Hydrogeochemistry (460G)

Answer the following question:
1- **Explain the following:**   (16 mark)
   a- The impact of organic matter decay and Selective uptake of ions by vegetation on water quality
   b- Piper Diagram

2- **Discuss in detail:**   (16 mark)
   a- Field analyses and sample conservation
   b- Accuracy of chemical analysis
   c- Depth specific and depth integrated sampling
   d- Stiff's diagram

 3- **Explain Sulin`s diagram for genetic classification of groundwater (16 mark)**

Answer

1-Explain the following: **(16 mark)**
 a- The impact of organic matter decay and Selective uptake of ions by vegetation on water quality
-*Selective uptake of ions by vegetation*
Some elements are heavily up taken by plants because its importance for plant growth (K and P and N).
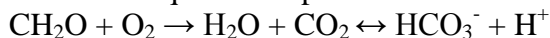Others are not important like Mg and S that is why it does not affected by plant uptake.
Vegetation can also adsorb gases from the atmosphere, for example SO_2, NH3 and NO_2. These gases may partly be taken up and incorporated in the plant, while the remainder is flushed away with the rain
 Uptake rate differ from plant to another and also depends on the age of the plant.
-*Decay of organic matter*
This process means **oxidation** of fossil organic matter (peat, lignite etc.) which occurs in the soil or within the aquifer and produces carbonic acid;
   $CH_2O + O_2 \rightarrow H_2O + CO_2 \leftrightarrow HCO_3^- + H^+$
Organic matter is very complex containing humic and fulvic acids etc, also contains minor constituents such as P, K, N, S, etc., which are released upon degradation.
Decomposition of organic matter in aquifers can occur associated with **reduction** of oxides, sulfate and nitrate, or the formation of methane.
In addition, the production of CO2 may have a great influence on reactions involving carbonate minerals $SO_4^{2-} + 2CH_2O$ $H_2S + 2HCO_3^-$

b- Piper Diagram
        A piper diagram is a graphical presentation of the chemistry of a water sample or samples. The cations and anions are shown by separate ternary plots. The apexes of the cation

plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus bicarbonate anions. The two ternary plots are then projected up onto a diamond **(Fig).** The diamond is a matrix transformation of a graph of the anions and cations. In Piper diagrams the concentrations are expressed as % meq/L.
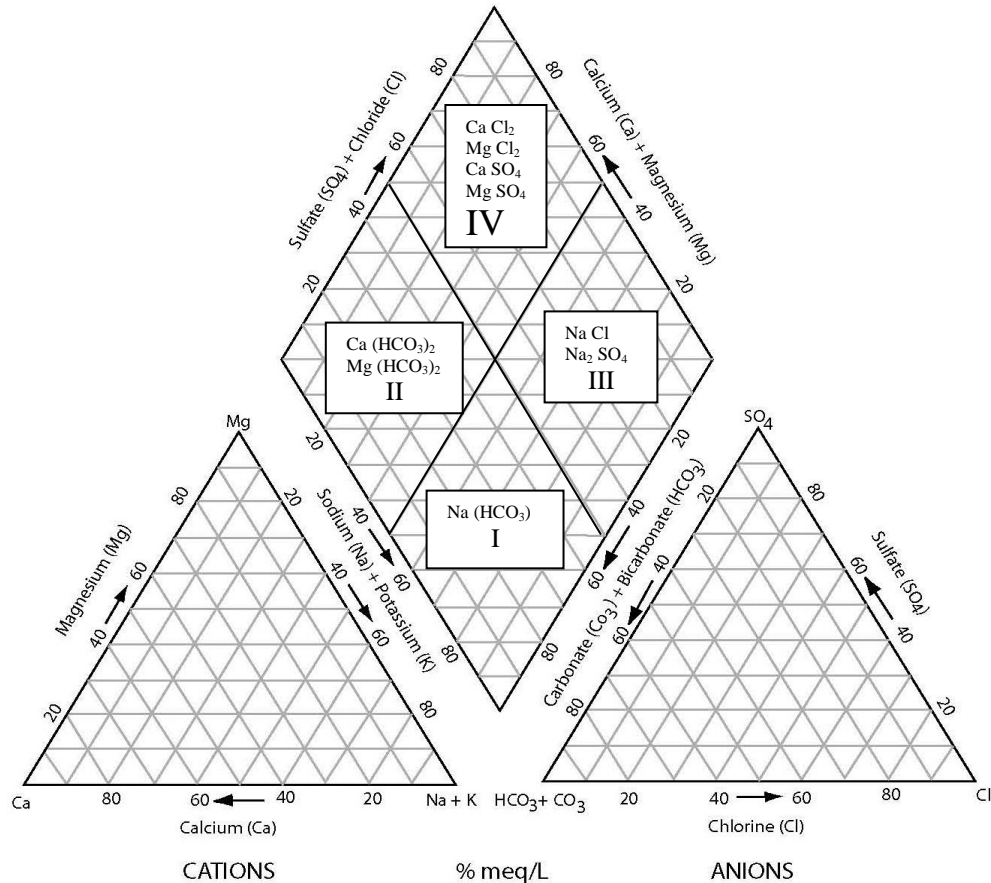
Zone I Characterized by Na (HCO_3) shallow meteoric water, soft and alkaline in reaction. At high depths It is formed according to the following equation:

