

Soil Chemistry

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Basics of physical chemistry

Chemical bonds

Covalent
Metallic
Coordination
Electrostatic
Van der Waals

Chemical equilibrium

Precipitation, dissolution
Water ions, pH, pOH
Redox equilibrium, Nerst function

Thermodynamics

Energy, Enthalpy, Entropy, Free energy, Free enthalpy
Diffusion, Fick's I, II law

Basics of colloid chemistry

Definition of colloids

Materials, where the energy surface processes are same magnitude as other physicochemical processes.

High specific surface area. In spherical particles $A=4\pi r^2$, $V=4/3\pi r^3$

Type of colloids

Structural

Diffuses – In one or two small dimension
Disperses – in three small dimension

Phase

Solids in solids – alloys (steel), minerals, composites
Solids in fluids – suspensions, sols, gels (**SOIL**)
Solids in gases – smog, pollens (**SOIL**)
Fluids in solids – microcapsules, water saturated pore systems (**SOIL**)
Fluids in fluids – emulsions, liquid films (milk, oil film on water, pesticides)
Fluids in gases – fogs, aerosols
Gases in solids – air saturated pore systems (**SOIL**)
Gases in fluids – foams
Gases in gases – not colloid system, because there are not different gas phases

At pore systems, as can be seen, there is not so easy to decide which the disperse phase is.

Surface forces

Covalent
Coordination
Electrostatic
Van der Waals

Surface properties

Hydrophobic, hydrophilic properties
Surface charge
Double layer
PZC (Point of Zero Charge)

Surface processes

Cohesion - adhesion
Adsorption - desorption
Ion change processes
Precipitation – dissolution

Soil materials

Mineral materials

Silicates

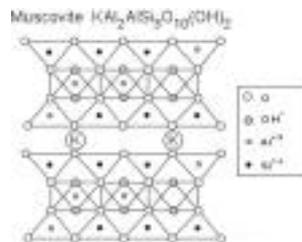
Tectosilicates tetrahedral SiO_4

Quartz – big, hard crystallizes, low specific surface area

Feldspars – orthoclase $\text{K}(\text{Si}_3\text{AlO}_8)$, plagioclase $\text{Na}(\text{Si}_3\text{AlO}_8)$, low specific surface area

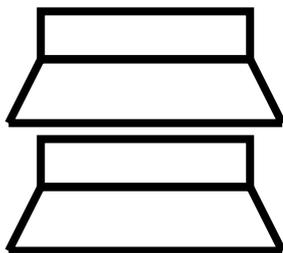
Phyllosilicates sheets Si, Al O

Micas

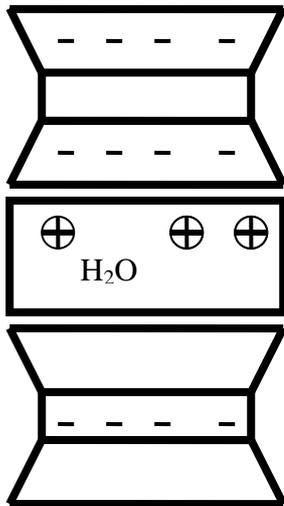


Clay minerals

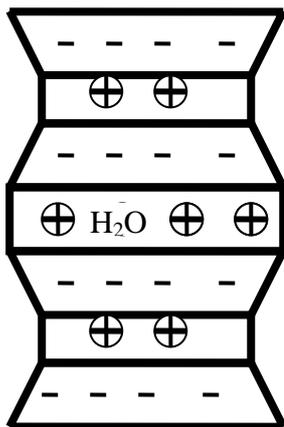
Kaolinite 1:1, $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$



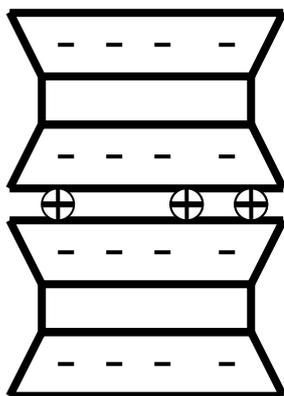
Smectite 2:1 $M^{x+y}(Al_{2-x}Mg_x)(Si_{4-y}Al_y)O_{10}(OH)_2$



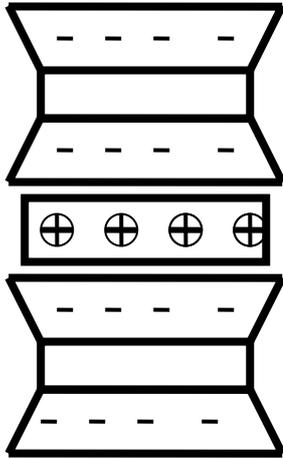
Vermiculite 2:1 $Mg_{0.33}(Mg,Al,Fe^{3+})_3(Si_3Al)O_{10}(OH)_2$



Illite Clay sized hydrous mica



Chlorite 2:1:1 $[(M^{2+} M^{3+})_3(Si,Al)_4O_{10}(OH)_2]^{x-} [(M^{2+} M^{3+})_3(OH)_6]^{x+}$



Inosilicates chains, SiO

Piroxenes

Nesosilicates

Olivine $(MgFe)_2SiO_4$

Non silicates

Oxides, hidroxides

$FeO(OH)_x$ – goethite, ferrifydrite, lepidocrocite

Fe_2O_3 – hematite, magnetite

Fe_3O_4 – magnetite

$AlO(OH)_x$ – diaspore, boehmite

$Al(OH)_3$ – gibbsite

MnO_4

Salts

$CaCO_3$ – calcite, aragonite

$CaMgCO_3$ - dolomite

$CaSO_4$ – gypsum

$Ca_5(PO_4)_3F$, $Ca_5(PO_4)_3OH$ – fluor-, hidroxiapatite

$Ca_3(PO_4)_2$ - phosphorite

Amorf materials

Non-crystallic materials

Silicates, oxides, hydroxides etc....

