RANGE AND AVERAGE OF HYDROCHEMICAL RATIOS OF THE DIFFERENT SURFACE WATER SAMPLES IN RIVER NILE AND CANALS

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Abstract

It is found that all River Nile and canals water samples are suitable for all kinds of fruits, vegetables and field crops, where EC values are (< 4) m mhos/cm, while the rest of samples (mixed water samples) are unsuitable for irrigating any type of crops, since their salinities are over (16) mmhos/cm.

The study indicated that, all River Nile and canals water samples can be classified as water of the first grade (class I) while mixed water samples can be classified as water of the third grade (class III) of irrigation water.

Introduction

In this paper deals with a systematic hydrochemical study carried out at proximity basalt to assess groundwater quality and evaluate the hydrochemical processes. A total of 40 water samples were collected equally from these areas and analyzed. Results showed that the waters rich in alkaline earth in the basalt and alkali rich element in the granite[1].

The dominancy of cations was observed as $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ in the basalt and $Na^+ > Mg^{2+} > K^+ > Ca^{2+}$ in the granite, whereas anions as $HCO_3^- > Cl^- > SO_4^{-2}$ and $Cl^- > HCO_3^- > SO_4^{-2}$, respectively. Hydrochemical processes were identified with the helps of ion exchange, carbonate weathering and dissolution, multiple ionic ratios, and silicate weathering, which shown the predominance of carbonate, dolomite, calcite and silicate (anorthite) weathering in basalt, but in granite, silicate (alkali feldspar) weathering was dominated, [2].

The study finds, from hierarchical cluster analysis that there as two main hydrochemical faciesnamely the calcium-sodium-chloride-bicarbonate waters and the magnesium-polassium-sulfate-nitrate waters in the northern and southern sections respectively[3].

Hydrochemical conditions up to depths of 1000 m below ground level around the Mizunami Research Laboratory were invesligated to a construct a "baseline condition model" describing the undisturbed hydrochemical environment prior to excavation of the underground facilities at Mizunami, Gifu, Japa[4].

Experimental

Measurements of the constituents of surface water samples, (5,6):

These measurements contain the following topics:

- **Hydrogen ion concentration (pH):**

pH-meter, WTW model LF 538.

- **Specific electrical conductance(EC):**

Electrical conductivity meter, Model 35, Yellow Springs Instrument Company, U.S.A.

- **Total dissolved solids (TDS):**

Total dissolved solids of any water sample can be determined using the following method:

- **Calculation method:**

In This method TDS in ppm can be determined as follow;

$$TDS=Ca^{2+} + Mg^{2+} + Na^+ + K^+ + CO_3^{2-} + 1/2\ HCO_3^- + SO_4^{2-} + Cl^-$$

- **Carbonate and bicarbonate constituents:**

Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) constituents are determined titrimetrically against sulfuric acid by neutralization method.

Pipet a volume of sample into a porcelain dish and add one drop of phenolphthalein, if solution turns pink, titrate against sulphuric acid (0.01N) from a burretdropwise until the colour just disappears, and designate this burret reading as (y) and add 2 drops of methyl orange and titrates against sulphuric acid 0.01N to the just orange colour, designate the new burret reading as (z).

- **Calcium and magnesium constituents:**

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations are determined titrimetrically against (Na_2EDTA) by complexometric method, calcium is determined by using murexid indicator while magnesium is estimated by subtracting the calcium value from the total hardness value after determining them using Eriochrome Black T in presence of suitable buffer solution.

- **Total hardness (Calcium and magnesium hardness):**

Pipet a volume of sample containing less than 25mg hardness into a porcelain dish and add 1ml (3%) NH_2OH. and add 1ml buffer solution andadd 2ml Eriochrome black T indicator and titrate with Na_2EDTA (1.00ml=1.00mg $CaCO_3$) until the colour of the solution becomes clear blue.

- **Calcium hardness.**

Pipet a volume of sample containing less than 25mg hardness into a porcelain dish and add1ml NaOH solution and add 0.2g murexidindicator or 5 drops and add

the titrant (Na_2EDTA) slowly with continuous stirring until the colour changes from pink to purple.

- **Magnesium hardness:**

Mg^{2+} hardness (in ppm) as $MgCO_3$ = total hardness - calcium hardness.