$2C + H_2O + Na_2 SO_4 \longrightarrow 2 Na (HCO_3) + H_2S$
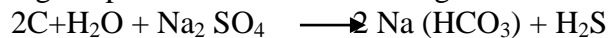
Note : one composition and one formation

Zone II Characterized by Ca (HCO_3)$_2$ and Mg (HCO_3)$_2$ salts.

Note: the formation (genesis) is the same as meteoric water leaching to carbonate rocks. The composition is different and it is difficult to identify the lithology

Zone III Characterized by Na Cl and Na$_2$ SO$_4$ salts.

Note: The composition and the formation (genesis) are different. The Na Cl may be meteoric or marine water and the Na$_2$ SO$_4$ is meteoric water of deep percolation

Zone IV Characterized by Ca Cl$_2$, Mg Cl$_2$, Ca SO$_4$ and Mg SO$_4$ salts.

Note: The composition and the formation (genesis) are different. The Ca Cl$_2$ and Mg Cl$_2$ are marine water origin and the Ca SO$_4$ and Mg SO$_4$ Characterizes either meteoric water or marine water. If salinity low, the meteoric water leaching to sulfate cement. If salinity high, the meteoric water leaching to evaporates (Gypsum or anhydrite)

ADVANTAGES

Many water analyses can be plotted on the same diagram.

-Can be used to classify waters by Hydrochemical facies.
- Can be used to identify mixing of waters.
DISADVANTAGES
-Neglect gas analyses
-Different water formation (genesis or origin) are plotted in the same zone

2- Discuss in detail: **(16 mark)**
  a- Field analyses and sample conservation
        When a groundwater sample is brought to the surface, it is exposed to physico-chemical conditions which are different from those in the aquifer. For example, atmospheric oxygen may readily oxidize components like Fe^{2+} , H_2S, etc. which are commonly present in anoxic groundwater. Furthermore, degassing of CO_2 may occur, causing changes in pH, alkalinity and total inorganic carbon, which may also induce carbonate precipitation. Thus, measures are needed to prevent changes in the chemical composition of the sample before analysis. Such measures are of two kinds: conservation and field measurements.
        Conservation is in most cases done by adding acid to the sample until the pH is < 2. (0.7ml of 65% HNO_3 is usually enough to neutralize alkalinity and to acidify 100ml sample). Acidification stops most bacterial growth, blocks oxidation reactions, and prevents adsorption or precipitation of cations. Prior to acidification, the water sample has to be filtered to remove suspended material which could dissolve when acid is added.
     Field analyses are usually carried out for parameters like pH, EC, Eh, O_2, which are measured by electrode, and sometimes also for alkalinity and Fe^{2+}.

