

Hydrochemical study of Rain Water In Baghdad city-Iraq

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Received on:14/6/2006

Accepted on:5/7/2007

Abstract:-

The chemical substance dissolved in rain water are generally considered to have two atmospheric sources, dry fallout and/or soluble salts. The present study deals with the rain water year 1995-1996 at Baghdad city were expressed in term of monthly averages of the collected samples . The concentrations values of cations (Ca, Mg, K and Na) and anions (Cl, SO₄ and HCO₃), were expressed as average annual. All ions concentration, are found to be within the excepted range of fresh water. These results were compared with rain water year 1985-1986. Appreciable reduction in concentrations of both cations and anions have been recorded, and the percentages of reduction are ranging between 28% to 84%. Moreover, by adopting fractionation factor, the results revealed that the sea water have less contribution of all ions concentration than other sources (local activities). The results of the chemical analysis were dealt with statistically by using cluster and factor analysis .

Key words

Rain water – Fresh water – Fractionation factor – Cluster analysis – Factor analysis.



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Introduction

The chemical substance dissolved in rain water are generally considered to have two atmospheric sources. They may be derived from fairly unreactive dust particles in which case they are deposited as dry fallout, or it may be present as gases or soluble salts which dissolved in rain water itself. The fallout deposited in amount independent of the quantity of precipitation, where as the substance dissolved in precipitation should have concentration that vary with rainfall amount. It has been demonstrated that much of the total dissolved and ionic load of many streams has been contributed by rainfall (Juang and Johnson,1967;Al-Jabbori,1989). Thus the magnitude of the atmospheric contribution must be known. The composition of rainwater is determined by the source of the water vapor and by the ions which are acquired by water (or lost from it) during transport through the atmosphere. Near the coast, the composition of rainwater strongly resembles diluted seawater. As the distance from the coast increases the concentrations of ions that are directly derived from seawater decreases.

The study area (Baghdad city) is located in the Mesopotamian alluvial plain

between latitudes $33^{\circ}14'$ $33^{\circ}25'$ N and longitudes $44^{\circ}31'$ - $44^{\circ}17'E$. The area is characterized by arid to semi arid climate with dry hot summers and cold winters, however, the source of the rain at Baghdad city is from the aerosols blowing from the Mediterranean sea west of the study area. The mean annual rainfall is about 151.8 mm (Al-Adili and Ali,2005). Table-1, showed the hydrochemical results of rain water components analysis at the rain year period 1995 – 1996 at Baghdad city. The sampling and chemical analysis were carried out at by the University laboratories. The aim of this paper is to find out the variation of ions concentrations between the tow different water years (1985 – 1986 to 1995 – 1996), and revealed the causes of these variations by using the fractionation factor and statistical analysis.

Analysis of the Results :-

The Hydrochemical analysis results of the water year 1995-1996 were expressed in term of monthly averages of the collected samples (Table-2). Different ions exist within the atmosphere around the year. Their existence are characterized by different rates and they are controlled by many factors, partly climatologically, wind systems in the region and partly local conditions. The main components of rain water are: Ca , Mg , Na

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and K as cations , Cl , SO_4 , HCO_3 as anions. Due to the fact that early events brings down the long existed dust and chemicals in the air prior to the rainfall events (Al-Jabbari et al. ,1989), it can be seen from Table-2, that the concentrations of chemicals at November 1995 are fairly higher than those analyzed within the following months.

The concentrations of cations (Ca , Mg and K) during the examined period were ranging between 0.66-1.5 , 0.4-4.5 and 0.012-0.07meq/l respectively, where their averages annual values are 0.908 , 0.6905 and 0.0287 meq/l respectively. Soil dust is the main possible source of these ions especially the Ca in rain water, due to Ca make the principle crystalline constituents of the urban dust which is easily eroded by wind action (Al-Jabbari et al.,1989, Gambell and Fisher, 1966).

Comparison has been made with the results obtained by Al-Jabbari 1989 for the water year 1985-1986 . As can be seen from Table-3,generally, the concentration of cations and anions decreases and the percent reduction within the last ten years were 59% , 28% and 44% respectively.

