Chemical and Isotopic Content and LMWL of Rainwater in Baghdad/Iraq

Ahmad A. Ramadhan

Petroleum Technology Department -University of Technology-Baghdad-Iraq.

ahmad_2009_61@live.com

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Abstract

Rainwater samples were collected from different areas in Baghdad city of 9 samples for the rainy season 2007-2008, and 14 samples for the rainy season 2008-2009. The objective of this work is to identify the chemical and physical properties as well as isotopes contents of the rainwater, in addition, the LMWL was also carried out for the rainwater in Baghdad city. The results show that the pH was in the range from (5.5-6.44) which is moderately acidic and the TDS was in the range (84-189 ppm). As for cations and anions concentrations, they were in the range of (11.59-28 mg/l) for Sodium, (0.05-1.05 mg/l) for Potassium, (2.2-9.7 mg/l) for Magnesium, (11.22-36.2 mg/l) for calcium, (17.5-39.82 mg/l) for chloride, (18.3-49.57 mg/l) for Bicarbonate and (12.47-38.34 mg/l) for sulfate. On the other hand, the isotopic concentrations of 9 samples of rainwater, which include Deuterium, and Oxygen-18, were determined to be in the range of (-0.79-7.25‰) and (-48.78-18.75‰) respectively. The local meteoric water line for Baghdad city is represented by the following equation: ($^{2}H = 8.538 * {}^{18}O + 26.175$).

Key words: rainwater, chemical, isotopic content.

المحتوى الكيميائي والنظائري لمياه الامطار واعداد الخط المطري في مدينة بغداد/العراق

احمد عبدالله رمضان

قسم تكنولوجيا النفط - الجامعة التكنولوجيا - بغداد - العراق .

الخلاصة

تم التقاط نماذج مياه الامطار من مناطق مختلفة من مدينة بغداد للموسم المطري 2007-2008 وبواقع 9 نماذج والموسم المطري 2008-2009 وبواقع 14 نموذج. الهدف من هذا البحث هو تحديد خواص مياه الامطار الكيميائية والفيزيائية والنظائرية فضلا عن اعداد الخط المطري لمدينة بغداد . كانت النتائج كما ياتي : تراوحت قيم الاس الهيدروجيني (5.5-6.44) وهي خفيفة الحموضة الى متعادلة ومجموع الاملاح الذائبة من (84-189) جزء بالمليون، اما بالنسبة للايونات السالبة والموجبة فقد تراوحت قيم ايون الصوديوم (11.59-28) ملغم/لتر وايون البوتاسيوم (0.05-1.05) ملغم/لتر وايون المغنيسيوم (2.2-9.7) ملغم/لتر وايون الكالسيوم (11.22-36.2) ملغم/لتر وايون الكلوريد (17.5-39.82) ملغم/لتر والبيكاربونات (18.3-49.57) ملغم/لتر وايون الكبريتات (12.47-38.34) ملغم/لتر ، كما تم تحديد المحتوى النظائري لـ(9) عينات لمياه الامطار وتشمل الديتيريوم والاوكسجين-18 ، اذ تراوحت قيم الديتيريوم (-7.25-0.79‰) والاكسجين-18 (-48.78-18.75‰) ، معادلة الخط المطري لمدينة بغداد تتمثل بالمعادلة الاتية ($^{2}H = 8.538 * {}^{18}O + 26.175$) .

الكلمات المفتاحية : مياه الامطار ،كيمياء ، المحتوى النظائري .

Introduction

The rainwater or precipitation is considered as the beginning of hydrological cycle on the terrestrial [1], and the effective parameter in surface and groundwater recharge, where most studies of water resources require water balance to calculate the water surplus available from rainwater. The climate of study area lies within the semi-arid region and effected by Mediterranean climate which characterized by rare rainfall of less than 200 mm.[2]

The importance of determining the physical and chemical properties of the rainwater is considered as the first step in a number of studies of environmental and climatic changes as well as the impacts and air transport of pollutants [3].

The importance of studying isotopes characteristics and its concentrations in rainwater is to verify scientific facts of any study on water resources and other studies dealing with this object, there are two types of using this approach, the first one is radioactive isotope such as Tritium and the second one is stable isotopes such as Deuterium and Oxygen-18 [4].