b- Accuracy of chemical analysis
        The accuracy of the analysis for major ions can be estimated from the eletro-Neutrality (E.N.) condition since the sum of positive and negative charges in the water must balance:

$$\text{Electro Neutrality (E.N., \%)} = \frac{(Sum\,cations + Sum\,anions)}{(Sum\,cations - Sum\,anions)}\,100$$

where cations and anions are expressed as meq/1. The sums are taken over the cations Na^+, K^+, Mg^{2+} and Ca^{2+}, and anions Cl, HCO^-_3 and SO^-_4. Sometimes other elements contribute significantly, like for example Fe^{2+} or NH_4^+ in reduced groundwater, or H^+ and Al^{3+} in acid water. The presence of the last two substances in significant amounts requires more accurate calculations of E.N. balances using special computer. Differences in E.N . of up to 2% are inevitable in almost all laboratories. Sometimes an even larger error must be accepted, but at deviations of more than 5% the sampling and analytical procedures should be examined.
        Another useful technique is to compare calculated conductivities with measured electrical conductivity. At 25°C, the EC divided by 100 yields a very good estimate of the sum of anions or cations (both in meq/1).

$$\sum \text{anions} = \sum \text{cations (meq/1)} = EC/100 \; (\mu \text{ S/cm})$$

        This relation is valid for EC values up to around 2000 μ s/cm.
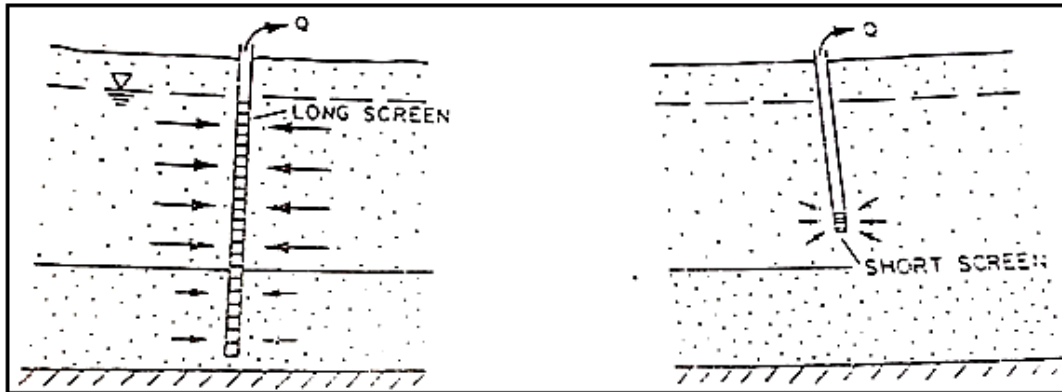**c- Depth specific and depth integrated sampling**
        Most chemical analyses of groundwater are found in the files of governmental and water works offices. Their prime function is to monitor the groundwater quality in production wells.

Such wells are typically installed with a screen of at least several meters length (Figure). Accordingly, the listed chemical composition of the groundwater reflects integrated sample over the whole screen interval. Note in Figure, that the sample obtained is integrated over the length of the screen as well as over the permeability of the formation. Thus the screen interval with fine grained sand will contribute relatively less to the total yield than the coarse grained sand with a much higher permeability.

Chemical groundwater data obtained from depth integrated samples can be useful in identifying regional patterns in groundwater composition and its relation to rock types.

Depth integrated versus depth specific groundwater sampling. Coarse dotted areas represent coarse grained sand and densely dotted areas fine grained sand. The size of the arrows reflects the flow rate

However, in many cases groundwater compositions show major variations with depth, even on a small scale. Integrated samples over a screen interval of several meters may accordingly represent mixtures of waters with different compositions and the mixing process may also induce chemical reactions during the sampling process. Therefore, depth specific sampling is usually required in order to study chemical processes in detail. An illustration of a groundwater chemistry profile, obtained with a depth specific device, of a sandy aquifer with a well-defined oxic zone and anoxic zone containing Fe^{2+}, is shown in Figure. Suppose that a screen is installed so that it draws water from both the oxic and anoxic zones. Then the O_2 containing water will mix and react with Fe^{2+} and pH or alkalinity by the reaction:

$$2Fe^{2+} + 1/2O_2 + 3H_2O \rightarrow 2FeOOH + 4H^+$$
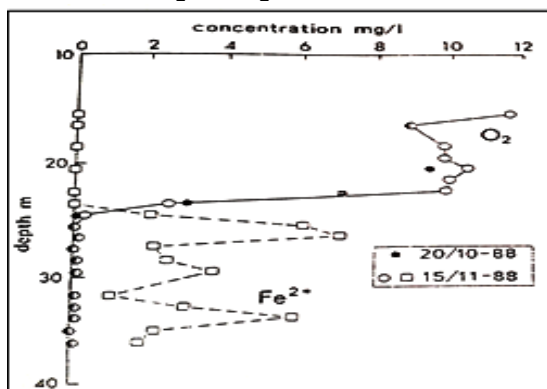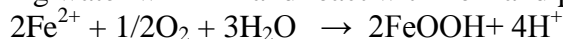
**The distribution of O_2 and Fe^{2+} in a sandy aquifer**

