Salahaddin University, College of Agricultural Engineering Sciences ,Soil and Water Department

Adv. Soil Chemistry,MSc. level

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References

*A.A.S (1981). Chemistry of soil environment. USA.
Alfred. and Conklin J.R.(2014) Introduction to soil chemistry.2nd edition ,Canada.
*Bohn, H.L., L. M. Brian and George A. O. (2001). Soil chemistry. 3rd ed. New York.
Garrison Sposito (2012) The chemistry of the soils.2nd edition.
*Lindsay, W. L. (1979). Chemical equilibria in soils. USA.
Lindsay,(2023). Chemical equilibria in soils.3rd edition. USA.
*Parker, D. R., R. L. Chaney and W. A. Norvell (1995). Chemical equilibrium and reaction models. SSSA special publication No. 42.
*Sparks, D. L. (2008). Environmental soil chemistry. USA.2nd edition..
*

Sposito, G. (1989). The chemistry of soils. New York.

*Wolt, J. D. (1994). Soil solution chemistry. John Wiley .

*Zasoki, R. J. and R.G. Buran (2002). Soil and water chemistry. Course notes and Graphical materials, winter quarter 2002.

*Alvarez- Benedi, J. & Munoz- Carpena R. (2005) Soil- Water solute process characterization. First Edition ,Printed in USA.

*Benjamin M.M. (2002) Water chemistry. Univ. of Washington.

*Zasoski R. J. and Burau R. G. (2002) Soil and Water chemistry.

*Weiner Eugene R. (2007) Applications of environmental aquatic chemistry. First edition printed in New York.

Introduction:

1- Definition of soil chemistry.

2-Goals of studying soil chemistry.

Home work: Write the goals of studyig depending on time series as follow:

-The 19th century .

- The end of the 19th and the beginning of the 20th century.

-The 20th century .

- The end of the 20th and the beginning of the 21st century.

What are the main components of soil?

Soil composition concerns the geochemistry of that portion of the mantle of the earth currently exposed to the atmosphere and subjected to biotic influences

The earth mantle (given) mineral matter

Organisms (introduce) organic matter into soil

Both of them together make up solid phase.

Definition of soil chemistry:

It is a branch of edaphology which deals with studying of the chemical reactions, properties and processes of the soil pertaining(يتعلق ب) to plant and animal growth and human development environments.

Chemistry of the soil plays a vital role in the development of natural recourses, the protection of environment and sustainability of ecosystem health.

1-pH.

2-EC (Electrical conductivity)dSm^{-1}.

3-Cation exchange capacity(meq /100g oven dry soil or cmole$_c$/kg soil)

4-Organig matter%.

5-Calcium carbonate content or% (CaCO3%).

6-Concentation of cations and anions.

7-Concentration of heavy metals.

Type of clay minerals.

8-Gypsum %

9-Others.

Modern soil chemistry

Modern soil chemistry involves three points.

1- Descriptive chemistry of the soil components.

2- Thermodynamic equilibrium among soil phases (or between nutrients in soil phases)

3- Kinetics of the movement rate of elements between phases.

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Soil chemistry traditionally had two branches:

1-Inorganic soil chemistry like :soil chemistry ,soil physics ,soil pollution ,soil genesis…..etc

2- Organic soil chemistry :like soil biochemistry ,soil microbiology….etc.

But strict separation of the mentioned two branches or fields is difficult and may be rather pointless in many cases.

Quiz :Fill the following blanks with the suitable terms:

Soil chemistry had ------------- branches which are --------- and ------------- but ------------------------------------- between them is -------------------------------or -------------------------------------.

D 1. 1- Soil in space and time	C1. 1. Soil Morphology
	C1. 2. Soil Geography
	C1. 3. Soil Genesis
	C1. 4. Soil Classification
D 2. **2- Soil properties and processes**	C2. 1. Soil Physics
	C2. 2. Soil Chemistry
	C2. 3. Soil Biology
	C2. 4. Soil Mineralogy
D 3. 3- Soil use and management	C3. 1. Soil Evaluation and land use planning
	C3. 2. Soil and water conservation
	C3. 3. Soil fertility and plant nutrition
	C3. 4. Soil engineering and technology
	C3. 5. Soil degradation control, remediation and reclamation.
D 4. 4- the role of soils in sustaining society and the environment	C4. 1. Soil and the environment
	C4. 2. Soil, food Security and human health
	C4. 3. Soil and land use change
	C4. 4. Soil education and public Awareness
	C4. 5. History, philosophy and sociology of soil science.