The Na and Cl ions concentrations were ranging between 0.123-0.869 and 0.46-3.5 meq/l and their annual averages were 0.254

and 0.75 meq/l respectively. The local atmospheric dust from plantation areas , roads believed to be one of important sources which can contribute appreciable amount of Na and Cl to the atmosphere beside other artificial sources. As concluded by Gambel and Fisher 1966 , revealed that Na and Cl within the rain water is not only affected by sea salt , thus it is important to taking into account their local conditions (study area), unlike the coastal regions where the concentrations depends mainly on sea salts.

Referring to Table(3),also , the reduction in concentrations of Na and Cl were observed clearly within the last ten years and the percent reduction was 84% and 50% respectively .

The sulfate ion concentration were ranging between 0.61-2.1 and its average value within the water year 1995-1996 is 1.061 meq/l, the percent reduction during ten years were 38%. The main possible sources of sulfate in rain water can be primarily attributed to the gases of sulfur compound which released to the atmosphere by human activities as well as the manufactured process and air craft exhaust. Thus the sulfate volume in rain water is dependent upon the precipitation volume . The effect of fuel sulfur are most marked in the rain water of industrial

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and urbanized areas (Junge 1960). However the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) particles in air are another source of sulfur when it wash out by the rain events.

The concentrations of HCO_3^- were ranging between 0.44-1.73 meq/l and its average value 0.599 meq/l . The main source of this anions is the CaCO_3 dust which is dominated within the top dry soil, as well as, the agricultural activities (plantation regions). Also this anion is reduced within the last ten years, and its percent reduction was 59% .

Concentration Analysis

The composition of rainwater is determined by the source of the water vapor and by the ions which are acquired by water (or lost from it) during transport through atmosphere. Near the sea coast the composition of rainwater strongly resembles the dilution of seawater. As the distance increase towards the urban areas , the concentrations of ions that are directly derived from seawater decreases (Plummer,1996). In industrialized areas additional sources are burning of wastes , power plants and other industry factories will be another contribution during rain events especially for Cl ion. However , Na in aerosols may also originate

from soil dust particles in arid climates in addition to sea salt (Plummer,1996). Accordingly the distribution of depletion or addition of ions must be non for both rain water and sea water. This situation can be get it by adopting fractionation factor. This reflects the changes of ionic concentrations ratio in rain water with respect to the ionic concentration in sea water, where :

$$F_{\text{Na}} = \frac{(\text{Cl}/\text{Na})_{\text{Rain}}}{(\text{Cl}/\text{Na})_{\text{Seawater}}} \text{ ----- (Plummer,1996)}$$

In this formula, the Cl and Na concentrations in rain or seawater can be expressed as mol/l , mg/l or any other units, also the above feature of factor means that the concentration is calculated relative to Na. It can be calculate this factor relatively to any cations or anions.

Table-4 demonstrate that the main enrichment ions of marine aerosols are Na and Cl, thus it can be adopted Na or Cl as a respective ions , here using the Na to finding F_{Na} for all cations and anions and hence, reflects the depletion or addition of ions in rainwater with respect to seawater. As can be observed from fractionation factor that, generally, all cations and anions have a high values which indicating an enrichment of ions with respect to Na due to a presence of inland

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atmospheric factors such as wind system, local conditions, urbanization activities ...etc.

The fractionation factors of SO_4 , Ca and HCO_3 shows a higher values comparing with other ions. As aforementioned those ions in rain water resulting mainly from activities of urbanized areas. It can be concluded , however , during transport the aerosols over land , the air masses and clouds pick up dust and gases from natural and industrial factors which modifies the composition of rainwater leading more different contributions in ionic concentration than near coastal aerosols.

To facilitate the interpretation of these analysis and to illuminate supplementary sources, the seawater contribution can be subtracted from the rainwater analysis (Plummer,1996). This calculation requires the selection of a conservative component for which Cl is a suitable, since it shows little fractionation (Table -4). The calculation proceeds constructed on the ratio of Cl and Na ions concentrations in seawater (Plummer,1996). Table-5 showed the concentration of ions in seawater and rain of Baghdad city, as well as, the depletion or addition of ions in rain water other than the concentration of marine aerosols, which indicates the contribution of other sources of ions in the rain water. Thus, the results revealed

that the seawater have less contribution of ions concentration than the other sources in the study area, that is may attributed to a far distance between a study area (Baghdad city) and a coastal (Mediterranean sea) . On the other hand, the contributions of local activities may be the main sources of ions concentrations in rain water, such as existed dust and chemicals in the air (as a gaseous).

