybdenum exist as anions H_2BO_3^- and MoO_4^{2-} . Other substances such as pesticides: 2,4-D, 2,4,5-T and DDT or rock weathering product H_2SiO_4 [or $\text{Si}(\text{OH})_4$] are present as non-charged or molecular species in soils.

Although the anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity, their retention mechanisms are much more complex than the simple electrostatic attractions involved in most cation adsorption.

II. Nonspecific Anion Adsorption.

A. Anion Repulsion (negative adsorption)

An anion approaching a charged surface is subject to

- a.) attraction by positive charges on the surface, or
- b.) repulsion by negative charges.

Because layer silicates in soils are normally negatively charged, anions tend to be repelled from the soil mineral surfaces.

*** The diffuse double layer concept**

If a dilute solution of KCl is added to a dry montmorillonite, the Cl^- concentration in the bulk solution at equilibrium will be greater than the Cl^- concentration originally added.

Ex: An original solution has 0.01M Cl^- (as KCl), after dry montmorillonite is added to this solution and after a while when equilibrium has been reached, we'll find the Cl^- concentration would be, say, 0.011 M.

This process is called anion repulsion or negative adsorption and can be explained by the diffuse double layer concept, as follows.

Because the clay minerals such as montmorillonite have negative charges on their surface, more cations are attracted to the surface and anions are repelled from the surface.

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This results in an uneven distribution in the diffuse double layer. Therefore, anion concentration in the bulk solution is higher than originally added.

An additional explanation is that when an electrolyte solution is added to a dry clay, some water is used to form the double layer, leaving less water to the salt. This reduction in volume of H₂O coupled with the uneven distribution of ion in the diffuse double layer results in an increase in the anion concentration in the bulk solution.

Ex: We add 1000 ml of 0.01 M Cl⁻ to a 100g montmorillonite. 100 ml of H₂O is used to form the double layer around the clay, therefore at equilibrium, we only have: 0.01 mole Cl⁻ in 900ml H₂O $\hat{=}$ $0.01 / 900 = 0.011M$ (Cl⁻)

* **Donnan Concept.** This can be used to explain the increased conc. of anion in the bulk solution.

Donnan was the first to propose that for any charged surface, an electrical potential field will develop. At the boundary of the field, according to thermodynamics, the chemical potentials of a given electrolyte in 2 phases (namely bulk solution vs. electrical field) must be equal:

Ex:
$$\underbrace{(K^+)_0(Cl^-)_0}_{\text{Inside the field}} = \underbrace{(K^+)_1(Cl^-)_1}_{\text{outside the field or in bulk solution}} \quad (1)$$

When you increase (K⁺)₀ and reduce (K⁺)₁ by electrical attractions to the negative surface, then you must reduce (Cl⁻)₀ and increase (Cl⁻)₁ so that equation (1) is always maintained. That's why chloride concentration in the bulk solution increases.

B. Factors affection anion repulsion

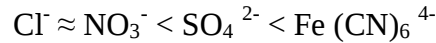
1.) Charge of the colloid surface

The greater the negative charge on the soil solid, the greater the anion repulsion. That is why montmorillonitic soils exhibit greater anion repulsion than kaolinitic soils. This is especially true at low pH where kaolinite may even develop positive charge.

2.) Anion charge and concentration

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The higher the charge of anions, the greater the anion repulsion. For Na-montmorillonite, anion repulsion increases in the order:



Similarly, increasing the anion concentration increases anion repulsion. The reason is that the higher the concentration of electrolytes, the thinner the double layer, and the repulsion becomes greater with decreasing double layer thickness.

3.) pH effect

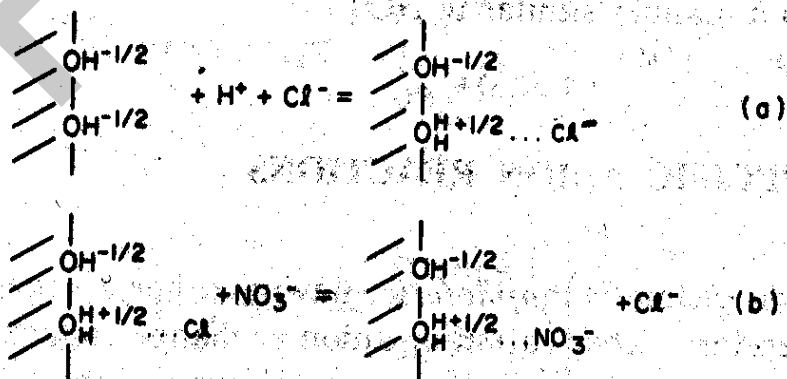
In soils with pH-dependent charge, lowering the pH decreases the net negative charge of the system. Anion repulsion thus decreases as the soil pH decreases.