The main goals of studying soil chemistry :

1. Studying the chemical properties of the soil, like EC, pH, CEC, concentration of cations , anions soil organic matter content, soil $CaCO_3$ content and soil gypsum content…etc.
2. Studying the availability of nutrients for plants or determining the amount of available nutrients for plants.
3. Determining total concentration of nutrients in the soils.
4. Studying micro nutrient status in the soils.
5. Studying mineralogical properties of the soils.
6. Reclamation the soil which not suitable for agriculture purpose.

7-Understanding of soil chemistry reactions and how the soil relates chemically with the environment.

8. Studying the applications of thermodynamic concepts in soil science.

Decreasing O_2 Content →

Protecting organic matter content

Solid phase make up only about 50% of Soil volume .Since the density of O.M is about 0.5 g cm^{-3} and mineral material = 2.7 g cm^{-3} Other half filled with water and air ? (Figure next slide)

Gas phase occupies about fourth of soil volume

CO_2 in good drain soil =0.1% ,while in Bad aeration (Poor aeration) soils = 5 -10 % and may rise to 20% in frozen soil horizon they replace all O_2 . The rare gas also occurs in soil (Ne , Kr , Ar ,Xe).

Does the chemical composition of the soils are similar? Or not? Why?

Mechanisms of ion-soil interaction:

This mechanism can remove and replace ions in the soil solution . The mechanism of ion entry into the soil solution includes:

1-Mineral weathering.

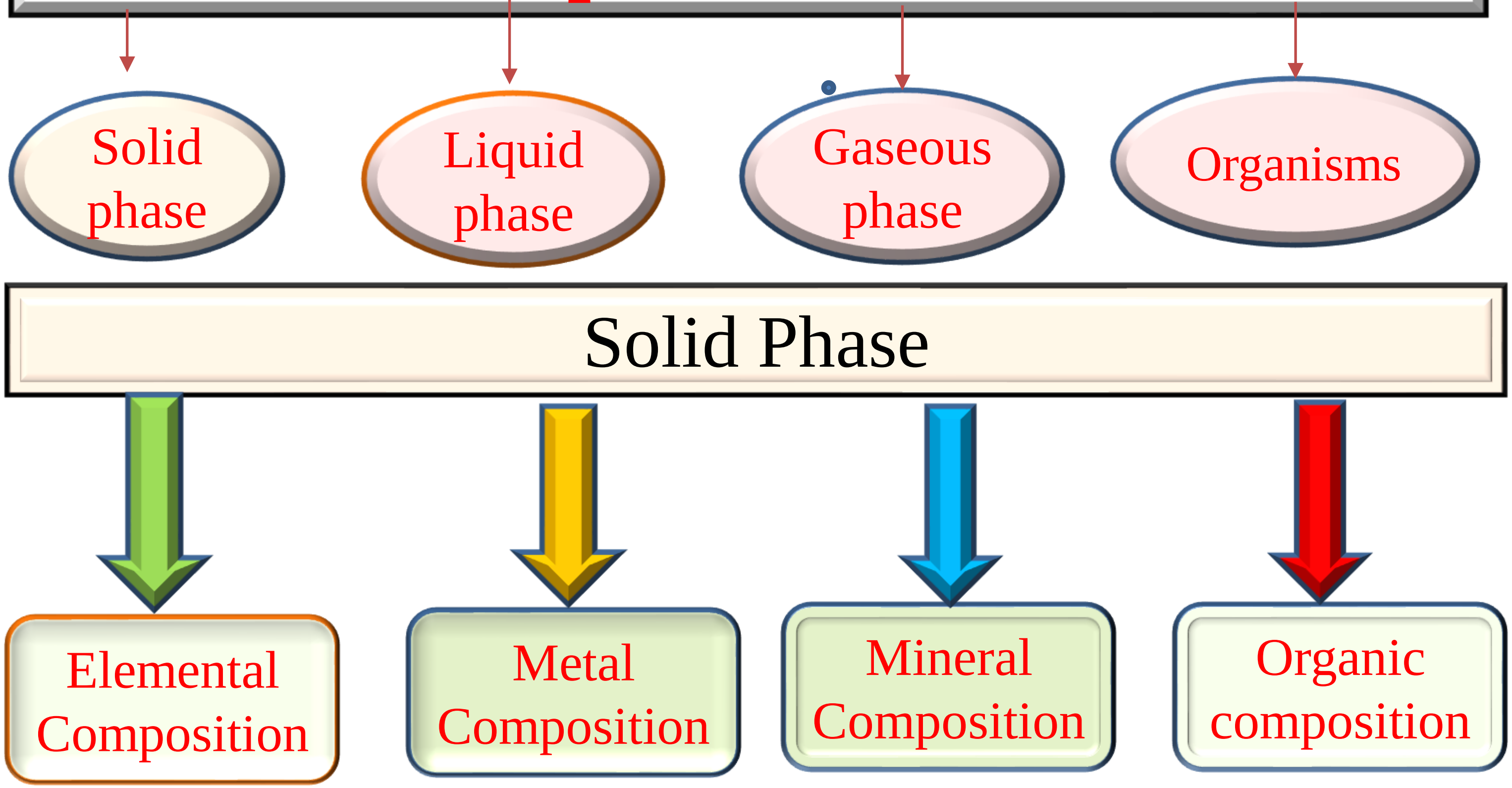
2-Organic matter decay.