By comparing the concentrations of cations (Ca , Mg , Na and K) and anions (Cl , SO_4 and HCO_3) with the normal ranges of concentrations in unpolluted fresh water (Table-6). The concentrations of Cl are exceeds the average range of concentrations in fresh water that is referred, as mentioned previously , the soil dust in Baghdad area especially within the earlier events , have appreciable contribution in rain water contamination by increasing a concentrations of Cl. Also, however , the concentration of SO_4 is located within a fifty percent of an average concentration at a fresh water, which is refer to an enrichment of a sulfate due to industrial activities where the location of rain station region is within an industrial and very density urbanized area . The enrichment of Na cation in rain water was also located within the first half of the average range of fresh water which can be attributed to the

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contribution of local atmospheric dust, plantation area and roads in aerosols when it approaching the region of study. Generally, all ions concentrations as listed in Table-6, are located within an excepted range of fresh water. It should be noted here, that some higher ranges were recorded at event occurred at Nov.1995 (Table-1), where this is the first event and the higher concentrations are due to the fact that the early events brings down the long existed dust and chemicals in the air prior to the rainfall event (Al-Jabbari et al. 1989).

Statistical analysis of Baghdad rain water (1995-1996) :-

The results of the chemical analysis were dealt with statistically by using cluster analysis. This analysis is depended on counting several variables of different samples, as well as, finding out the ratio of similarity among variables after comparison with each other ,and arrangements in the form of clusters or dendograms depending on the extent of their presence in the different samples. This is called (R - mode) where pairs of variables were compared with each other for all samples. When comparing these samples with each other depending on variables presence and the arrangement of their correlations in the form of clusters(Q-mode) and by explaining these correlations

,the relationship between all the samples and classification could be defined.

Pyramid (WARD) method was used in the two types of cluster analysis as it was considered the most modern and best method in such sort of studies. While, the factor analysis was used to minimize the big number of bilateral correlations at developed form and to classify into simple clusters. It was also, considered as one of the branches of multivariable aiming at putting new variables to replace those in the original findings. As with regard to hydrochemical and hydrological studies, the theoretical factors derived and physical operations affecting the rain water during flowing from source till precipitate, as wall as, the new operation (altering operations) such as the ionic exchange, concentration increase and decrease, reaction between water and dusts. In order to find out the similarity matrix bilateral correlations were used in (R-mode) among variables (Al-Adili,1995; Davis,1973).

(I) Cluster analysis (R-mode):-

The R- mode depended completely on bilateral correlation coefficients among different variables (elements) which disclosed the similarity in hydrochemical behavior of the variables. Likewise the bilateral correlation coefficients would't show clearly

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if that group of variables have similar behavior. The value ($r = \pm 0.4$) for 99% confidence level was taken as a minimum limit for measuring the degree of correlation between clusters of variables. The cluster analysis R-mode for rain water resulted in the appearance of three major groups A, B and C (Fig.1).

This analysis has revealed with three major groups. Group – A, consists of the anions which included in the rain water, group – B, consists the cations and trace elements, as well as total hardness (T.H.). Trace elements in rain water associated with the cations, but with less correlations. Total soluble solids (TSS) correlate with all these in low relation, it could be interpreted and referring that the total soluble solids is sum of cations and anions.

(II) Cluster analysis (Q-mode) :-

The purpose of conducting this mode of analysis was finding out the similarity between samples one or all cases depending on measuring the Euclidean distance. The rate of resemblance among samples increased when the distance became closer and vice versa (Al- Gieali, 1989). This was done by comparing samples with each other depending upon their variables. It was provided in applying this mode, that the

number of these samples was greater than the calculated variables for each sample or at least be equal in number (Aqrabi and Al-Basree 1988). The number of samples in this analysis was amounted to 20 ones of 12 variables (12 elements). Due to numerous number of samples, Q-mode analysis results were classified rain water cases (event samples) into three main groups A, B and C, (fig.-2) thus, this mode assisted us to find out several groups representing the rain water samples.