The composition of the resulting sample will depend on the extent of mixing and reaction. In principle, even a sample which contains both Fe^{2+} and O_2 could be obtained although

such a water quality does not occur in the aquifer. In any case the resulting sample will not reflect the in situ conditions in the aquifer very well. It is obviously of great importance to realize whether the data one tries to interpret have been obtained using a depth specific or depth integrated sampling method and also to evaluate how the sampling procedure affected the measured water quality.

d- Stiff's diagram
Stiff diagrams are graphical representation of water chemical analyses, first developed by H.A. Stiff in 1951. A polygonal shape is created from three or four parallel horizontal axes extending on either side of a vertical zero axis. Cations are plotted in mill equivalents per liter on the left side of the zero axis, one to each horizontal axis, and anions are plotted on the right side. Stiff patterns are useful in making a rapid visual comparison between water from different sources.
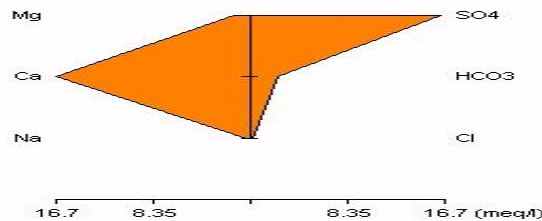
ADVANTAGES
•   Can help visualize ionically related waters from which a flow path can be determined, or
•   If the flow path is known, to show how the ionic composition of a water body changes over space and/or time .
DISADVANTAGE
•   Only one analysis per plot.

3-Explain Sulin`s diagram for genetic classification of groundwater (16 mark)
Sulins` Diagram is composed of two squares one of them represent the marine water genesis (where rCl>r(K + Na) and r(K + Na)/ r Cl< 1) and the other for meteoric water origin (where r(K + Na) > r Cl and r(K + Na)/ r Cl> 1). The two squares are joined at a transition point where r(K + Na)/ r Cl=1and ther are devided into four triangle I, II, iii and iv **(Fig)**.
Any point plotted in ***triangle No I*** means r(K + Na) - rCl/r SO_4> 1. Excess Na over Cl and SO_4 produces **Na (HCO_3)** water type of meteoric genesis, soft, alkaline in reaction. The water present near the surface in shallow aquifer. The hypothetical salt combinations are: KCl, NaCl, Na_2SO_4, **Na (HCO_3)**, Mg $(HCO_3)_2$ and Ca $(HCO_3)_2$. Sometimes **Na (HCO_3)** water type exists in deeper aquifer with H_2S and CO_2 gases due to reduction of sulfate and decaying of organic matter.
Any point plotted in ***triangle No II*** means r(K + Na) - rCl/ r SO_4< 1. Excess Na over Cl produces **Na_2 (SO_4)** water type of deep meteoric origin slightly alkaline in reaction. The hypothetical salt combinations are :KCl, NaCl, **Na_2SO_4**, $MgSO_4$, Mg $(HCO_3)_2$ and Ca $(HCO_3)_2$. Sometimes **Na_2 (SO_4)** water type exist in shallow aquifer due oxidation of sulfide deposits.
Any point plotted in ***triangle No III*** means rCl- r(K + Na) / r Mg < 1. Excess Cl over Na produces **Mg Cl_2** water type (normal sea water) or syngenetic marine water diluted by meteoric water within the rock pores. The hypothetical salt combinations are: KCl, NaCl, **$MgCl_2$**, $MgSO_4$, $CaSO_4$ and Ca $(HCO_3)_2$.

Any point plotted in ***triangle No IV*** means rCl- r(K + Na) / r Mg > 1. Excess Cl over Na and Mg produces old marine **CaCl₂** water type or oilfield water. The hypothetical salt combinations are: KCl, NaCl, MgCl₂, **CaCl₂,** CaSO₄ and Ca (HCO₃)₂.