610-280 Environmental Chemistry

Soil: Charge

- Soil pH
- Dynamic interactive processes
- Surface charge
- Cation exchange capacity
- CEC calculations

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References

- V. P. Evangelou, Environmental Soil and Water Chemistry
- D. J. Shaw, Colloid and Surface Chemistry
- D. L. Sparks, Soil Physical Chemistry
- M. B. McBride, Environmental Chemistry of Soils

Soil pH

- Affects plant growth and behaviour of ionic species in soil
- Normally between 4-8.5
- Increase pH by liming ($CaCO_3$)

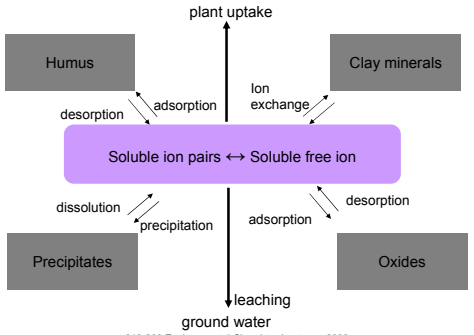
$Soil\}(H^+)_2 + CaCO_3(s) \rightarrow Soil\}Ca^{2+} + CO_2 + H_2O$

- Decrease pH by applying sulfur:

$2S(s) + 3O_2 + H_2O \rightarrow 4H^+ + 2SO_4^{2-}$

pH	
>10	Strongly alkaline
9-10	Moderately alkaline
8-9	Slightly alkaline
6-8	Neutral
5-6	Slightly acidic
4-5	Moderately acidic
<4	Strongly acidic

Dynamic processes



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Soluble free ion

- Although written as Ca^{2+}, Na^{+}, NO_3^{-} etc., in aqueous solution these ions have associated water molecules:

- Eg. $Fe^{2+}.6H_2O$

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Inorganic salts MW ?H_2O

"Soluble ion pair"

- Coordinated water molecules are not removed
- $CaSO_4$ (aq) ion pair

Outer sphere complex

Neutralization of the divalent ions

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Ion complexes

- When ions are attracted to each other chemically or electrostatically, and disrupt the individual hydration spheres

Inner sphere complex

- Much stronger association than ion pairs.

Surface charge

Two types of charge on surfaces of soil particles (mineral and organic colloids)

- Permanent charge
  - Results from isomorphous substitution of an ion within a clay mineral by an ion with lower valency
  - pH independent
  - Charge delocalized
- Variable charge
  - Due to terminal or “broken” bonds
  - pH dependent
  - Charge localized at specific sites
  - Sites are chemically active

Counter ions

Electrophoresis

Used to determine if particle is positively or negatively charged

Motion of particle in an electric field, E

Mobility $\mu=v/E=q/(6\pi r\eta)$

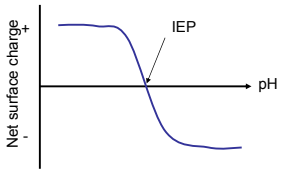
Surface charge

- Variable
  $>Al_2=OH_2^+ \leftrightarrow >Al_2=OH \leftrightarrow >Al_2=O^-$

pH < IEP < pH

- Isoelectric point (IEP or pzc - zero point of charge)
  - Flocculation greatest at pH=IEP

Isoelectric point



- The IEP is sensitive to adsorbed ions and molecules, and crystallinity of the particles

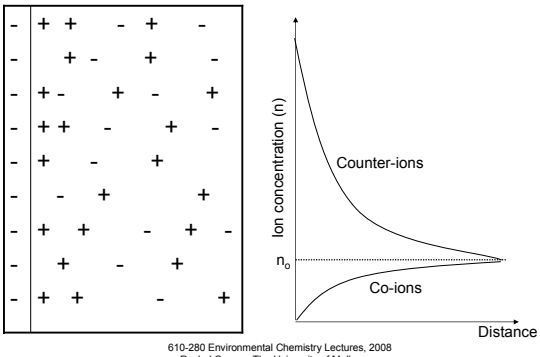
Mineral	pH_{IEP}
SiO_2	2
α-$Al(OH)_3$	5.0
Kaolinite	4.6
Montmorillonite	2.5
α-Al_2O_3	9.1
COOH	4-6

Harrison

Adsorption

- Chemical reaction between surface and ion, specific adsorption, and very strong association (inner sphere), some exchange
- Electrostatic reaction: localised electrostatic charge neutralisation, non-specific adsorption (outer sphere), weaker interaction, exchangeable cations

Guoy-Chapman model



Cation concentration

- Increases dramatically from the bulk solution to the surface of negatively charged soil particles.
- Cation retention in soil is directly related to the CEC – why is leaching so small in soils with typical CEC, say 10 cmol/kg?

Cation exchange capacity

- Defined as the quantity of cations that are reversibly adsorbed per unit mass of the material
- Both mineral and organic portions exchange cations
- (NOTE anion adsorption also occurs, generally soil has much smaller capacity for anion exchange)
- Mechanism by which K, Ca, Mg, and essential trace elements are made available to plants
- Exchangeability of the cation is dependent on its valency, diameter in hydrated form, the type and concentration of other ions present in soil solution.

Cation exchange capacity

- The higher the valency, the greater the degree of adsorption.
- Ions with large *hydrated* radius have a lower replacing power than ions with smaller radii.
- CEC dominated by Ca, Mg, Na, K and Al

	Ionic radii (A) hydrated
Na^+	7.90
K^+	5.32
Mg^{2+}	10.8
Ca^{2+}	9.6

CEC ≈ 2[Ca] + 2[Mg] + [Na] + [K] + 3[Al]

- Relative order of replaceability:

$Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Al^{3+}$

CEC

- Given a soil containing 20 % smectite, 5 % kaolinite and 3 % humus estimate the soil CEC from these approximate CEC values:

Humus at pH 7 200 cmol/kg,
smectite 100 cmol/kg and
kaolinite 5 cmol/kg.

- Q: If there was an increase of 1 % humus in soil, how much will the CEC of soil at pH 7 increase? As many soils have a CEC between 5-20 cmol/kg, is this a significant increase?

How is CEC determined

For example,

- DRY soil of known mass is extracted with ammonium solution.
- Filter and run filtrate through atomic absorption spectroscopy.
- Compare with standards to determine concentration of cations.
- Calculate total positive charge associated with ions.

Wikipedia

Example

1.00 g of soil extracted with 100 mL ammonium chloride solution. Concentrations of the principal cations are as follows:

- Ca 50 μg mL^{-1}
- Mg 3 μg mL^{-1}
- Na 2 μg mL^{-1}
- K not detected

Determine the CEC of the soil.

Example

By convention result is expressed in terms of cmol kg^{-1}

This calculation is repeated for each cation and then summed:

In summary

Soil: Charge

- pH of soil
- Ion interactive processes in soil
- Sources of surface charge
- Cation exchange capacity and related calculations