C. Electrostatic attraction of Anions

Anions approaching positively charged sites on layer silicates or hydrous-oxide minerals are attracted electrostatically in the same manner as cations are attracted to negatively charged soil colloids.

Anions that are retained electrostatically are called nonspecifically adsorbed anions. This kind of adsorption can be shown as follows:

First the colloid surface is protonated (by obtaining an H^+), then the positive charge will attract a Cl^- ion. This Cl^- can be exchanged with another nonspecifically adsorbed anion such as NO_3^- .



The anions Cl^- , NO_3^- and ClO_4^- are generally considered to be non-specifically adsorbed.

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If you look at table 7.1, there are 2 things that need to be noted:

- 1.) At $\text{pH} > 7.0$, both kaolinite and montmorillonite have virtually all negative charge, therefore they repel anions. There is no anion adsorption whatsoever.
- 2.) Kaolinite generally adsorbs more anions than montmorillonite at the same pH, due to the higher positive charge density on kaolinite.

TABLE 7.1

Adsorption of Cl^- and SO_4^{2-} by a Kaolinitic Soil and of Cl^- by a Montmorillonitic Soil in Relation to pH^a

KAOLINITIC SOIL (mmole sorbed kg^{-1})			MONTMORILLONITIC SOIL (mmole sorbed kg^{-1})	
pH	Cl^-	SO_4^{2-}	pH	Cl^-
7.2	0	0	6.8	0
6.7	3	10	5.6	0
6.1	11	27	4.0	0.5
5.8	24	36	3.0	1
5.0	44	52	2.8	4
4.0	60	—		

^aFrom F. E. Bear (Ed.), *Chemistry of the Soil*, ACS Monograph Series No. 160, 1964, p. 198.

III. Specific Anion Reactions

A. Oxyacid anions and Al-Fe oxides

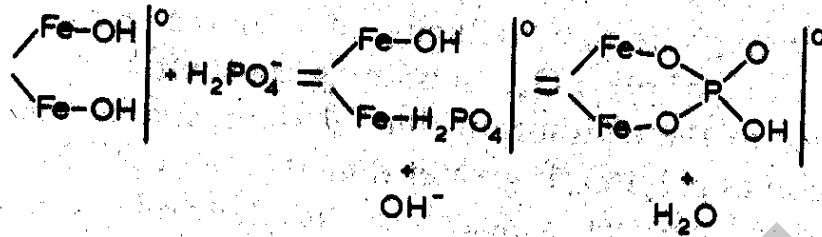
1.) Amphoteric nature of Al and Fe oxides

An amphoteric system can have either a negative or positive charge depending on the environment; and hydrous oxides of Al and Fe are such a system. Therefore, hydrous oxides of Al and Fe have either cation or anion exchange capacities, depending upon the pH.

2.) Ligand exchange or anion penetration.

Besides the electrostatic attraction or nonspecific adsorption, these oxides are capable of adsorbing some anion's specifically. Specifically adsorbed anions often are HPO_4^{2-} , H_2PO_4^- , H_2AsO_4^- (arsenate), and F^- . These anions can enter 6-fold coordination with Al^{3+} or Fe^{3+} ions and replace OH^- ions on hydrous oxides surfaces. This exchange is known as ligand exchange or anion penetration.

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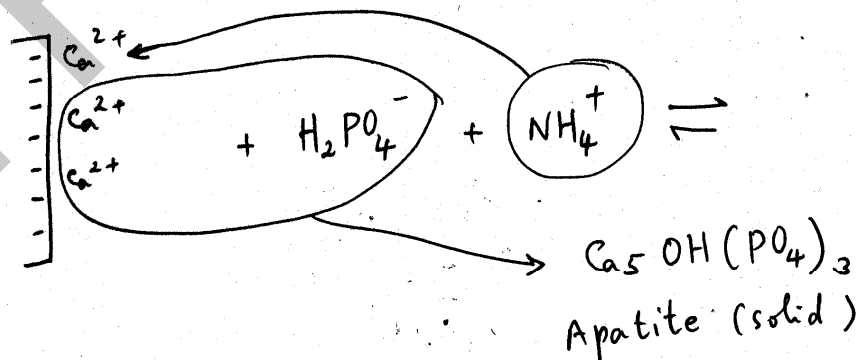
So, the mineral changes from hydroxyl surface to phosphate surface.