Rainwater is considered as a good cleaner for atmosphere through removing the suspended dust particles in high layers of air by complex reactions [5]. So the chemical contents of rainwater reflect the amount of dissolved dust from air, and they vary within locations and from rain storm to another. The sources of dust particles in atmosphere come from the sea salt, continental aerosol, biogenic material and anthropogenic release, where these sources are controlling the chemical composition of rainwater by dissolving in rain and giving the chemical content behavior of rainwater [6].

Generally, the physical and chemical contents of rainwater represent the amounts of dissolved solids and particles in the atmosphere, and the chemical composition of rain are changed due to the amount of dust in high layers of air because the fresh vapor from the sea is changed during transition phase from the sources until precipitation. This mechanism of changing in chemical and isotopic content is called fractionation of contents.

The main objective of this work is to put a corner stone in the observation network creation in order to evaluate changing in rainwater quality in Iraq as well as identifying the physical, chemical and isotopic contents to use this data in various studies of water resources management.

Baghdad city lies in the center of Iraq, within the latitude (33º 10′ -33º 29′N) and longitudes (44º 09′- 44º33′E) with an area of about 1350 km^2 [7] and the elevation is about 34 (m a.s.l.). The climate of Baghdad city is mainly arid to semi-arid, in correspondence to Mediterranean climate which affecting the region. According to the meteorological information during the period (1981 – 2000), the annual mean of meteorological data for rainfall is approximately 140 mm, relative humidity is (45 – 46) %, evaporation is about 3300 mm, temperature is 23° C and the wind speed is range of (3 – 3.5) m/sec. [8]

Materials and methods

This study has included two steps which are described as following:

1-Water sampling

Rainwater sampling was done manually by distributing plastic dishes with 90 cm diameter in random locations of the city of Baghdad, those dishes were placed on the roofs at 1 m height from the surface when it starting precipitation. Then they were emptied into plastic containers at the end of rain to avoid the effects of evaporation, later these samples were transported to the laboratory. The use of this method was as an alternative to sampling network which is not available in Baghdad city. The samples were collected during two rainy seasons from location pointed in map shown in figure.1.

a - Nine samples were taken from rainwater during rainy season of (2007-2008).

b - Fourteen samples were taken from rainwater during rainy season (2008-2009).

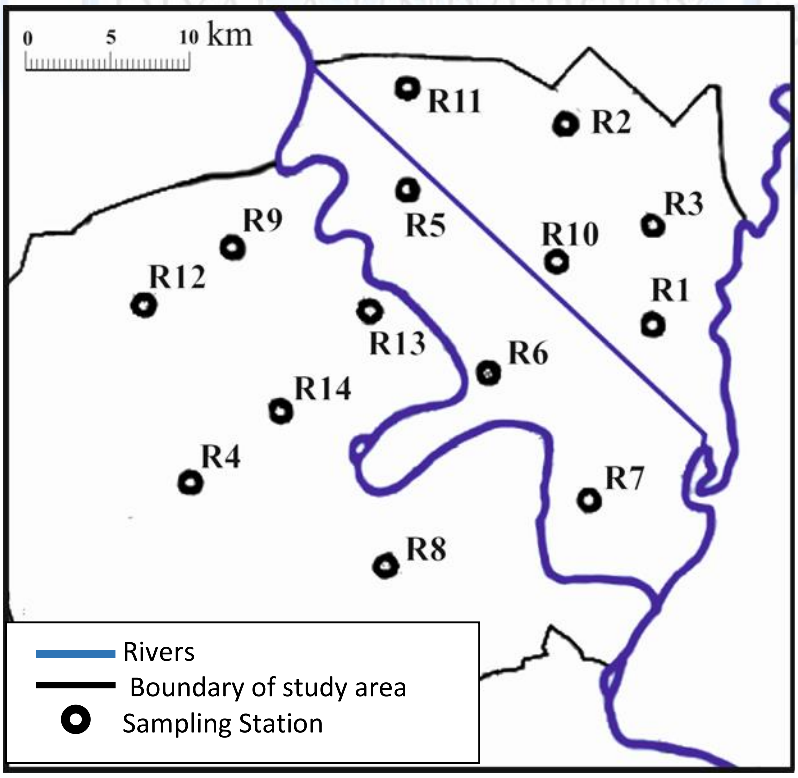

Fig. 1. Location map of study area with sampling points.