This analysis mode (Q - mode) showed that group – A, consists of 5 cases (samples) from the analyzed cases, which represents the moderate concentrations of the analyzed components. That is mean, the medium events of contribution to rain water sources. While, group – B, consists with 12 samples (with different degree of correlations). These samples have the lowest concentration of rain water components, and it could be explained as the fresh rain water type with the aerosols origins from the sea water. Nevertheless, the highest salinity and ions concentration are correlated in a group – C, this relationship represents the highest polluted cases (samples) due to different sources such as manufacturing process, fuel gaseous and human activities.

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This type of analysis, concluded the relationships of the analyzed samples depending on their components concentration and their origins at aerosoles .

(III) Factor Analysis (R- Mode) :-

The factor analysis was employed to minimized the great number of correlations among variables and classify them into simple groups finding out new variables in the original findings.

There are several types of factor analysis, but the present study focused on R-Mode for it was employed to find out the different correlations among variables (chemical analysis), it also contributed in understanding the nature of rain water origin and water quality. The values less than (± 0.4) were considered ineffective whether positive or negative on resulting factors. By using this analysis, three principal and important factors were appeared in explaining the results (Table - 8) and they were of eigen values higher than (1) as the eigen value showed the contribution ratio of explaining the variable responding factor (apparent) .

The selected factor should have an eigen value for more than (1). These factors had covered 70.15 % of the total variables of the rain water 1995-1996 year, as the first factor

formed 37.81 % of the total effects. It had been positively affected by TSS - Na - HCO_3 - Cl - Mg - T.H. - K, which showed the quality of rain water present in the study area reflected by the variables above. This factor indicated the source for these ions by the contributions of agricultural and human activities. While, the second factor, represent the total hardness and quality of rain water by covering the T.H. which is measuring of Ca and Mg ions, with effect = 20.24% from the total effects. However, Factor -2 consists Zn ion due to its origin, Ritter and Rinefierd(1983), mentioned that the high value of Zn is conduct from air born pollution, that's why associated with Mg and Ca because the main source of these ions is plant (Hem,1985).

The third factor, affect with 12.1 % from the total effects, it consists sulfate ion and lead with less contribution of iron in this factor, it can be attributed this factor to the effect of fuel and manufacturing factor on the rain water, due to fuel components of SO_4 , pb and Fe .

Councilusions

The results of the study of rain water year 1995-1996 at Baghdad city showed, by comparison with rain water year 1985-1986, appreciable reduction in concentration of both

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cations and anions, and the percent reduction ranging between 28% to 84%. The composition of rain water is determined by the sources of the water vapor, as well as, by ions which are acquired by water (or lost from it) during transport through atmosphere. Moreover, by adopting fractionation factor in this study, to conduct the distribution and contribution of the depletion or addition of ions in rain water and seawater, the results revealed that the sea water have less contribution of all ions concentration than the other sources in the study area, due to the far distance between Baghdad city and the costal (Mediterranean sea), also, the contribution of local activities such as, existed dust and chemicals in air as a gaseous which believed are the main sources of ions in rain water. However, the comparison of the concentrations of cations and anions with those in unpolluted fresh water indicate, that, generally, all ions are located within an excepted range of fresh water.

The results of the chemical analysis were dealt with statistically by using cluster and factor analysis. Cluster analysis, R –

mode showed 3 major groups, the first group (group – A), consists of the anions (with good correlations), while the major groups (group – B) included cations, trace elements, and total hardness, it could be explained by association of trace elements with cations in rain water. Cluster analysis, Q- mode, also, conduct three major groups of cases (group of samples), each group representing samples (rain water) with low, moderate, and high concentration of analyzed variables. Factor analysis, R – mode, revealed three major factors affecting with 70.15% of the total variables. The highest effected Factor (with 37.81%) representing the quality of rain water at the study area and sources of ions. While, the second factor effected with 20.24%, and can be interpreted as the plant contribution as a major source for the rain water. The last factor (with less effect = 12.1%) attributed this factor to fuel and manufacturing processing as consists of SO_4 , pb, and Fe variables, which means the contribution of those ions at rain water in urban areas.

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Table-1: Hydrochemical analysis of rain water at Baghdad city .