Organic matter

Humus substances

Fulvic acid – acid soluble

Humic acid – base soluble

Humin – insoluble

Functional groups

Anionic

Carboxyl

Phenol

Cationic

Amino

Imino

Amfoteric

Amid

Non-ionic, hydrophilic

Alcoholic

Keton

Aldehyd

Sulfo

Sulfate

Other organic matters

Saccharides

Polisaccharides

Amino-acids

Organic-acids

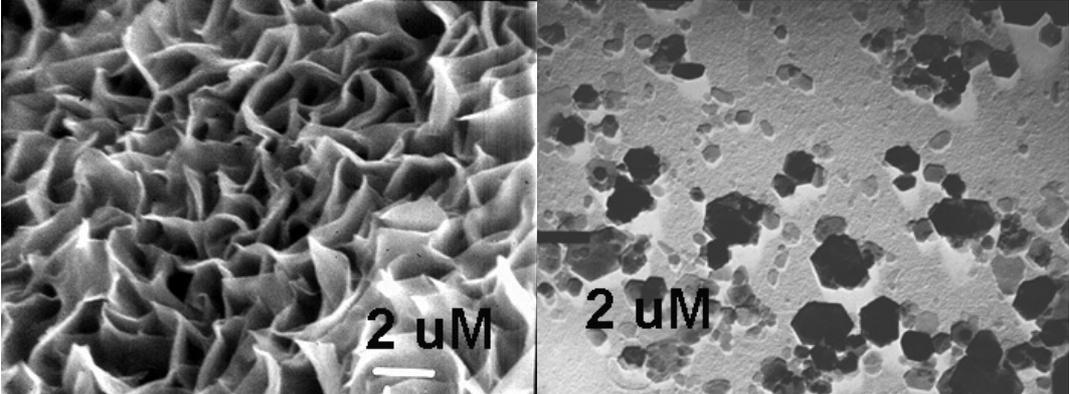
Alcohols

Amines

Living materials – biomass

Surface properties of inorganic soil materials

Surface area



Montmorillonite

Kaolinite

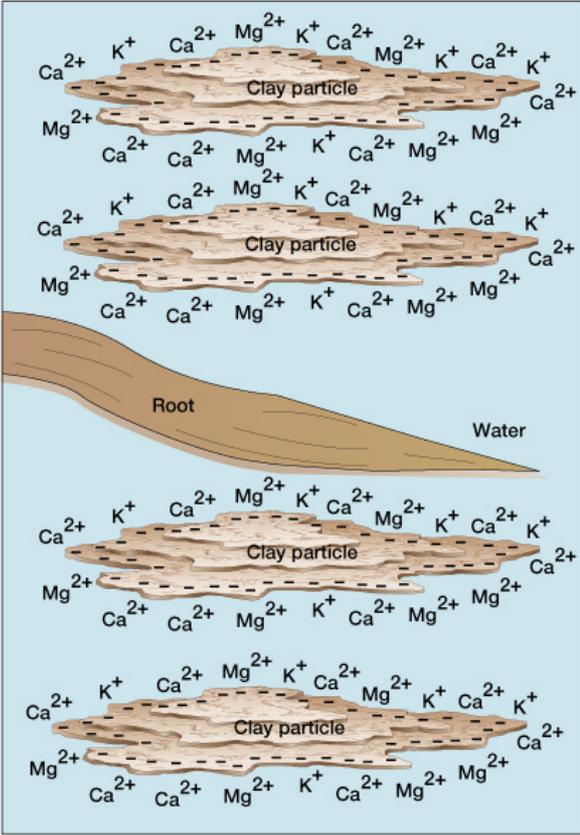
Charge of particles

Permanent charge

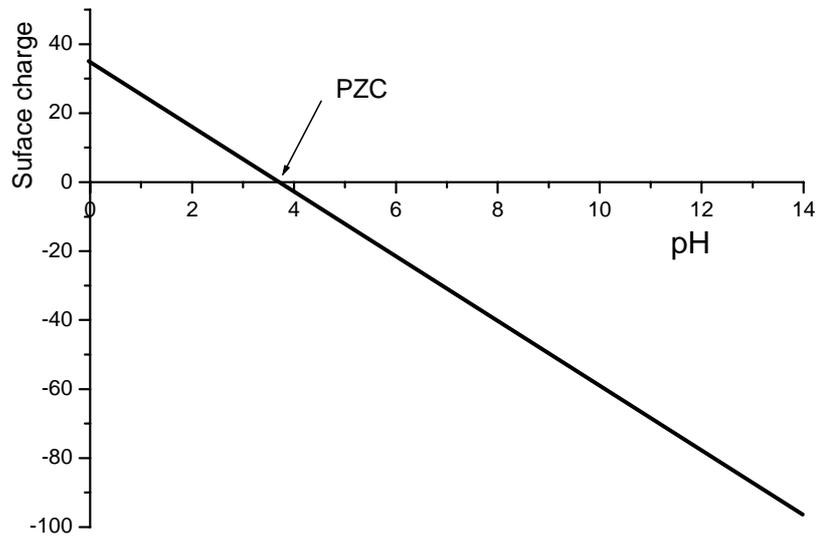
Substitution of clay minerals crystals - negative

Changeable charge

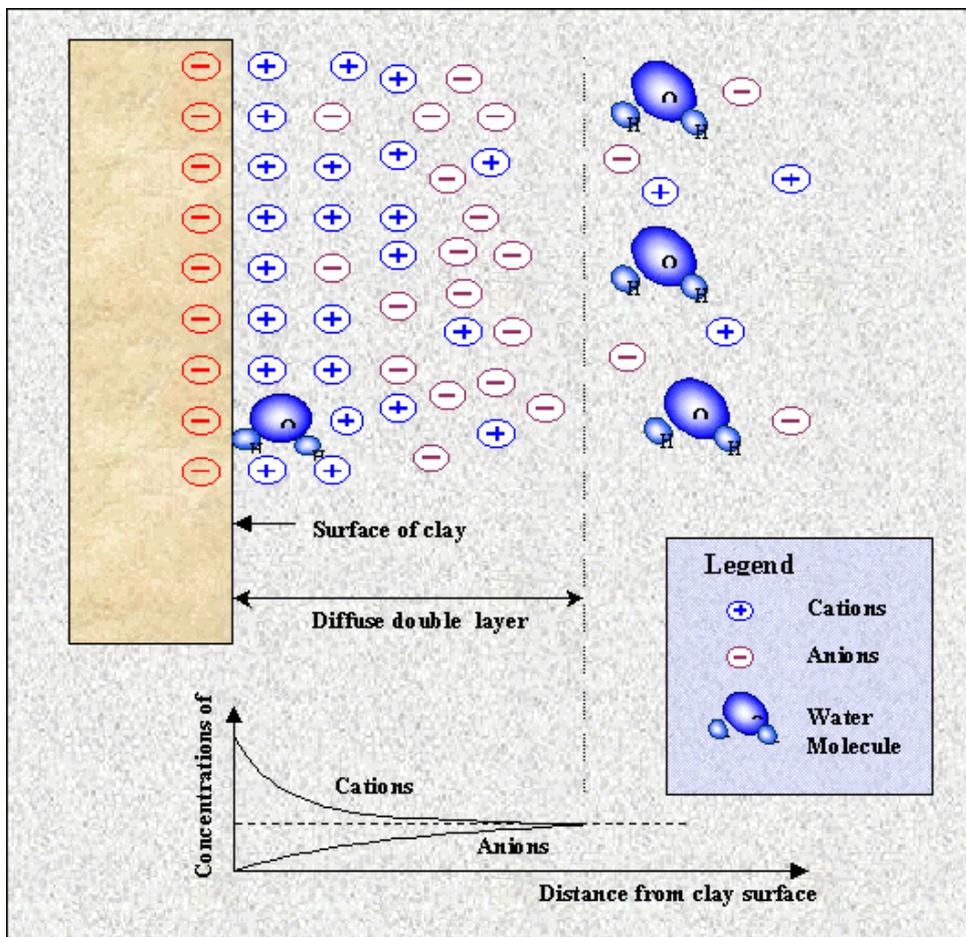
Depending on the pH- H^+ and OH^- adsorption

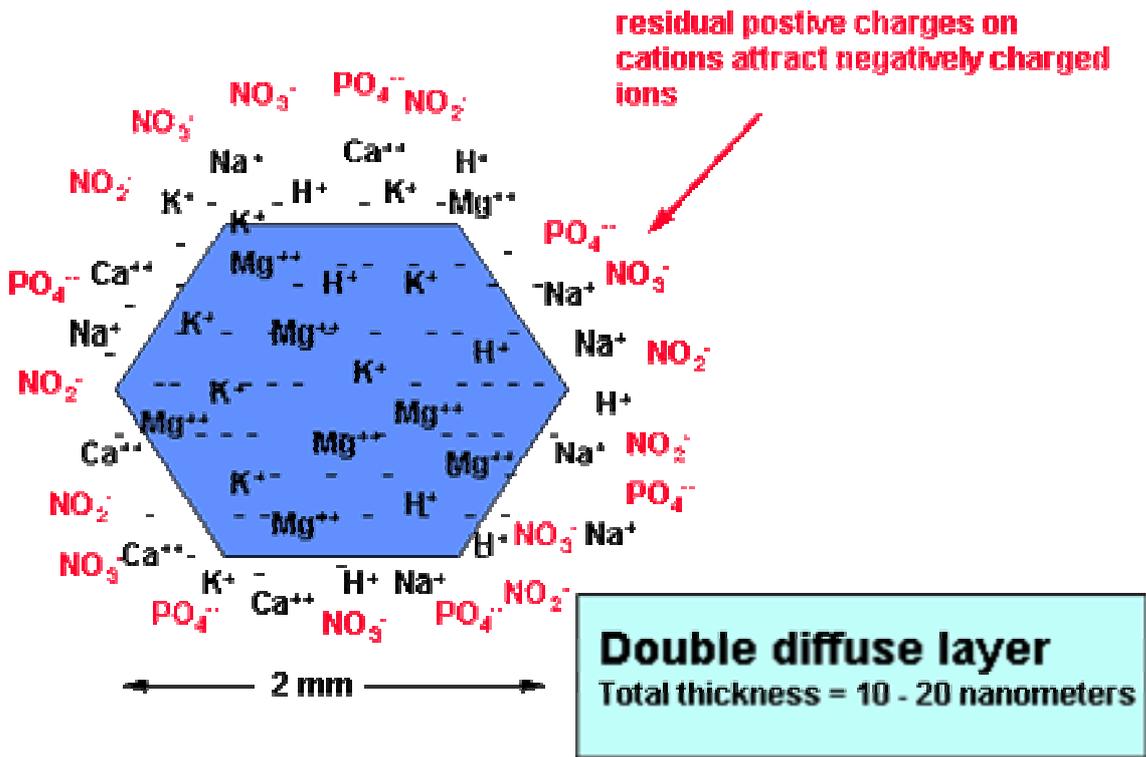


Point of Zero Charge (PZC)