3-Rain.

4-Irrigation water.

5-Release of ions retained by soil colloidal or clay fractions of soils.

Chemical composition of soils



Solid phase

Liquid phase

Gaseous phase

Organisms

Solid Phase

Elemental Composition

Metal Composition

Mineral Composition

Organic composition

The major elements in soils are those with concentrations that exceed 100 mg kg^{-1}, all others being termed trace elements. According to the data in tables 1.1 and 1.2, the major elements include O, Si, Al, Fe, C, K, Ca, Na, Mg, Ti, N, S, Ba, Mn, P, and perhaps Sr and Zr, in decreasing order of concentration. Notable among the major elements is the strong enrichment of C and N in soils relative to crustal rocks (Table 1.1), whereas Ca, Na, and Mg show significant depletion (Table 1.2). The strong enrichment of C and N is a result of the principal chemical forms these elements assume in soils—namely, those associated with organic matter. The average C-to-N, C-to-P, and C-to-S ratios (8, 61, and 13 respectively) in soils, indicated by the data in Table 1.1, are very low and, therefore, are conducive to microbial mineralization processes, further reflecting the active biological milieu(environment) that distinguishes soil from crustal rock.

The major elements C, N, P, and S also are macronutrients, meaning they are essential to the life cycles of organisms and are absorbed by them in significant amounts. The global biogeochemical cycles of these elements are therefore of major interest, especially because of the large anthropogenic influence they experience. Mining operations and fossil fuel production, for example, com- bine to release annually more than 1000 times as much C and N, 100 times as much S, and 10 times as much P as is released annually worldwide from crustal weathering processes. In soils, these four elements undergo biological and chemical transformations that release them to the vicinal atmosphere, biosphere, and hydrosphere, as illustrated in Figure 1.1, a flow diagram that applies to natural soils at spatial scales ranging from Pedon to landscape. The two storage components in Figure 1.1 respectively soils can continue to accumulate C for several millennial(2000 year), only to lose it over decades when placed under cultivation. The importance of this loss can be appreciated in light of the fact that soils are the largest store or repository(مستودع أو المخزن) of no fossil fuel organic C on the planet, storing about four times the amount of C contained in the terrestrial biosphere.

The picture for soil N flows is similar to that for soil C, in that humus is the dominant storage component and emissions to the atmosphere are an important pathway of loss. The emissions send mainly N_2 along with N_2O and NH_3 to the atmosphere

The picture for soil N flows is similar to that for soil C, in that humus is the dominant storage component and emissions to the atmosphere are an important pathway of loss. The emissions send mainly N_2 along with N_2O and NH_3 to the atmosphere. The N_2O, like CO_2 and CH_4, is of environmental concern because of its very strong absorption of terrestrial infrared radiation (greenhouse gas). Unlike the case of CO_2 and CH, however, the source of these gases is dissolved inorganic N, the transformation of which is termed denitrification when N_2 and N_2O are the products, and ammonia volatilization when NH_3 is the product. Denitrification is typically mediated by respiring microorganisms, whereas ammonia volatilization results from the deprotonation of aqueous NH^+_4

Important losses of C from soils occur as a result of leaching, erosion, and runoff, but most quantitative studies have focused on emissions to the atmosphere in the form of either CO_2 or CH_4 produced by respiring microorganisms. The CO_2 emissions do not arise uniformly from soil humus, but instead are ascribed conventionally to three humus “pools”:

1-An active pool, with C residence times up to a year.