- **Chloride constituent:**

Chloride is determined volumetrically by titration against silver nitrate using potassium chromate as indicator.

Pipet a volume of sample containing less than 50mg Cl^- into a porcelain dish and add 10 drops K_2CrO_4 indicator andwith continuous stirring titrates with $AgNO_3$ until the pink-red Ag_2CrO_4 persists for 10-15sec.

- **Sodium and potassium constituents:**

Sodium (Na^+) and potassium (K^+) constituents are determined by means of flame photometer model PFP 7, Jenway, (UK). The obtained standard curve and the sample readings can be calculated in ppm (less than 100ppm).

- **Sodium constituent:**

Measure the blank and the standards of Na^+ ppm by the flame photometer and record the readings and measure the samples containing less than 100ppm Na^+ and record the readings.

- **Potassium constituent:**

Measure the blank and the standards of K^+ ppm by the flame photometer and record the readings andmeasure the samples containing less than 100ppm K^+ and record the readings.

- **Sulfate constituent:**

Sulfate (SO_4^{2-}) is determined by the turbidity method using spectrophotometer single beam, model (20D), Milton Roy Company, U.S.A. To every 10ml of the blank and the standards add 5ml of acid salt and few crystals of barium chloride and measure transmitance at wavelength 420nm and in a semi-logarithmic paper plots a relation between the standards concentrations and %T and from the plot, the sample reading can be obtained at concentrations less than 50ppm SO_4^{2-}.

Results and Discussion

The relationship between the different major components can be studied through the determination of the ionic ratios. The expression of the ionic relationship in terms of mathematical ratios is quite helpful in establishing chemical similarities among water.

Ions ratios expressed as me/l are also useful in detecting surface water contamination (pollution) or mixing with other water resources. The ions ratios are important for possible determination of the origin of surface water and the different processes contributing to water quality development.

The significance of these ratios in the concerned area, as in (Table 1), can be evaluated as follows:

Table (1): Ranges and mean values of hydrochemical ratio of the different surface water samples in Egypt.

Hydrochemical Ratios	River Nile and canals		Mixed		Rain water	Sea water
	range	mean	range	mean	mean	mean
rNa^+/rCl^-	1.1-1.95	1.54	0.81-0.91	0.86	0.65	0.84
rSO_4^{2-}/rCl^-	0.5-1.18	0.84	0.08-0.12	0.11	0.86	0.1
$rCl^-/r(HCO_3^-+CO_3^{2-})$	0.13-0.62	0.35	43.88-251.4	148.1	0.65	189.9
rCa^{2+}/rMg^{2+}	1.46-2.53	2	0.18-0.31	0.25	7.22	0.17

1. Sodium-chloride ratio (r Na$^+$/r Cl$^-$):

The variation in (rNa^+/rCl^-) ratio is used for differentiating fresh and saline water. The values of this ratio are always higher than unity in fresh and meteoric water, while it is less than unity in sea water or saline water.

All water samples collected from River Nile and its canals have (rNa^+/rCl^-) values greater than unity ($Na^+>Cl^-$), where the (rNa^+/rCl^-) ratio ranges from (1.1 to 1.95) with a mean value 1.54 for River Nile and its canals.

The increasing ratio in surface water in River Nile may be attributed to the cations exchange process and leaching of terrestrial salts, this refers to the Nile water is fresh and meteoric water. In Mixed waters the ratio ranges from (0.81-0.91) with a mean value (0.88) less than unity:

($Cl^->Na^+$) where NaCl represent the dominant in sea water [7].

2. Sulfate -chloride ratio (rSO_4^{2-}/r Cl$^-$):

Sulfate – chloride ratio can be taken as a guide for detecting any excess of sulphate in the surface water due to ($CaSO_4$) dissolution or ($CaCO_3$) precipitation. The solubility of sulfate mineral components gradually increased in the hydro-chemical composition by depth and distance from the recharge to discharge area [8].

Consequently, the percolation of meteoric water and the greater distance of recharge area are the main factors of increasing the sulfate concentration by direct action of leaching processes.

With respect to the surface water samples collected from River Nile and its canals water have the values of (rSO_4^{-2}/rCl^-) ranges from (0.5 to 1.18) with mean value (0.84) is closed to rain water where the samples have values of (rSO_4^{-2}/rCl^-) more than unity is due to the dissolution of a local terrestrial source of sulfate such as gypsum, ($CaSO_4.2H_2O$), epsomite ($MgSO_4.7H_2O$), glauberite ($Na_2SO_4.10H_2O$) and anhydrite ($CaSO_4$).