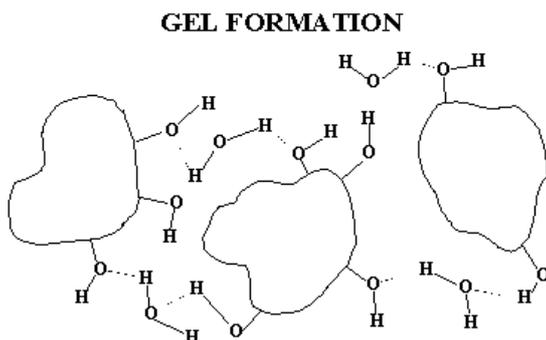
Double layer



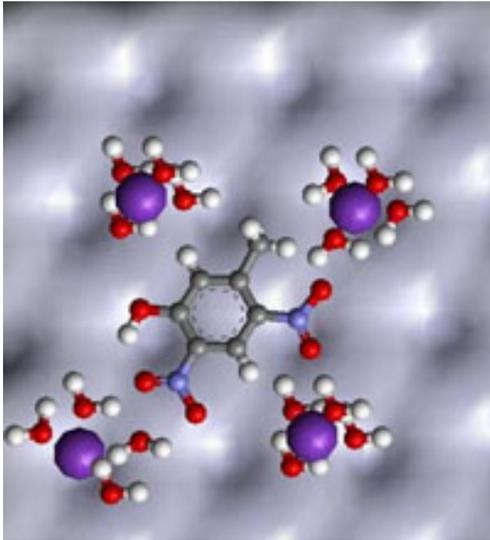


Peptization – coagulation

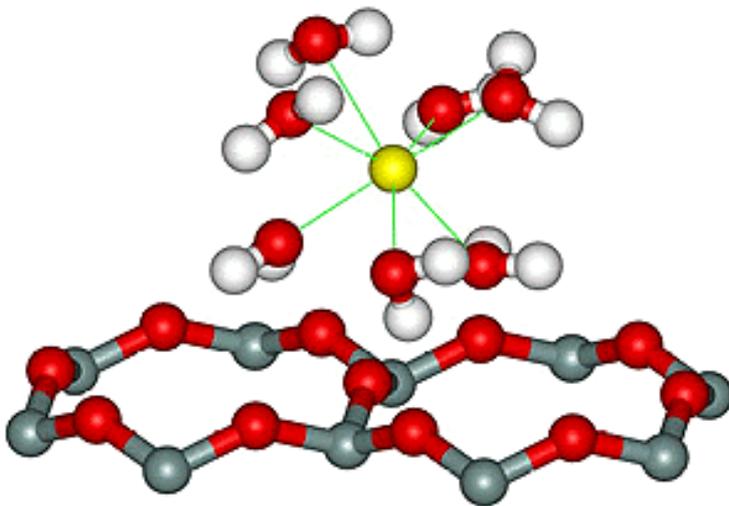
Charge depending = pH depending



Hydrate sphere



Na effect on peptization



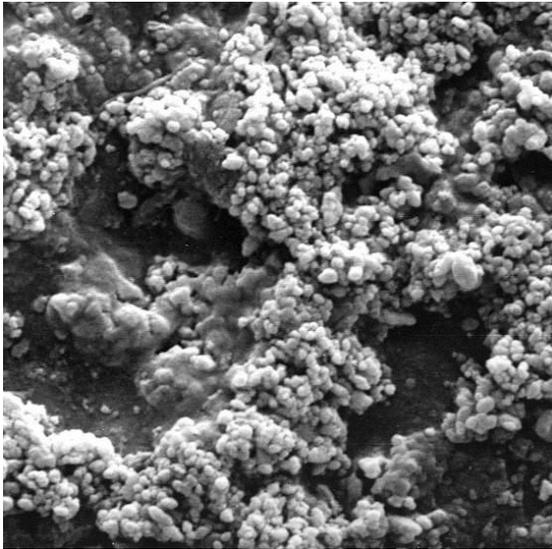
Surface and colloid properties of soil organic matters

Classification

Fulvic acid – soluble in water or acids

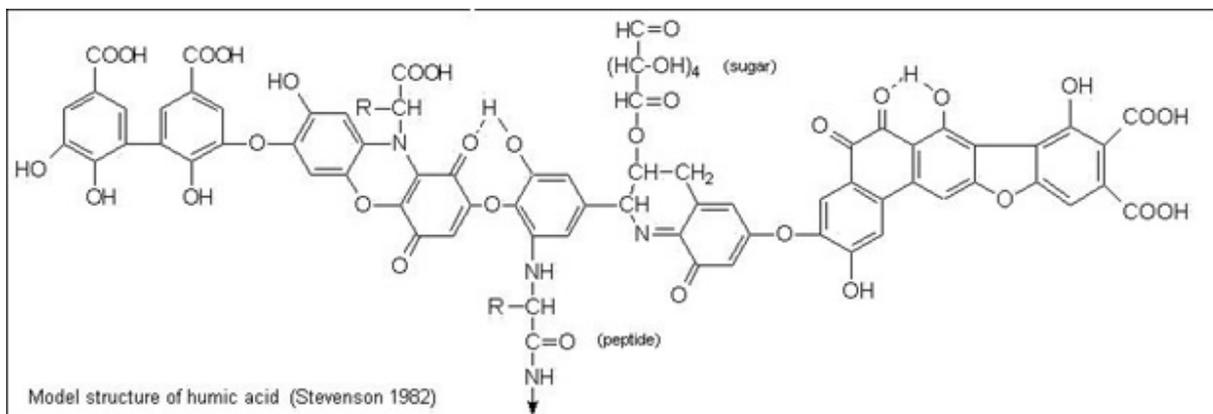
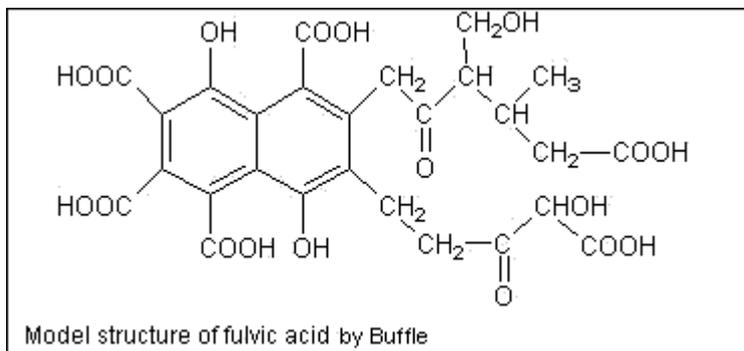
Humic acid – soluble only in bases (NaOH)