2- A slow pool, with residence times up to a century.

3-A passive pool, with residence times up to a millennium (Thousands).

Nature soils can continue to accumulate C for several millennial, only to lose it over decades when placed under cultivation. The importance of this loss can be appreciated in light of the fact that soils are the largest repository(store) of no fossil fuel organic C on the planet, storing about four times the amount of C contained in the terrestrial biosphere

Cultivated soils, on the other hand, often show excessive leaching and runoff losses of N, as well as significant emissions .

Sulfur flows in soil for example mineralization of organic S by microorganisms to SO4 ,which can be leach or absorb by plants and living organisms. In flooded soils ,soluble H_2S and other potentially volatile sulfides are produce from degradation of humus or reduction of sulfate (Electron transfer to sulfate to produce sulfide), they can lost by emission.

Phosphorus flows in soils is important that inorganic-P reservoirs—phosphate on particle surfaces and in solid phases can sometimes be as large as or larger than that afforded by humus, depending on precipitation. Leaching losses of soil P are minimal, and gaseous P emissions to the atmosphere essentially do not occur from natural soils.

The four elements become oxyanions (CO_3^{2-}, NO_3^-, SO_4^{2-}, PO_4^{3-}, and their proton complexes) when humus is mineralized by microorganisms under aerobic conditions at circumneutral pH. The affinity of these oxyanions for particle surfaces, as well as their susceptibility to precipitation with metals, has been observed often to increase in the order $NO^-_3 < SO_4^{2-} \leq CO_3^{2-} \leq PO_4^{3-}$. This ordering is accordingly reversed for their potential to be lost from soils by leaching or runoff processes, whereas it remains the same for their potential to be lost by erosion processes.

An important question about the previous slides or explanations:

Why the focus was on four elements (C,N, S and P) ?

The focusing was on the above four elements due to the following reasons:

1-The are four of the essential macronutrients for plants and organisms.

2-Their concentration in deserts ,forest and other soils are strongly or significantly affecting by temperature and rainfall.

3-In most soils ,the microbial degradation of litter and humus is the process through which (C,N, S and P) were releasing to aqueous or liquid phase, then absorption by biota or losses by the following processes:

A- Leaching . B-Erosion and runoff. C-Emission to atmosphere in gaseous form.

4- They are more affecting by human activities in comparing with other macro nutrients.

5-Their cycle are most interesting in comparing with other macro nutrients.

6- They are forming oxyanions with oxygen as follow:

CO_3^{2-} ,NO^{3-} ,SO_4^{2-} and PO_4^{3-} .

Gauss's law: It indicated that oxygen has two negative charges ,it means it able to bonding till 2 vu with oxyanions or between central cation and oxygen as follow:

1-For NO_3^- equal to 2-1.67 =0.33
2-For SO_4^{2-} equal to 2-1.50 =0.50
3- For CO_3^{2-} equal to 2-1.33 =0.67
4-For PO_4^{3-} equal to 2-1.25 =0.75

Depending on above value the series of oxyanions is as follow:

$NO_3^- < SO_4^{2-} < CO_3^{2-} < PO_4^{3-}$
$0.33 < 0.50 < 0.67 < 0.75$

Q_1: Why for monovalent cations if radius equal or more than 0.033 nm has capability to dissolve in water or aquatic solution. Q_2: Mention the factors affecting the ionic radius.

Q_3: How bond valency parameters affects on bond strength between Metals and oxygen?

consider Al^{3+}, for which Eq. 2.3 takes on the form

$s = \exp[27.03(0.1651 - R)]$ ----------(2.4)

$s = \exp[27.03(0.1651 - 0.185)] = 0.58$

$s = \exp[27.03(0.1651 - 0.197)] = 0.42$ and so on for all elements.

where R is now the length of an Al–O bond in nanometers. In the aluminum oxide mineral corundum (Al_2O), Al is in octahedral coordination with O_2. Two different Al–O bond lengths are actually observed in this mineral (0.185 nm and 0.197 nm), corresponding to s values of 0.584 and 0.422 vu respectively. These two bond strengths bracket theAl^{3+} ideal value of 0.50 calculated with Eq. 2.2 using Z 3, CN 6. When bond strength is calculated with Eq. 2.3 instead of Eq. 2.2, it is termed bond valence, not only to avoid confusion with the original Pauling definition, but also to emphasize its chemical interpretation as an effective valence of the ion to which it is assigned.