While the Mixed water have the values of rSO_4^{-2}/rCl^- ranges from (0.08 to 0.12) with mean value (0.11) is closed to Sea water(0.1) this is due to mixing of River Nile waters with Mediterranean water in the end of River Nile.

3. Chloride – Carbonae and bicarbonate ratio $rCl^-/r(HCO_3^- +CO_3^{2-})$:

All water samples from River Nile and its canals have values of:

$rCl^-/r(HCO_3^-+CO_3^{2-})$ ranges from (0.13 to 0.62) with mean value (0.35) indicating normal good water [9] while in Mixed water the values of:

$rCl^-/r(HCO_3^-+CO_3^{2-})$ ranges from(43.88 to 251.4) with mean value (148.1) closed to sea water .

4. Calcium/magnesium ratio (rCa^{2+}/rMg^{2+}):

According to[10] reported that rCa^{2+}/rMg^{2+} gives certain indications with regard to the nature of the carbonate layer. When this ratio has a value close to unity, it is concluded that surface water is flowing entirely through dolomite terrain. However, when the ratio is equal to, or greater than four, the surface water is likely to have flowed in pure limestone.

The values of (rCa^{2+}/ rMg^{2+}) of all collected samples from River Nile and its canals have the values ranges from (1.46 to 2.53), with mean value (2) are more than unity and less than four $(Ca^{2+} > Mg^{2+})$, indicating these waters is likely flowed in dolomitic-limestone terrain within the aquifer matrices and passing into matrices rich in (Ca^{2+}) and (Mg^{2+}) minerals, with some contribution of Cations exchange while in Mixed water values ranges from (0.18 to 0.31) with mean value (0.25) and less than unity $(Mg^{2+}> Ca^{2+})$, indicating these waters is closed to sea water.

5. Other ratios:

According to Heba [11] she has documented the use of a set of three ionic ratios that can be used in revealing the chemical genesis of surface water as in Table (2, 3). Ratios from (I) to (V) are shown as follow:

[I] $\{r (CO_3^{2-}+HCO_3^-)-rSO_4^{2-}\}/r(Anions)X100$

This parameter mainly assists in distinguishing water circulation through calcareous terrains and those occurring in evaporitic rocks.

All River Nile and Canals water samples have positive ratio values. This means that $(CO_3^{2-}+HCO_3^-)$ exceeds (SO_4^{2-}), indicating the River Nile and Canals water passage in carbonate materials and weathering basement rocks as in (Table 2 and 3) .

On the other hand, salinity of mixed water is linearly increased by evaporation. All mixed water samples (have a ratio negative values), show that mixed water acquires sulphate from sulphate minerals (gypsum, anhydrite, alunite, mirabilite,----- ect), dissolution and evaporitic rocks as in (Table 4).

[II] {rSO$_4$$^{2-}$/ r(Anions) – rNa+ /r(Cations)}X100

This parameter discriminates between sulfate–enriched water circulating in evaporitic terrains and sodium–enriched water that encountered in marly and clays sedimentary terrains.

All water samples (River Nile, Canals and Mixed) have negative values of this ratio. This means that (Na^+) is more than (SO_4^{2-}), this indicating the impact of Mediterranean Sea in Mixed water, (Na^+) is the dominant because it form NaCl as in Tables (2 and 3).

Table (2): Range and average of Hydrochemical ratios in River Nile, Egypt, (The ratios are expressed by   ml eq/l).