Humins – not soluble



Electron microscope picture of humic acid

Structure of SOM

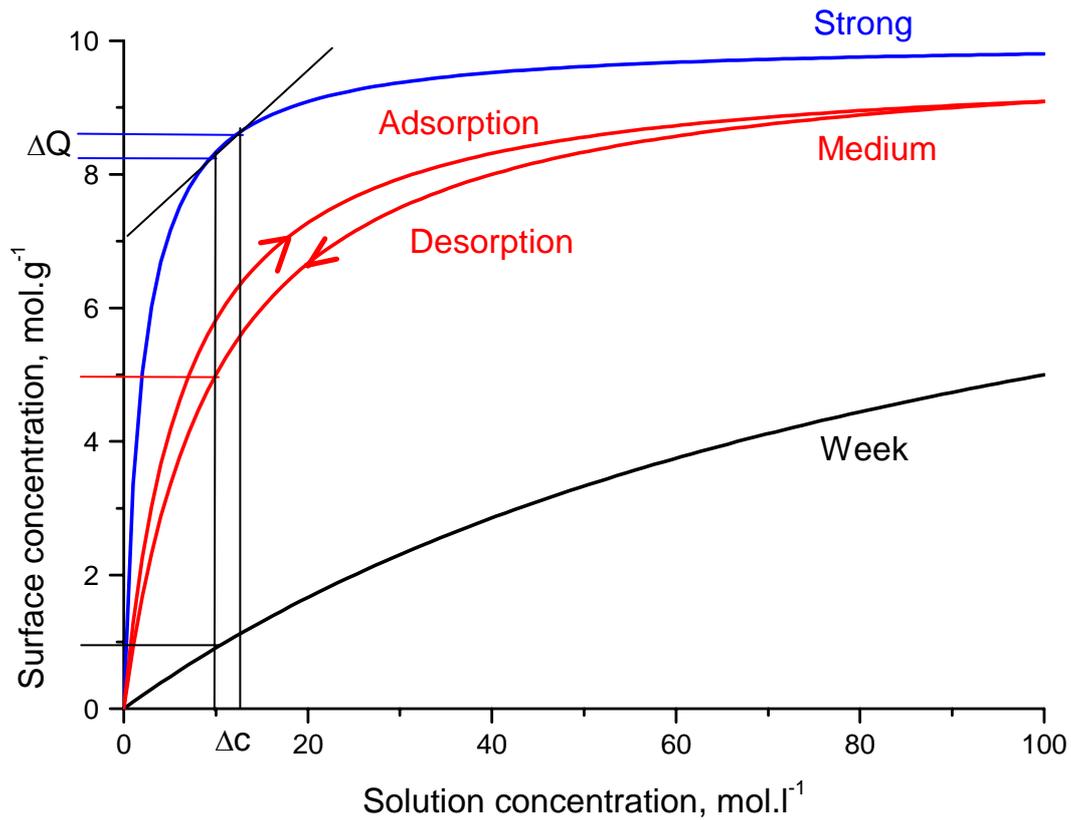


Sorption processes in the soil, ion change

Adsorption – Increasing the surface concentration

Desorption – Decreasing the surface concentration

Adsorption isotherms



Most frequently used adsorption isotherms:

Langmuir: $Q = \frac{A \cdot k \cdot c}{1 + k \cdot c}$, Freundlich: $Q = A \cdot c^b$

Adsorption hysteresis:

The adsorbed amount always lower than desorbed (see graph).

Buffering capacity

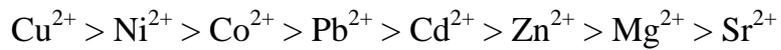
The adsorption can decrease the concentration changing in the soil solution (see

graph). $B = \frac{\Delta Q}{\Delta c}$

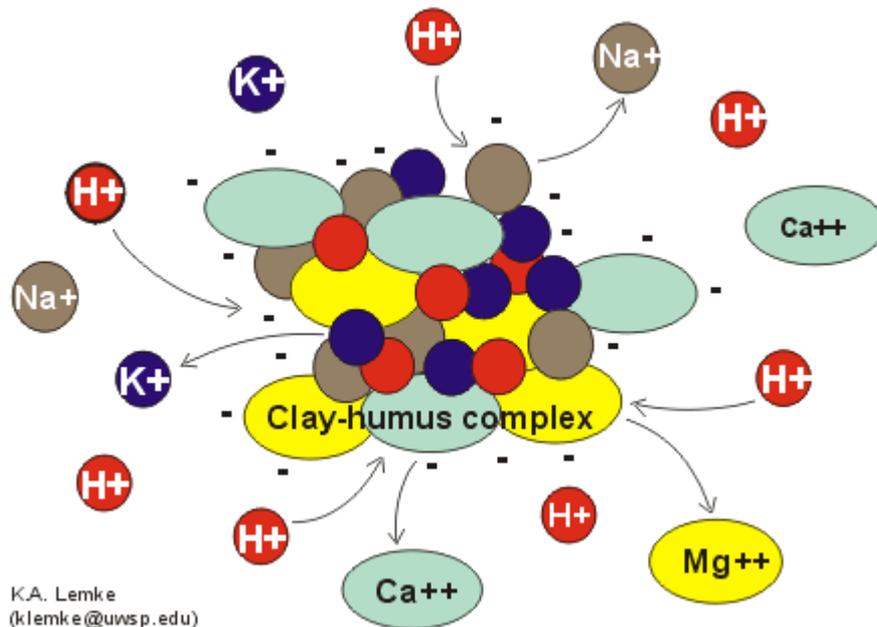
Chemisorption

Precipitation on the surface, it's an irreversible reaction!

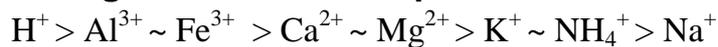
The order of precipitation:



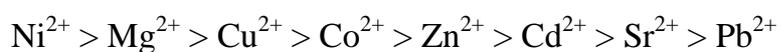
Cation exchange



Strength of cation adsorption



Order of other bivalent ions:



Cation Exchange Capacity CEC

The maximum equivalent exchangeable ions [cmol/kg]

Measured by Ba^{2+} adsorption.

Because of the changeable surface charge it must be measured in constant pH.

Base saturation

Adsorbed equivalent Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , Na^+ ions [cmol/kg]

Percentage base saturation

Base saturation/CEC*100 [dimensionless]

Soil acidity, alkalinity

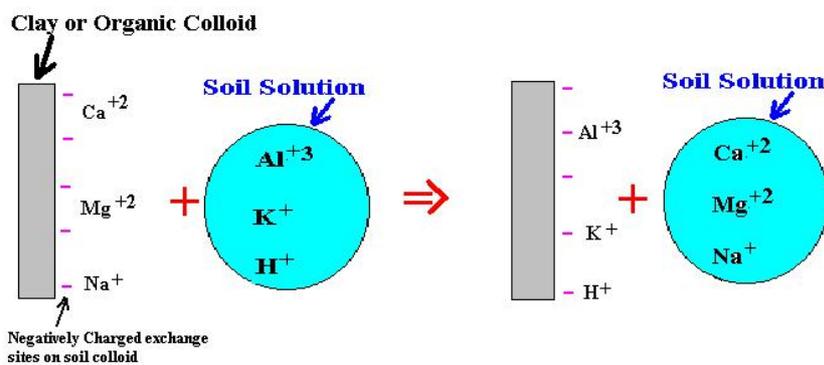
pH measurement

one part of soil + 2.5 part of solution, measurement by glass electrode

H₂O pH – using distilled water for pH measurement

KCl pH – using 1 mol/l KCl solution for pH measurement

The H₂O pH less than KCl pH, because of the ion change.



Soil acidity

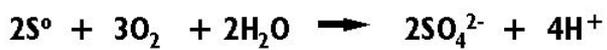
Sources of Soil Acidity



Carbonic acid



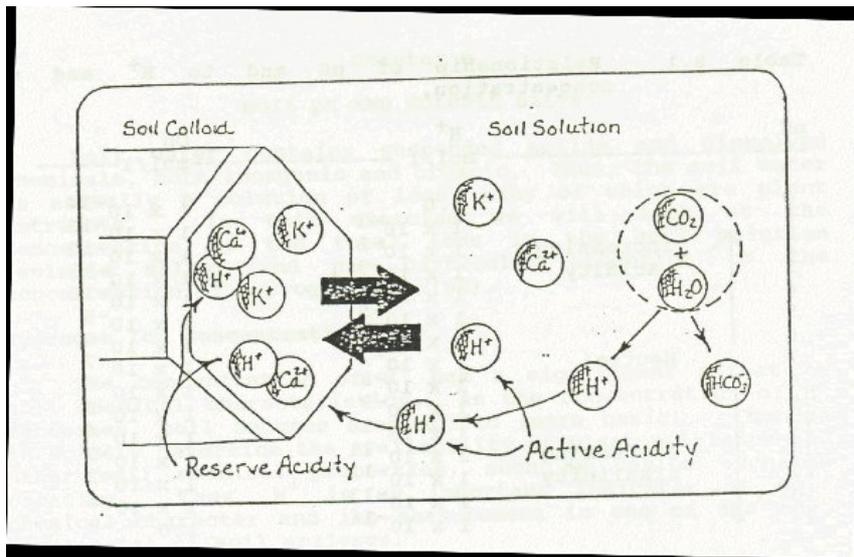
Nitrification



Sulfur oxidation

Active acidity – soluble acidity, in the solution

Reserve acidity – adsorbed acidity, on the surface of particles



Adsorbed acidic ions: H^+ , Al^{3+} , Fe^{3+}

Why are the trivalent ions acidic?