Var. TSS	T.H.	SO ₄	Cl	HCO ₃	Ca	Mg	Na	K	Pb	ZN	Fe
Date	(ppm)	(ppm)	epm	epm	epm	epm	epm	epm	(ppm)	(ppm)	(ppm)
Nov./95 447	2.2	2.10	3.50	1.73	.66	4.50	.87	.070	.030	.020	.020
Dec./95 84	1.2	1.60	.60	.77	.70	.50	.52	.055	.030	.019	.020
Dec./95 75	1.3	.560	.70	.61	1.00	.30	.01	.055	.030	.019	.020
Dec./95 96	1.8	.400	.70	.77	1.09	.70	.01	.055	.029	.018	.019
Dec./95 177	1.0	2.40	.40	.52	.71	.30	.10	.055	.030	.018	.020
Dec./95 131	.60	1.90	.30	.54	.30	.30	.52	.030	.030	.019	.020
Dec./95 101	.70	1.77	.30	.50	.40	.30	.16	.011	.030	.019	.020
Jan./96 66	1.2	.430	.50	.36	.70	.50	.16	.022	.030	.018	.020
Jan./96 145	1.4	1.04	.50	.58	1.00	.40	.26	.030	.030	.019	.019
Jan./96 62	1.1	.340	.50	.41	.70	1.09	.12	.012	.029	.019	.020
Jan./96 116	1.4	.790	.40	.68	.90	.50	.10	.012	.030	.019	.020
Jan./96 74	.90	.450	.40	.26	.30	.60	.16	.026	.029	.019	.020
Feb./96 290	2.2	1.08	1.40	.70	1.70	.50	.84	.016	.030	.018	.020
Feb./96 32	.80	.180	.40	.42	.50	.30	.17	.016	.030	.019	.020
Mar./96 79	.90	1.02	.50	.31	.60	.30	.02	.028	.030	.019	.020
Mar./96 73	1.4	1.02	.60	.45	.90	.50	.01	.005	.030	.019	.020

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Mar./96 95	1.9	1.37	.60	.56	1.50	.40	.68	.040	.029	.018	.019
Apr./96 157	1.7	1.04	.60	.70	1.30	.40	.35	.025	.030	.019	.020
Apr./96 250	1.5	1.27	1.41	.41	2.00	1.02	.01	.005	.030	.019	.020
Apr./96 100	1.6	1.01	.60	.70	1.20	.40	.01	.005	.030	.019	.020

Table-2:- Monthly average results of rain water chemical analysis during the water year 1995-1996 (meq/l) .

Month	K	Na	Mg	Ca	Cl	SO ₄	HCO ₃
Nov.95	0.07	0.869	4.5	0.66	3.5	2.1	1.73
Dec.95	0.0185	0.205	0.4	0.7	0.5	1.35	0.618
Jan.96	0.02	0.16	0.618	0.72	0.46	0.61	0.458
Feb.96	0.016	0.505	0.4	1.1	0.9	0.63	0.56
Mar.96	0.024	0.237	0.4	1.0	0.567	1.137	0.44
Apr.96	0.012	0.123	0.607	1.5	0.87	1.107	0.603

Table-3:-Comparison between average concentration of rain 1985-1986 and rain year 1995-1996 .(meq/l).

Year	K	Na	Mg	Ca	Cl	SO ₄	HCO ₃
1985-86	0.0513	1.637	0.96	2.203	1.493	1.727	1.453
1995-96	0.0287	0.254	0.6905	0.908	0.75	1.061	0.599

Table-4:- Fractionation factors of Baghdad rain water 1995-1996 .

Ions	Sea water mmol/l	Rain water 95-	Fractionation factor F _{Na}
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	(Plummer,1996)	96mmol/l	
Na	485	0.3431	1
K	10.6	0.0292	3.89
Mg	55.1	0.3458	8.87
Ca	10.7	0.43932	58
Cl	566	0.7442	1.86
SO ₄	29.3	0.5312	25.6
HCO ₃	2.4	0.6	353.4

Table-5 :- Concentration in rainwater from sources other than sea water .