Sample No	Hydrochemical ratios				
	I	II	III	IV	V
1	67.295	-18.179	9.452	0.656	-3.332
2	70.709	-16.346	9.654	-2.318	-4.020
3	70.487	-20.263	10.889	2.015	-6.058
4	69.279	-18.867	8.317	-0.877	-3.464
5	60.900	-22.491	12.520	3.687	-3.574
6	55.397	-20.892	8.521	0.333	2.340
7	59.727	-21.206	9.450	2.319	-0.419
8	60.758	-19.984	7.229	-2.168	1.052
9	49.955	-21.870	8.435	1.980	4.349
10	55.24	-24.429	11.512	4.924	-1.094
11	51.6397	-21.775	8.307	2.494	3.799
12	49.8597	-21.132	7.325	0.001	5.602
13	56.7397	-24.375	13.798	1.335	-2.584
14	39.970	-29.532	7.296	7.712	6.347
15	45.168	-28.011	9.561	5.114	3.839
16	40.0899	-30.050	6.947	8.846	6.186
17	39.970	-29.966	7.750	8.026	5.864
18	46.382	-28.117	11.367	14.399	1.187
19	50.098	-26.241	12.062	5.416	0.838
20	42.461	-28.571	7.925	8.187	4.944
21	37.598	-30.857	5.128	9.834	8.318
22	39.510	-31.545	8.122	9.729	6.263

Table (3): Range and average of Hydrochemical ratios in Canals of River Nile, Egypt, (The ratios are expressed by (ml eq/l).

Sample No	Hydrochemical ratios				
	I	**II**	**III**	**IV**	**V**
1	63.665	-16.512	8.798	-7.661	0.239
2	28.118	-16.021	9.460	-7.558	35.311
3	57.956	-24.709	15.566	4.969	-4.551
4	58.369	-22.759	12.119	3.121	-2.096
5	42.478	-28.204	8.954	6.159	5.289
6	37.538	-28.129	5.842	7.154	9.152
7	43.659	-29.437	7.239	7.332	4.968
8	46.424	-21.663	2.329	-1.800	9.821
9	47.212	-24.959	3.996	3.338	6.769
10	35.073	-35.798	6.130	15.622	5.565
11	41.219	-36.008	11.306	15.825	-0.241

[III] {r Na$^+$ / r(cations) – rCl$^-$ / r(Anions)}X100

This parameter tends to distinguish between waters derived from flysch or volcanite's and those coming from carbonate–evaporitic series or from a regional quartzitic schistose basement. Both types of waters have relatively high (Na$^+$) concentrations, but the former have a very low (Cl$^-$) content and the latter has (rNa$^+$ / rCl$^-$) ratio near unity.

All mixed water samples have negative values of this ratio. This means that (Cl$^-$) exceeds (Na$^+$), indicating the (Cl$^-$) forms (NaCl) and (MgCl) as in (Table 4). The River Nile and canals water samples have positive values of (C) ratio, reflecting the presence of carbonate materials in the matrix and evaporites or may be derived from volcanic rock since these samples have very low (Cl$^-$) content as in (Table 2 and 3).

Table (4): Range and mean values of the major dissolved ions in the surface water.

Surface water	Ca^{2+}	Mg^{2+}	Na$^+$	HCO$^-_3$	Cl$^-$	SO$_4^{2-}$	
Nile water	26.4-48	6.72-17.76	11.4-47.5	116-194	9-59	9.93-47.19	Range
	34	11	26	142	27	27	Mean
Canals water	28-45.6	10.08-18.24	13.9-58.7	116-184	11-72	16.56-49.69	Range
	36	13	32	148	35	32	Mean
Mixed water	160-520	312-1512	2600-11750	148-196	4902-22200	546.88-3725	Range
	333	946	8108	171	14646	2228	Mean

[IV] {r(Na^+- Mg^{2+})/r(Cations)}X100

This parameter individuates water that have circulated in dolomitized limestone or carbonate – evaporitic.

Most of water samples, about 85%, have positive value for this ratio, indicating the surface water passage in carbonate–evaporitic rocks. The rest of surface water samples (15%) have negative value that indicates surface water passage in dolomitized-limestone rocks as in (Table 2, 3 and 5).

[V] {r(Ca^{2+}+Mg^{2+})/r(cations) - r(CO_3^2+HCO_3)/ (Anions)} ×100

This parameter mainly distinguishes between circulation in carbonate reservoirs and in sulfate – bearing reservoirs. Most of surface water samples (72%) have positive value of this ratio, indicating the surface water passage in carbonate clays (settling). Some of surface water samples (28%) have negative value of this ratio, indicating surface water passage in sulfate sediments as in Tables (2, 3 and 5).

From the study of these ionic ratios, the main finding is that the surface waters have a meteoric origin. The surface water acquires its quality from leaching and dissolution of salts by its passage into the carbonates, clays, gypsum, basement, rocks and evaporates along the River Nile. While in the end of River Nile the water samples have marine origin as in:

(Table 2, 3 and 5).