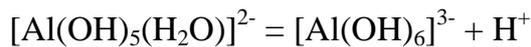
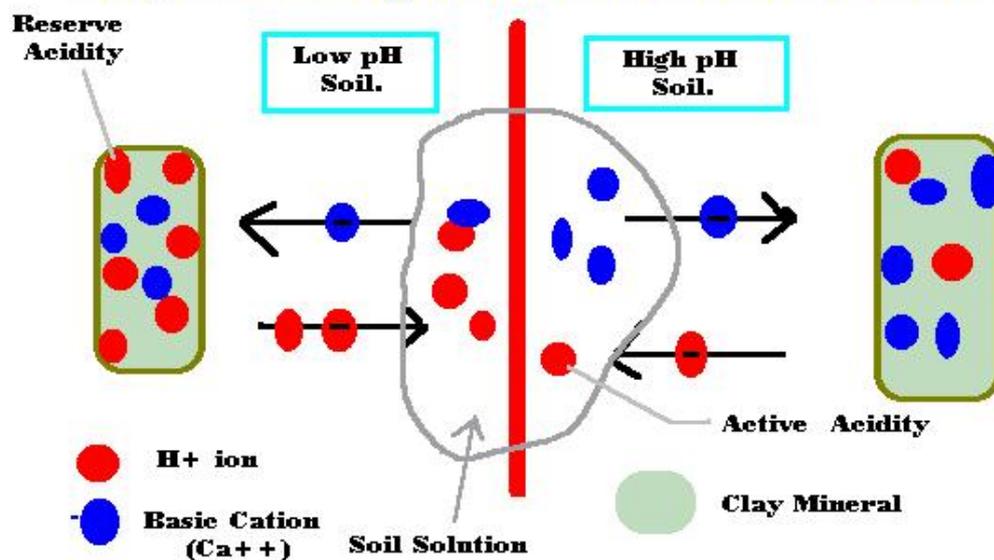


Diagram of Soil pH and Active and Reserve Acidity



Exchangeable acidity

More than active acidity, less than reserve acidity.

The K^+ can not exchange all of the adsorbed acidic ions.

soil + 1 mol KCl, shaking, titrating NaOH using indicator

Dimension [cmol H^+ /kg]

Hydrolytic acidity

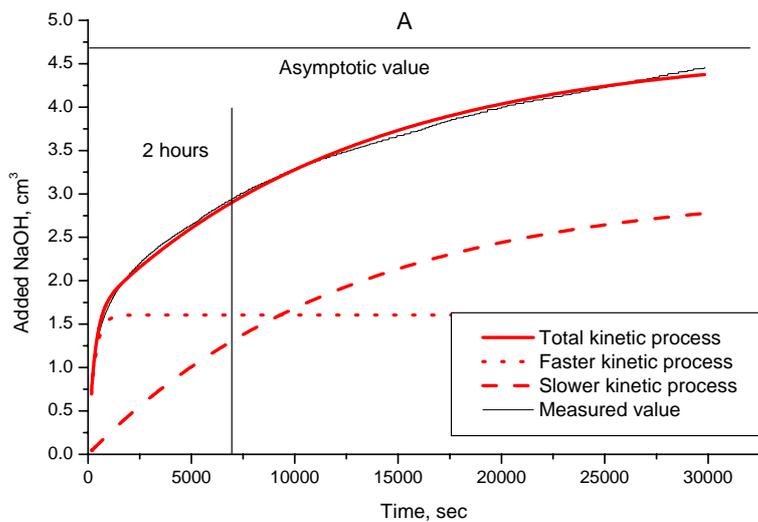
More than exchangeable acidity, less than reserve acidity.

The Ca^{2+} can exchange more adsorbed acidic ions, the acetate can buffering the system, forming acetic acid with the H^+ .

soil + 1 mol $Ca(CH_3COO)_2$, shaking, titrating NaOH using indicator

Dimension [cmol H^+ /kg]

Kinetics of acidity



Liming



Calculation of lime amount:

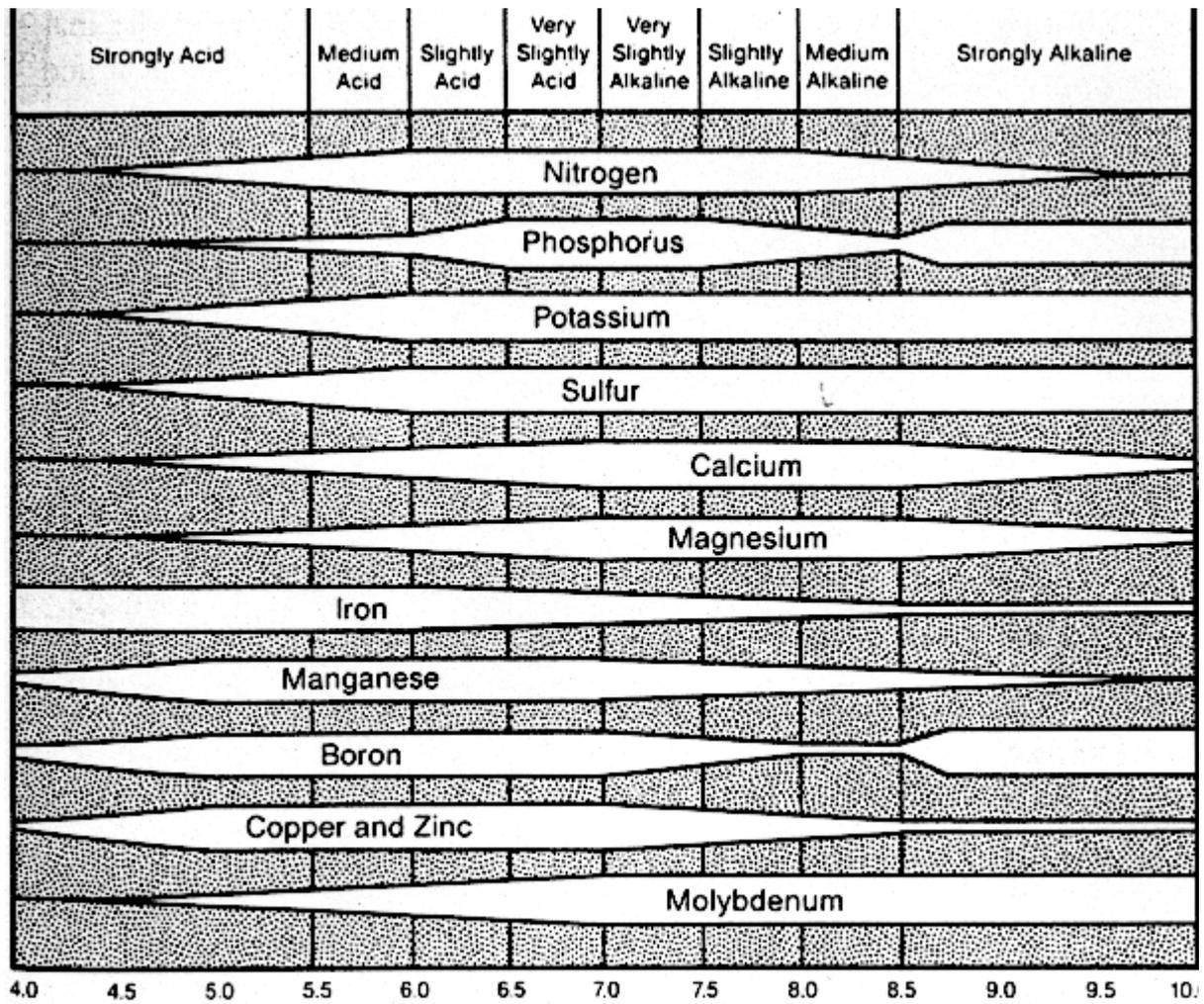
Hydrolytic acidity modified by the kinetic effect.

Soil alkalinity

Lime content pH~7-8

Sodic soils pH > 8

Effect of soil pH on nutrient uptake



Redox properties of soil

Sources of oxidation:

Atmospheric oxygen

Low diffusion if the soil pores are full by water.