Ions	Sea water mmol/l	Rain water 1995-96 (mmol/l)		
		Rain	Seawater	Other source concentration
Na	485	0.3431	0.64	-----
K	10.6	0.0292	0.0139	0.0153
Mg	55.1	0.3458	0.0724	0.2734
Ca	10.7	0.43932	0.0141	0.4253
Cl	566	0.7442	-----	-----
SO ₄	29.3	0.5312	0.0385	0.4927
HCO ₃	2.4	0.6	0.003	0.597

Table-6:- Ranges of concentrations of ions in 1995-1996 rain water and unpolluted fresh water in (mmol / l).

Ions	Concentration of fresh	Average concentration
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	water (mmol / l)	of Rainwater at Baghdad (mmol/l)
Na	0.1 – 2	0.3431
K	0.01 – 0.2	0.0292
Mg	0.05 – 2	0.3458
Ca	0.05 – 5	0.43932
Cl	0.05 – 2	0.7442
SO ₄	0.01 – 5	0.5312
HCO ₃	0 - 5	0.6

Table-7: Correlation coefficients for rain water at Baghdad city

	TSS	T.H.	SO ₄	Cl	HCO ₃	Ca	Mg	Na	K	Pb	Zn	Fe
TSS	1.0											
T.H.	.80	1.0										
SO ₄	.69	.49	1.0									
Cl	.94	.72	.62	1.0								
HCO ₃	.89	.69	.70	.92	1.0							
Ca	-.02	.49	-.06	-.22	-.20	1.0						
Mg	.81	.53	.54	.94	.89	-.46	1.0					
Na	.77	.88	.59	.73	.72	.36	.53	1.0				
K	.71	.73	.63	.76	.79	.11	.61	.85	1.0			
Pb	.28	.03	.26	.20	.30	-.10	.06	.03	.26	1.0		
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Zn	.35	-.14	.32	.46	.54	-.78	.64	-.07	.18	.17	1.0	
Fe	.05	-.29	-.18	.13	.05	-.49	.17	-.20	-.17	.26	.27	1.0

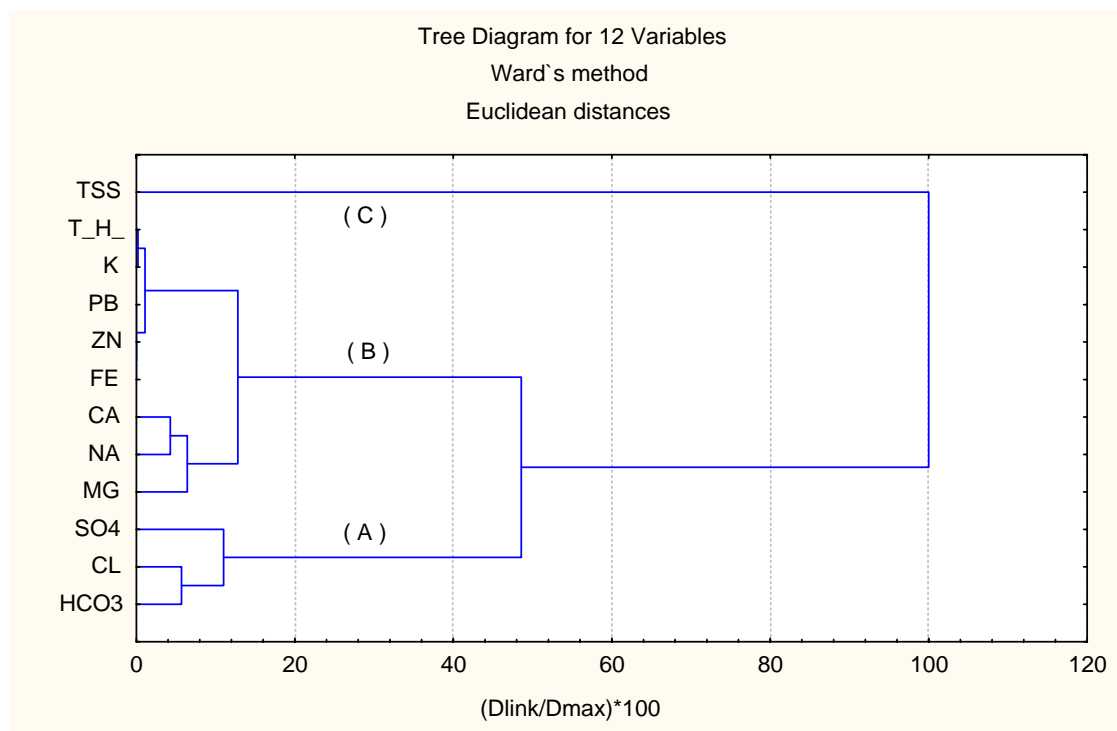


Fig. 1 : Cluster analysis R-mode for the rain water of the study area .