Ligand exchange is different from nonspecific anion adsorption in the aspect that while nonspecific anion adsorption can occur only on positively charged surfaces, ligand exchange or specific adsorption can occur on surfaces with negative, positive or neutral charge initially.

3. Surface dissolution and precipitation. A case of phosphate reactions.

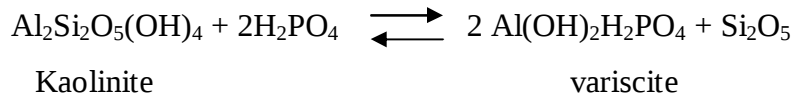
In fact, the reactions between phosphate and layer silicates consists of 2 steps: the initial step is rapid (complete is less than a day), which is considered as a combination of nonspecific adsorption and ligand exchange on mineral edges; the second step is much slower (it may take several days or weeks to complete), which is considered as the process of mineral dissolution and/or precipitation of added P with exchangeable or mineral lattice cations.

Example 1: Exchangeable cations



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Example 2 : with structured cations



Phosphorus forms sparingly soluble compounds with Fe^{3+} and Al^{3+} at low pH such as variscite, $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$, or strengite, $\text{Fe}(\text{OH})_2\text{H}_2\text{PO}_4$, at near neutral pH (pH 5.6-6.5). Phosphate is most soluble as you can see on Fig. 7.5 (page 192). That's why liming often tries to bring soil pH into this range. At high pH, phosphates becomes less soluble, again because of the formation of sparingly soluble Ca-phosphate compounds such as octocalcium phosphate, $\text{Ca}_4\text{H}(\text{PO}_4)_3$, or hydroxyapatite, $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$.

Stability Diagram

Diagrams such as Figure 7.5 are called stability or solubility diagrams. In this particular diagram, pH_2PO_4 , or $-\log(\text{H}_2\text{PO}_4)$ is plotted as a function of pH.

How do we construct this diagram? Well, we probably don't have time to go through all of it, but let me show you how to draw, say, variscite and hydroxyl apatite lines because these are the two most likely P minerals that control P concentration in soil solutions.

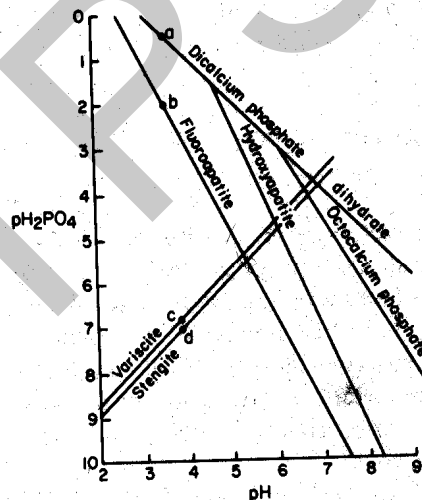
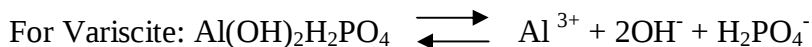


Fig. 7.5 Solubility Diagram for phosphorus compounds at 25°C and $5 \times 10^{-3} M$ calcium. (After W. L. Lindsay and E. C. Moreno, *Soil Sci. Soc. Amer. Proc.* 24:177-182 (1960).)



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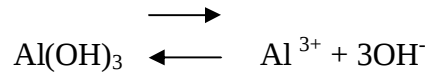
$$K_{sp} = (Al^{3+})(OH^-)^2(H_2PO_4) = 3.15 \times 10^{-30}$$

$$(H^+)(OH^-) = 10^{-14} \text{ from } H_2O$$

$$(OH^-) = 10^{-14} / (H^+)$$

$$(Al^{3+})(10^{-28}) / (H^+)(H_2PO_4) = 3.15 * (10^{-30} / 10^{-28}) = 3.15 * 10^{-2}$$

Soil solution Al^{3+} , in turn, is controlled by solubility of gibbsite:



$$(Al^{3+})(OH^-)^3 = 1.1 \times 10^{-33}$$

$$(Al^{3+}) = 1.1 \times 10^{-33} * (1 / (OH^-)^3) = 1.1 \times 10^{-33} \times (H^+)^3 / 10^{-42}$$

$$(Al^{3+}) = 1.1 \times 10^9 (H^+)^3$$

$$\frac{(H_2PO_4)}{(H^+)^2} * 1.1 * 10^9 (H^+)^3 = 3.15 \times 10^{-2}$$

$$(H_2PO_4)(H^+) * 1.1 \times 10^9 = 3.15 \times 10^{-2}$$

$$(H_2PO_4)(H^+) = \frac{3.15 \times 10^{-2}}{1.1 \times 10^9} = 2.85 \times 10^{-11}$$

$$\log(H_2PO_4) + \log(H^+) = -11 + 0.455$$

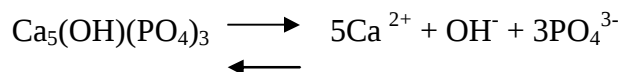
$$-\log(H_2PO_4) + [-\log(H^+)] = +10.545$$

$$\overset{\wedge}{pH_2PO_4} + \overset{\wedge}{pH} = +10.545$$

$$pH_2PO_4 = -pH + 10.545$$

as pH increases, pH_2PO_4 becomes smaller. That is H_2PO_4 concentration becomes larger, or variscite solubility increases.

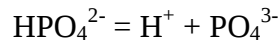
For hydroxyapatite:



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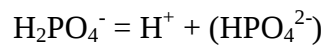
$$K_{sp} = (Ca^{2+})^5 (OH)(PO_4^{3-})^3 = 1.23 \times 10^{-56}$$

Now we have to convert (PO_4^{3-}) to $(H_2PO_4^-)$



$$K_3 = 4.35 \times 10^{-15} = \frac{(H^+)(PO_4^{3-})}{(HPO_4^{2-})}$$

$$(PO_4^{3-}) = \frac{k_3(HPO_4^{2-})}{(H^+)}$$



$$K_2 = 6.23 \times 10^{-8} = \frac{(H^+)(HPO_4^{2-})}{(H_2PO_4^-)}$$

$$(HPO_4^{2-}) = \frac{k_2 H_2PO_4^-}{(H^+)}$$

$$(PO_4^{3-}) = \frac{k_3 k_2 (H_2PO_4^-)}{(H^+)^2}$$

$$(Ca^{2+})^5 * \frac{(10^{-14}) * [k_2 k_3 (H_2PO_4^-)]^3}{(H^+)^6} = K_{sp} = 1.23 \times 10^{-56}$$

$$\frac{(Ca^{2+})^5 * (H_2PO_4^-)^3}{(H^+)^7} = \frac{K_{sp}}{10^{-14} * K_2^3 K_3^3} =$$

$$= \frac{1.23 * 10^{-56}}{10^{-14} * (4.35)^3 * 10^{-39} * (6.23)^3 * 10^{-24}}$$

$$= \frac{1.23 * 10^{-56}}{10^{-77} * 82.3 * 241.8} = \frac{1.2 * 10^{-56}}{1.99 * 10^{-73}}$$

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$$\frac{(\text{H}_2\text{PO}_4^-)^3}{(\text{H}^+)^7} = \frac{6.2 * 10^{16}}{(\text{Ca}^{2+})^5}$$

$$3 \log(\text{H}_2\text{PO}_4^-) - 7\log(\text{H}^+) = \log(6.2 * 10^{16}) - 5\log(\text{Ca}^{2+})$$

assume: act. of soil-solution Ca = $5 \times 10^{-3} \text{ M}$

$$\begin{aligned} -3\text{pH}_2\text{PO}_4 + 7\text{pH} &= 16 + 0.79 - 5\log(5 * 10^{-3}) \\ &= 16.79 - 5(0.7-3) \\ &= 16.79 + 11.5 \\ &= 28.29 \end{aligned}$$

$$3\text{pH}_2\text{PO}_4 = 7\text{pH} - 28.29$$

$$\text{pH}_2\text{PO}_4 = \frac{7}{3} \text{pH} - 9.43$$

As you can see from this equation and the diagram, the higher the pH, the higher the pH_2PO_4 or the lower the $(\text{H}_2\text{PO}_4^-)$ concentration in soil solution.