Sources of reduction:

Soil microbial activity

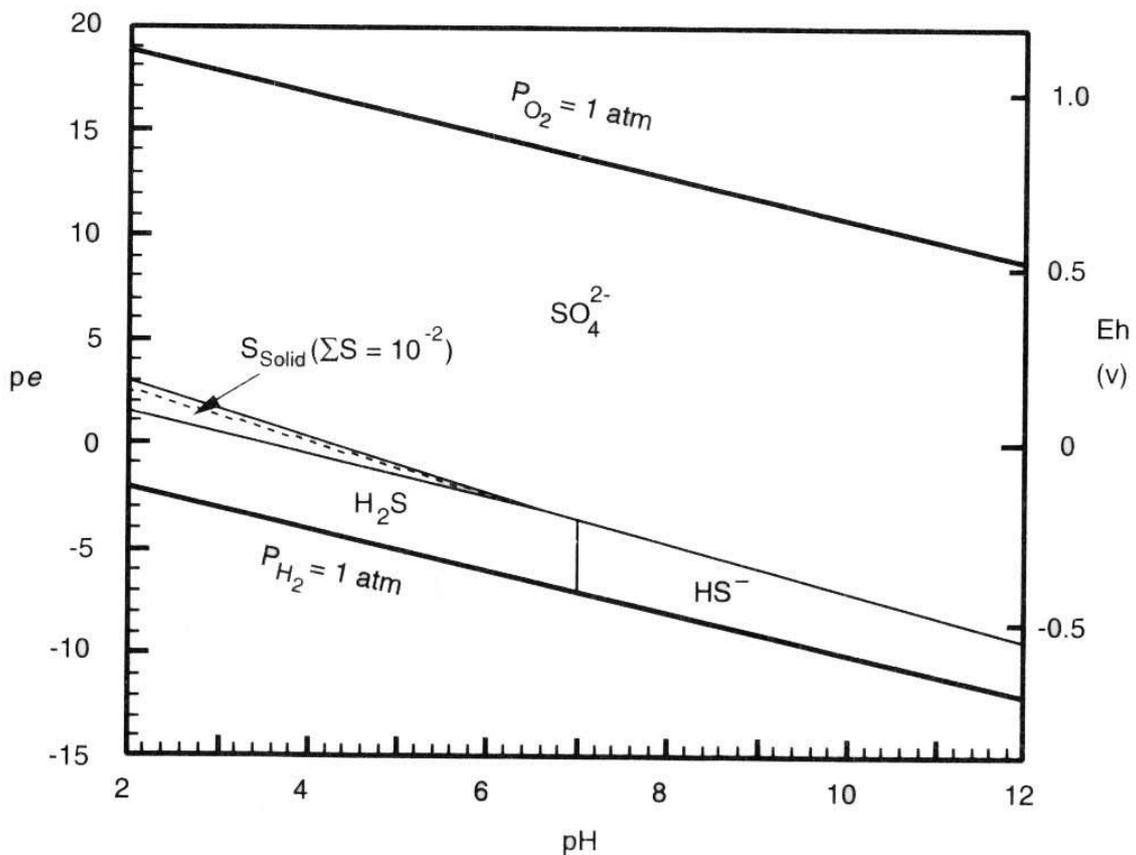
Electron donor soil organic materials (humus or non humus)

In high E_h aerobic organisms, using oxygen as electron acceptor

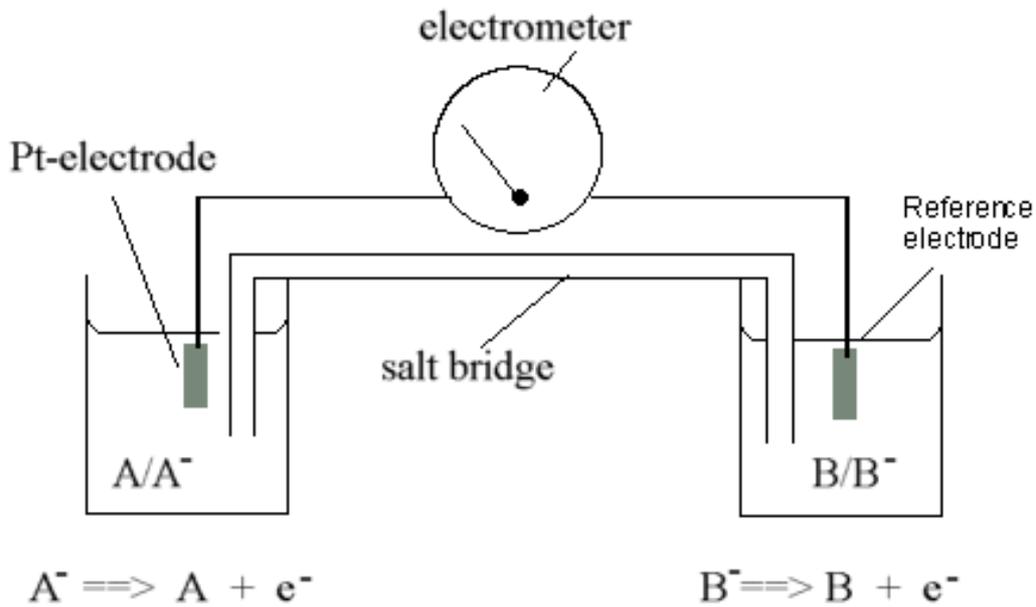
In low E_h anaerobic organisms, using other compounds as electron acceptor for

example: NO_3^- , SO_4^{2-} , Fe^{3+} , MnO_2 , COOH , R-OH

Redox potential depending pH



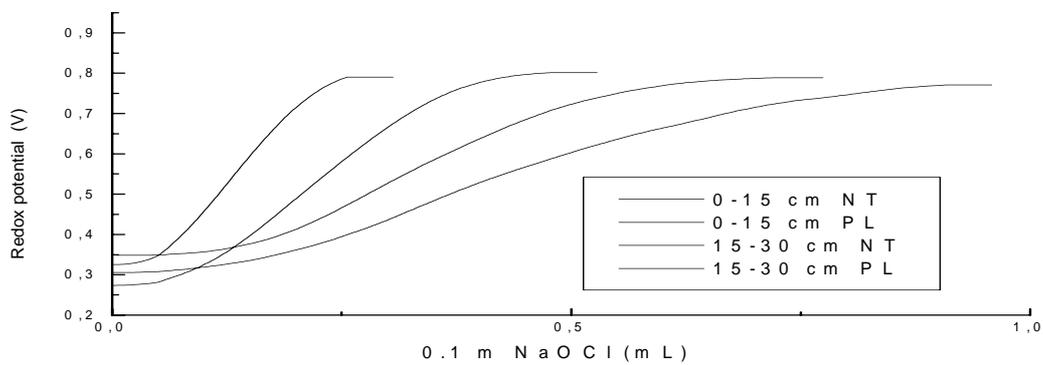
Measurement of redox potential



Using undisturbed soil or soil suspension.

Not well reproducible measurement.

Redox buffering properties



Redox titration curves of different soils.

The buffering capacity is the slopes of curves. (see above)

Describe of redox properties

Nernst equation

$$E_h = E_0 + R \cdot T \cdot \ln \frac{[\text{ox}]}{[\text{red}]}$$

dimension: Volts

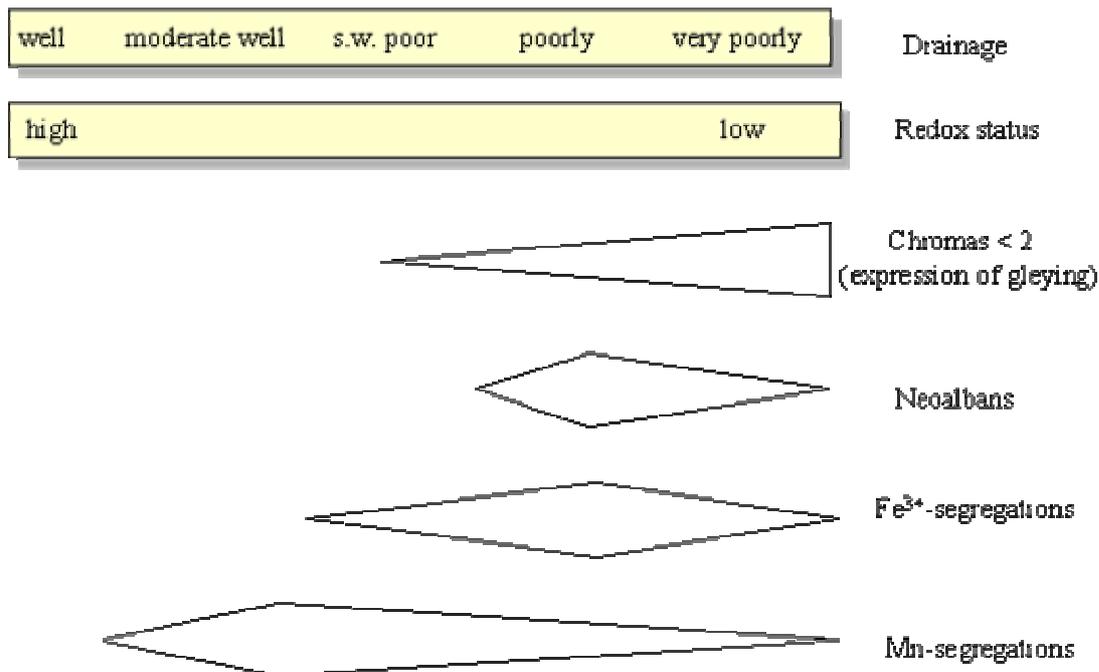
Soil is multiredox system, there are some processes with different E0

$$pe = - \lg[e^-] = 0.059 \cdot Eh$$

$$pe = 20.66 - pH \text{ (in aqueous system and 0.2 bar O}_2 \text{ partial pressure)}$$