Table (5): Range and average of Hydrochemical ratios in River Nile Water which mixed with Sea Water, Egypt, (The ratios are expressed by me/l).

Sample No	Hydrochemical ratios				
	I	II	III	IV	V
1	-9.955	-79.162	-10.077	63.376	18.855
2	-9.615	-78.767	-10.598	62.157	19.138
3	-5.386	-75.699	-14.745	58.558	20.483
4	-10.621	-75.791	-12.866	57.356	21.948
5	-8.306	-76.588	-13.129	58.606	20.806
6	-8.276	-77.374	-12.803	60.451	20.099

The range and average of Hydrochemical ratios in River Nile and canals are illustrated in the above Tables (2, 3 and 5).

(i) The assemblages of hypothetical salt combinations:

Hypothetically, the ions of the strong acids (Cl^- and SO_4^{2-}) form chemical combination with alkalis (Na^+ and K^+) and the rest of the acid radicals combine with the alkaline earths (Ca^{2+} and Mg^{2+}).

If the cations of alkalis and alkaline earths are surplus in water, they well combine with the weak acids (CO_3^{2-} and HCO_3^-). To clarify such combinations, the relations between cations and anions in the investigated waters, are illustrated in the form of bar graphs as outlined by Ragab [12].

In this method of representation, the concentrations of dissolved cations and anions, expressed in me/l, are represented by a vertical bar graph, the height of which is equivalent to the total concentration of either cations or anions. Each bar is subdivided into two longitudinal halves; the concentration of cations are plotted on the left half while the concentration of anions are plotted on the right one. Vertically, each bar is subdivided into several sections representing the present concentrations of the major cations and anions.

The deduced salt combinations on qualitative and quantitative bases are appended. The combination between major anions and cations reveals the formation of four main groups of hypothetical salts combinations in the surface water, (Table 6) and Figs. (1, 2 and 3).

In the surface water, three main groups (assemblages) of salt combinations are distinguished:

I- $(Na+K)Cl, (Na+K)_2SO_4, (Na+K)HCO_3$ Mg $(HCO_3)_2$ and Ca $(HCO_3)_2$.

I- $(Na+K)Cl, (Na+K)_2SO_4, MgSO_4$, Mg $(HCO_3)_2$ and Ca $(HCO_3)_2$.

II- $(Na+K)Cl, MgCl_2, MgSO_4, CaSO_4$ and Ca $(HCO_3)_2$.

Regarding the hypothetical salt combination in the River Nile, canals and mixed water, three main assemblage are detected: In River Nile and canals the assemblage (I) in (12) samples represent (32%), as in Table (6) and Fig (7). The presence of Na_2SO_4 salt in this assemblage is true indication of dissolution of terrestrial salts from continental deposits. Also, the presence of $NaHCO_3$, $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ salts indicates the origin of a meteoric water. Therefore, such water acquires its chemical composition from leaching and dissolution of terrestrial salts contents ,another main assemblage detected in River Nile and canals is assemblage (II) in (21) samples represent (54%). The assemblage (II) (two bicarbonate and sulphate salts) which is affected by leaching and dissolution of carbonate and sulphate minerals from channel matrices.

In mixed water one main assemblage is detected: assemblage (III) present in all samples of water (6) samples represent (15%) (two chlorides, two sulphates and one carbonates) as in Table (6) and Fig (3). Because of the chloride is dominant these indicate that the origin of the water is sea.

Table(6): Assemblages of the hypothetical salt combinations in the River Nile , canals and Nile mixed with sea water , Egypt.