These stability diagrams are very useful in predicting soil solution composition. For example, P concentration in soil solution. What we can tell from such a diagram is that a point above a compound's isotherm represents supersaturation with respect to that compound, indicating that precipitation of the compound is possible. Data below the isotherm indicate undersaturation of the soil solution with respect to the compound, so that the compound, if present, would be expected to dissolve. Intersections of 2 isotherms represent solutions in equilibrium with both compounds.

IV. Adsorption Isotherms

First let's define the 2 terms that are frequently used in adsorption.

Adsorbate: is a substance or an ion which is being adsorbed on a mother substance.

Ex: Phosphate is the adsorbate in a system of Phosphate solution and soil minerals.

Adsorbent: a substance which is doing the adsorbing action. For the above example, clay mineral is the adsorbent.

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The two most common adsorption equations are: Freundlich and Langmuir.

1.) Freundlich equation

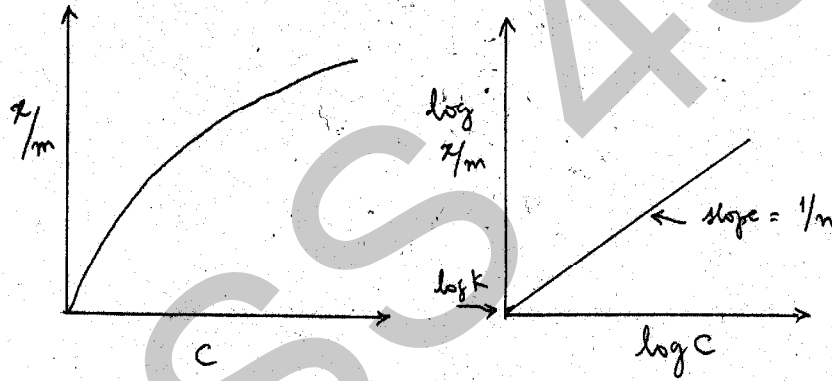
This is an empirical equation, which has the form:

$$\frac{x}{m} = kC^{1/n}$$

Where: x/m is the weight of adsorbate per unit weight of adsorbent

k and n are empirical constants.

C is the equilibrium concentration of adsorbate in question. When you draw the adsorption isotherm, this equation would have the form.



or:

$$\text{Log } (x/m) = \log K + 1/n \log C$$

2.) Langmuir equation

This equation was first derived for the adsorption of gases on solids. It requires 3 assumptions.

- constant energy of adsorption
- no interaction between adsorbate molecules
- a maximum adsorption is achieved when all reactive sites on the adsorbed surface are covered with a monolayer of adsorbate. The Langmuir equation is expressed as:

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$$\frac{x}{m} = \frac{KCb}{(1 + KC)}$$

where x/m : is the weight of adsorbate per unit weight of adsorbent.

C : concentration of adsorbate at equilibrium

K : a constant related to the binding strength between adsorbate and adsorbent

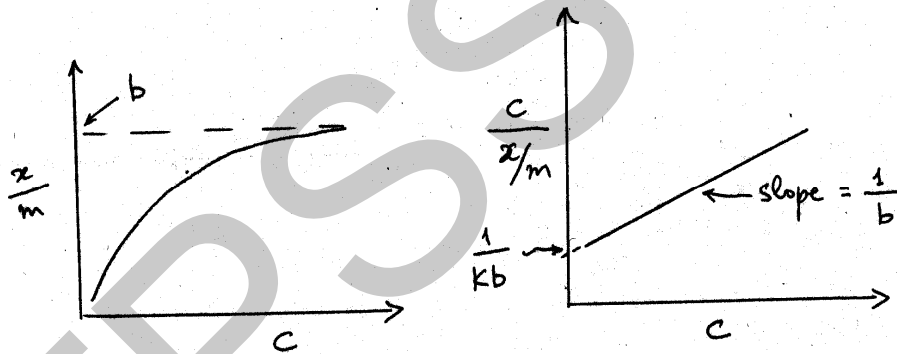
b : the maximum amount of adsorbate that can be adsorbed.

Divide both side of the equation by C .

$$(x/m)/C = Kb/(1+KC)$$

then invert this equation, we get the linear form of Langmuir equation.

$$C/(x/m) = 1/Kb + C/b$$



Langmuir equation is also used very often to estimate the adsorption capacity of soils for phosphate and SO_4 .