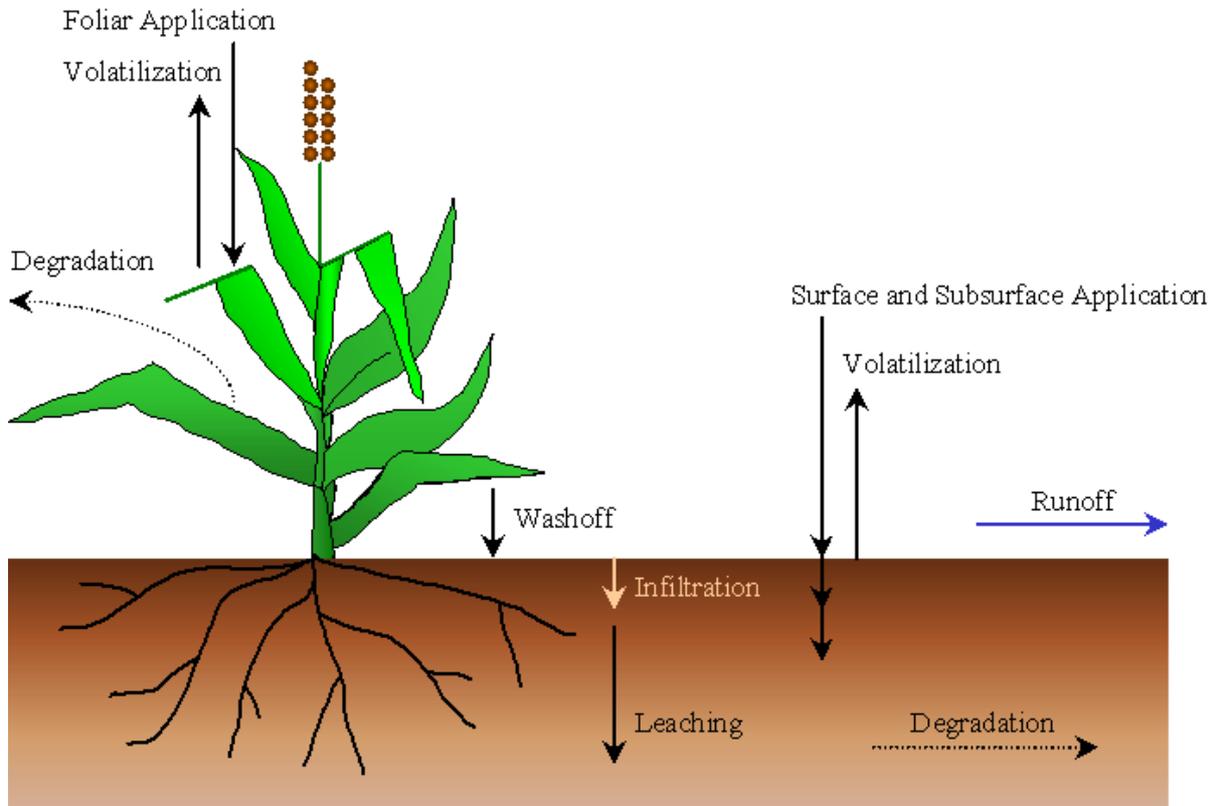
Soil properties depending redox status

Idealized Representation of Soil Morphological Features Associated with Wetness



Transport processes in the soil

Transport in the plant-soil system



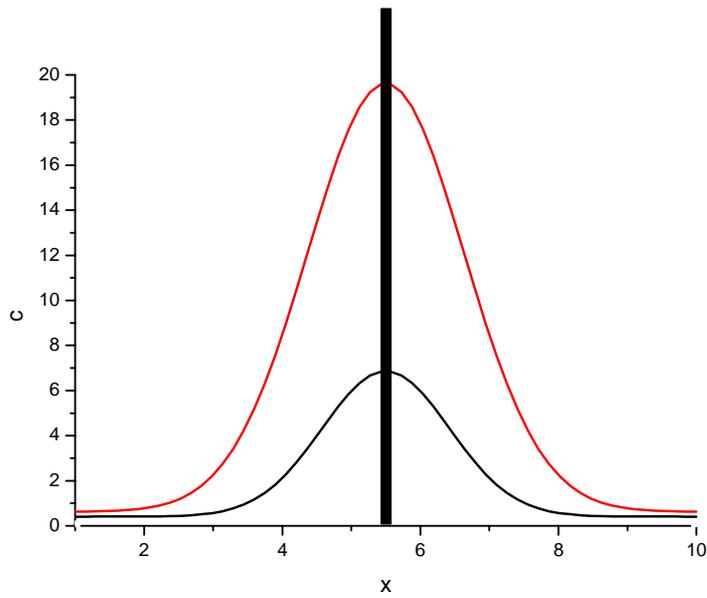
Why?

The materials on solid phase don't move.

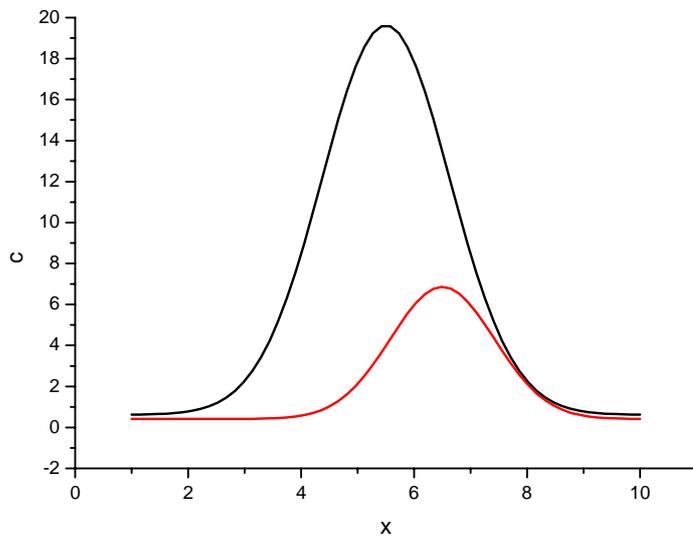
Chromatography model

Transport in the soil

Diffusion $\frac{dc}{dt} = -D \frac{\delta c}{\delta x}$



Diffusion and movement $\frac{dc}{dt} = -D \frac{\delta c}{\delta x} + v \cdot c$