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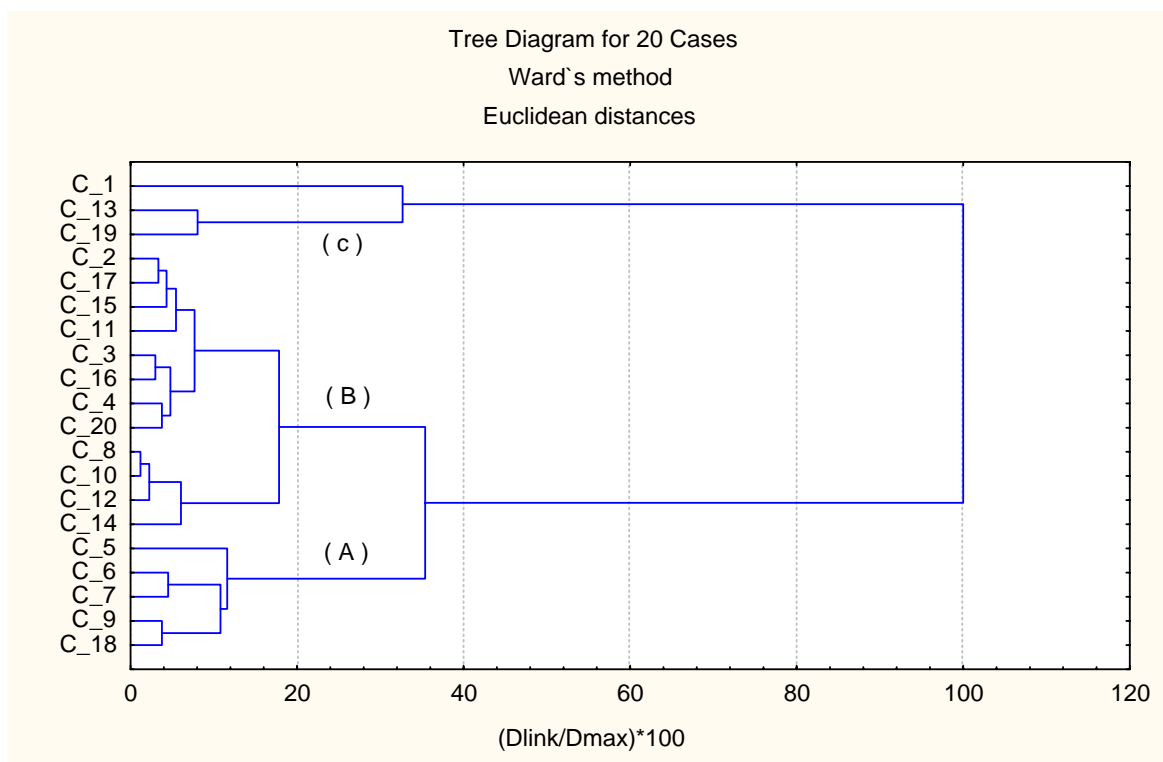


Fig.2 : Cluster analysis Q-mode , for the rain water of the study area.

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Table -8 :- Factor analysis R-mode for rain water

Elements	F1	F2	F3	Communality
Cl	0.953	-----	-----	0.983
Mg	0.854	-0.496	-----	0.979
T.H.	0.823	0.501	-----	0.923
K	0.756	-----	-----	0.863
SO ₄	-----	-----	0.631	0.779
TsS	0.879	-----	-----	0.937
Na	0.780	-----	-----	0.909
Ca	-----	0.832	-----	0.849
HCO ₃	0.866	-----	-----	0.915
Zn	-----	0.613	-----	0.627
Pb	-----	-----	0.667	0.774
Fe	-----	-----	0.413	0.553
Effects %	37.81	20.24	12.1	Total effects= 70.15%
Eigen value	4.53	2.42	1.46	

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