Rule 4: In a structure comprising different kinds of cation, those of high valence and small coordination number tend not to share polyhedron elements with one another. This rule tends to increase the distance between highly charged cations ,so as to reduce electro-statistic repulsion between them.

Rule 5: The number of essentially different kinds of ion in a crystal structure tends to be as small as possible. Thus, the number of different types of coordination polyhedral in a closely packed array of anions tends to be a minimum.

Lyotropic series

Ions with a higher valence are held more tightly than monovalent cations (exception, H+) the following relative ion replaceability has been called the Lyotropic series

$$H^+ > Al^{+++} > Ca^{++} > Mg^{++} > K^+ = NH_4^+ > Na^+$$

Strength of adsorption

– Based on charge and hydrated radius:-

- The smaller the radius and greater the valence, the more strongly the ion is adsorbed.

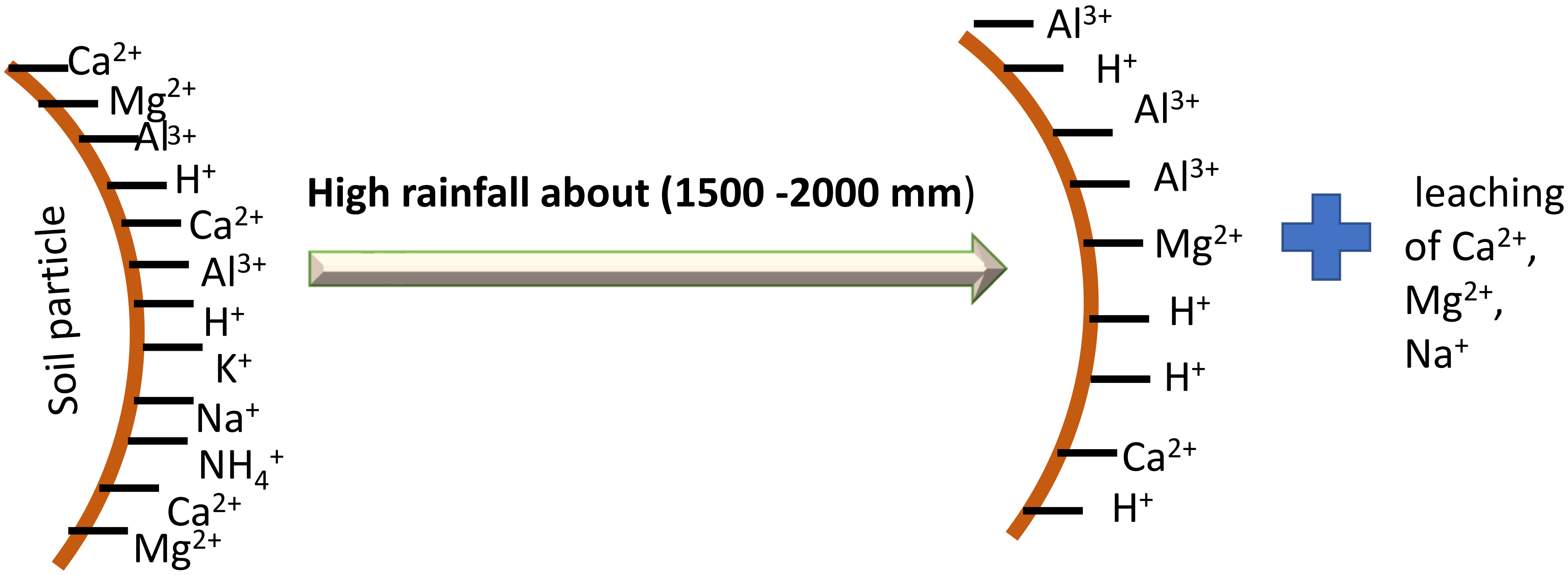
- The strength of adsorption increases as: –

- Cation valence increases
- Hydrated size decreases

Strength of adsorption = valence (charge) / hydrated radius

Application of lyotropic series:

1-Formation of acid soil:



High rainfall about (1500 -2000 mm)

leaching of Ca^{2+}, Mg^{2+}, Na^+

(Acid soil formation)