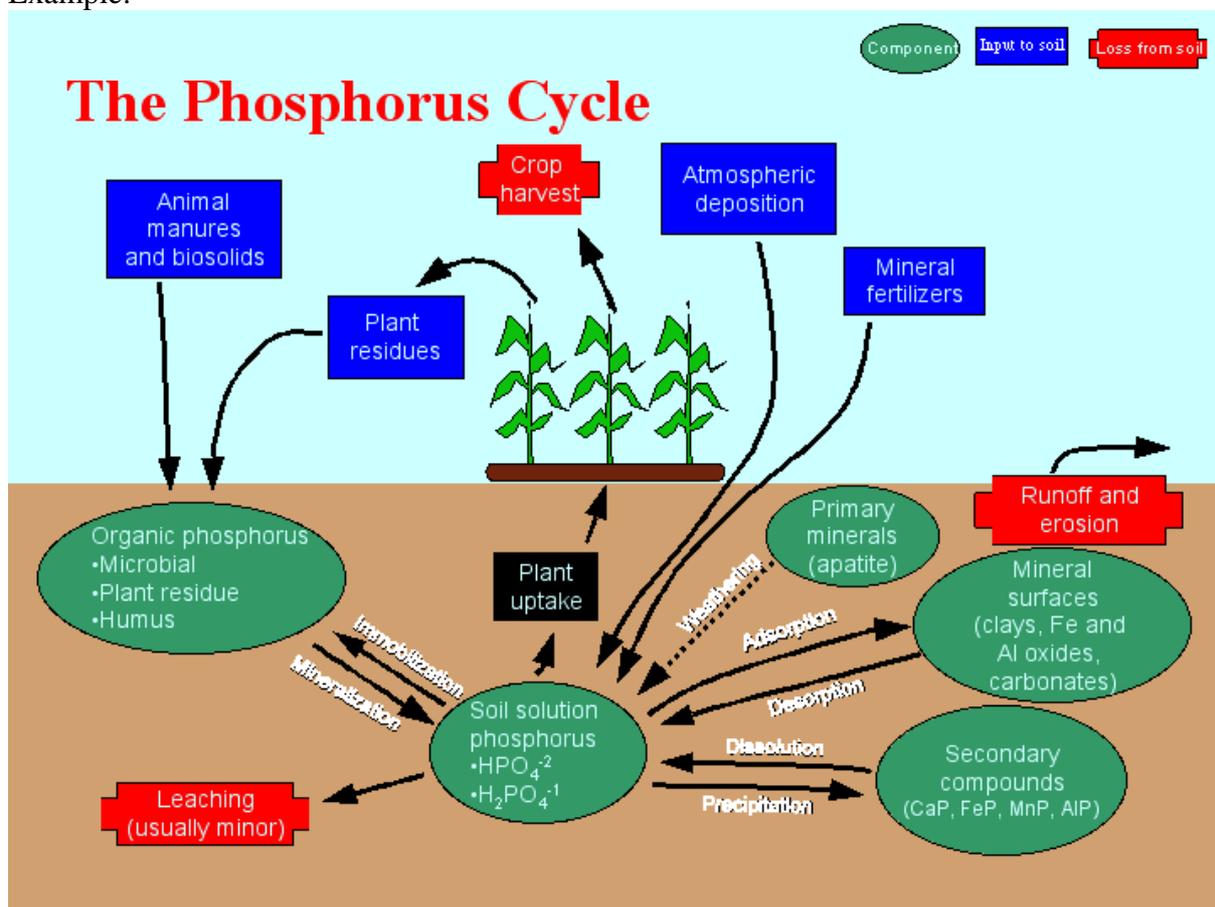
Diffusion, movement and degradation $\frac{dc}{dt} = -D \frac{\partial c}{\partial x} + v \cdot c - k \frac{\partial c}{\partial x}$

And so on, you can calculate all reactions, what you can imagine
 You must derive this differential equation in 3D (x,y,z)

Distribution between the solid and liquid phase

- Adsorption
- Precipitation
- Other chemical reactions

Example:



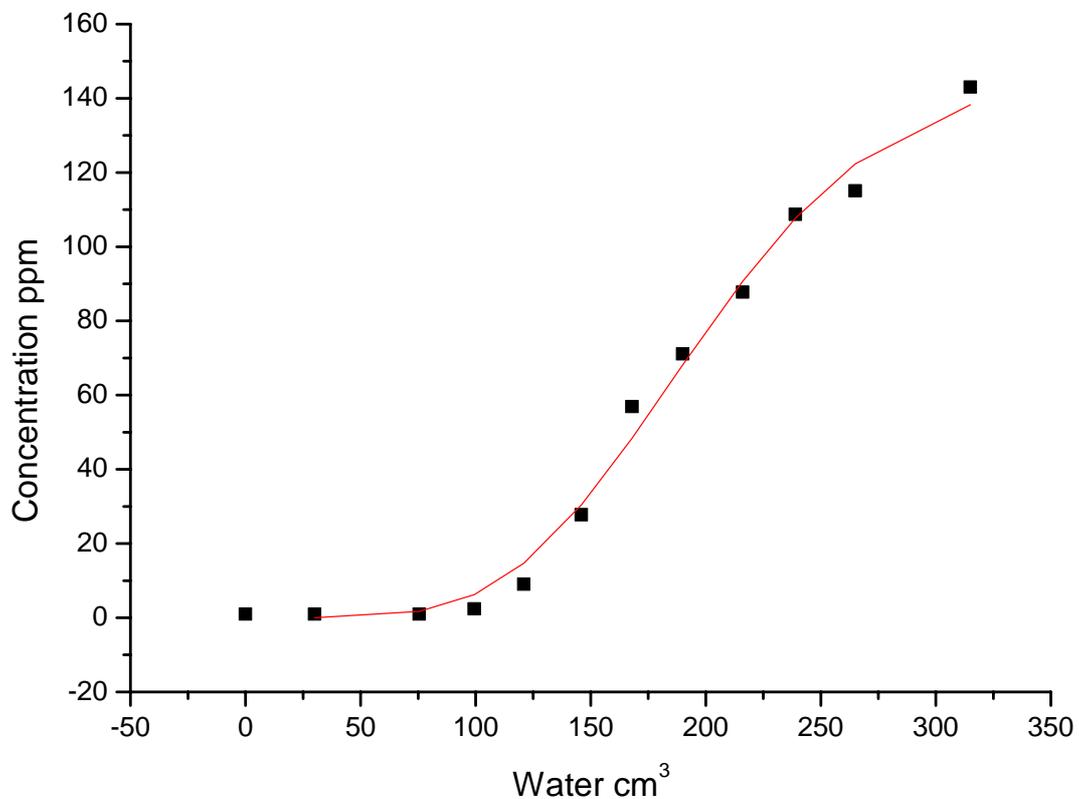
Modeling of soil transport

1. Water transport model
2. Solid – liquid phase reaction (sorption, precipitation....)
3. Degradation, sources
4. Using the transport differential equation
5. Almost every case the equation insoluble, computer simulation

Measurement of soil transport

Measurement all surface chemical reactions, almost impossible

Measurement of leaching or breakthrough curve, and calculation the parameters



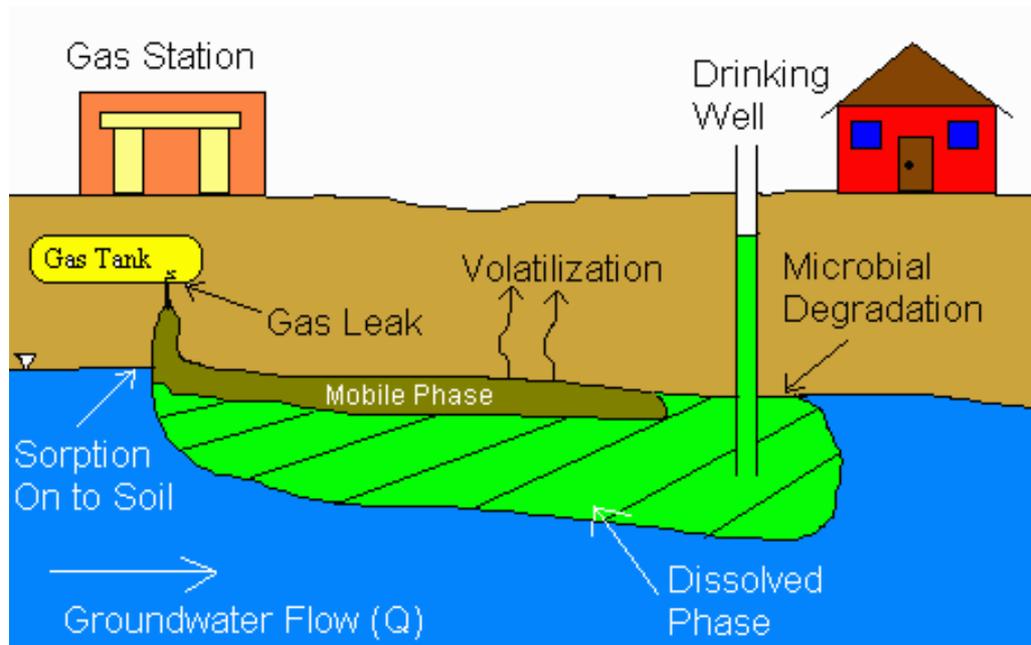
used function

$$y = c/2 * ((1 - \text{erf}(R * z - (x) / \sqrt{D * R * x / (v)})) + \exp(v * z / D) * (1 - \text{erf}(R * z - (x) / \sqrt{D * R * x / (v)})))$$

Parameters:

Retardation	Diffusion	Concentration	Velocity	Length of column		
	$m^2 \cdot s^{-1}$	$g \cdot m^3$	$m^3 \cdot s^{-1}$	m		
35.3	$3.03 \cdot 10^{-8}$	58.9	$9.9 \cdot 10^{-8}$	0.12	28.0	0.992
3.94	$1.0 \cdot 10^{-8}$	7.90				

Four phase transport



You must calculate the transport of two different liquid phase

Importance of soil transport

- Plant nutrition
- Soil formation
- Environmental protection