Hypothetical salt combinations	Assemblage	No of Samples	%
I-(Na+K)Cl,(Na+K)$_2$SO$_4$,(Na+K)HCO$_3$, Mg (HCO$_3$)$_2$ and Ca (HCO$_3$)$_2$	I	12	30.77
II-(Na+K)Cl,(Na+K)$_2$SO$_4$,MgSO$_4$, Mg (HCO$_3$)$_2$ and Ca (HCO$_3$)$_2$	II	21	53.85
III-(Na+K)Cl, MgCl$_2$,MgSO$_4$, CaSO$_4$and Ca (HCO$_3$)$_2$	III	6	15.38
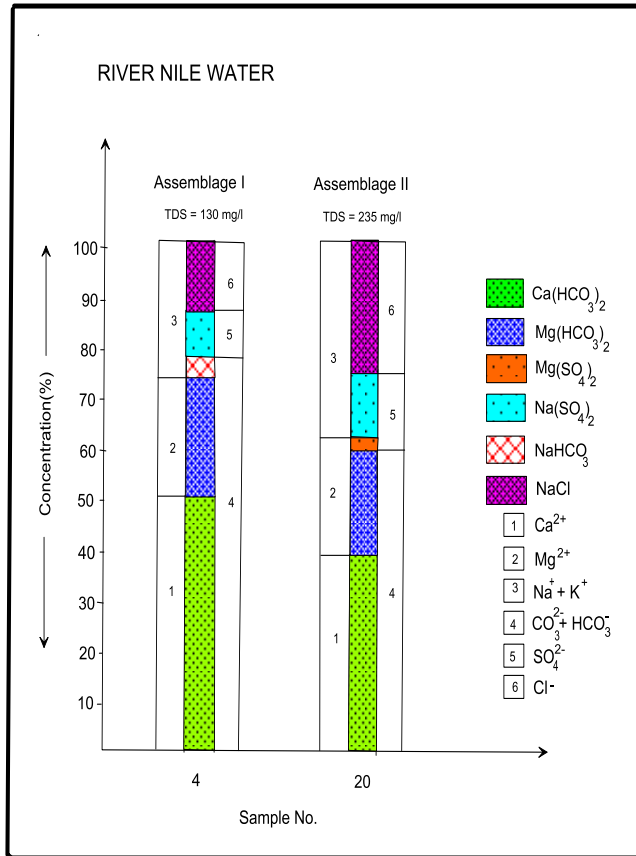
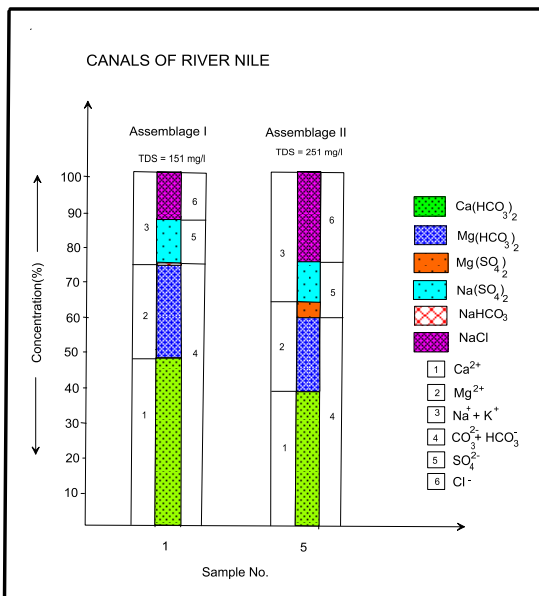**Fig. (1): Bar graphs representing the River Nile water samples .**

Fig. (2): Bar graphs representing the canals water samples .
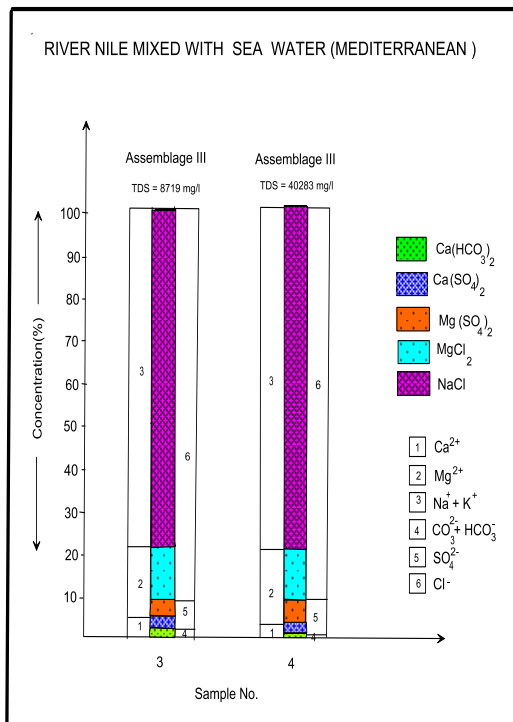

Fig. (3): Bar graphs representing the mixed water samples .

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