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2-Laboratory work

The laboratory work included the analysis of major ions (such as: Na, K, Ca, Mg, Cl, SO_4, HCO_3), in addition to the pH and Ec which were done for (2008-2009) rainy season samples. These analyses were carried out according to the standard methods in the Ministry of Science and Technology laboratories. [9,10]. As for the Isotopic contents were analyzed in the Jordanian Water Authority-Jordan, for the samples of (2007-2008) rainy season. These analyses included the measurements of Deuterium (^2H), and Oxygen-18 (^{18}O).

3-Local Meteoric Later Line (LMWL)

Local meteoric water line (LMWL) is one of important factors in using the environmental isotopes as tracer techniques in surface and groundwater studies [4], the goal of LMWL is to measure the fractionation process which happens on vapor from sources until reaching the rain points on continental area.

The environmental isotopes are considered as a good tracer regarding their properties like, mobile, soluble and not retained by the soil or aquifer materials. That means the tracer should be conservative and easily measurable. [11]

The Oxygen exists naturally in three stable isotopes: ^{16}O, ^{17}O, and ^{18}O. The ratios of their abundances are 99.76%, 0.04% and 0.20%, respectively. So the $^{18}O/^{16}O$ ratios are used because of their higher abundances and the greater mass difference between ^{16}O and ^{18}O. The hydrogen is also existed in nature forming three isotopes: ^1H, ^2H, ^3H, their relative natural abundances are 99.9885%, 0.0115%, respectively. The ^3H is abundance naturally in atmosphere in small amount because of reaction of cosmic rays with gases in the atmosphere layers. The basic determination of isotopic ratios is difficult work, so the result, as a relative isotopic ratios are measured as shown in the equation below. [12]

$$\delta^{18}O = (R_{sample}/R_{standard}-1)x1,000,$$

Where:

$\delta^{18}O$ = relative difference in concentration, in units of parts per thousand.

R_{sample} = $^{18}O/^{16}O$ in the sample.

$R_{standard}$ = $^{18}O/^{16}O$ in the standard.

Generally the fractionation is the change in $^{18}O/^{16}O$ from the sea vapor as a source point to the rainfall, the vapor deals with many processes during the movement just like condensation, temperature and height, which effect on the ratio.

Results

Tables (1) show the results of physical and chemical contents obtained for the samples of rainwater for the (2008-2009) season, while table (2) shows the statistical analysis for the chemical results for (2008-2009) samples. Table (3) shows the isotopic contents results of rainfall samples for the rainy season (2007-2008).

Table (4) shows the accuracy of chemical analysis results for (2008-2009) samples, which are in range of (-1.2% to 5.53%), and those accuracies are acceptable for interpretation. [13]

Table 1: Chemical contents of 2008-2009 samples in mg/l.

Sample No.	location	pH	Ec (µS/cm)	TDS	Na	K	Mg	Ca	Cl	SO_4	HCO_3
R1	Al-Mashtel	6.07	171	166	15	0.66	5.2	32	39	22	36.6
R2	Sadr city	5.87	178	160	22	0.08	6.2	20	35	28	44.4
R3	Ubidy	5.78	190	150	13	0.68	2.4	16	27.6	43	38.3
R4	Ameriya	6.31	185	168	13.5	0.24	2.2	36.2	31	26	33.5
R5	Al-Wazeriya	6.2	145	123	19	0.87	5.1	16	17.5	28	24.5
R6	Al-karrada	5.9	143	120	14	0.55	8.2	12	20.2	23.5	24.4
R7	Al-Zafaraniya	5.75	114	96	20	0.9	3.1	12	19.5	19.4	18.3
R8	Al-Durra	5.8	118	95	18	0.03	6.5	12	22.6	19.9	18.3
R9	Al-Kadhmiya	6.2	190	189	22	0.43	7.5	28.8	29.9	35.2	46.9
R10	Baladiyat	6.6	158	134	28	0.72	6.7	24.8	19.9	17.5	27.8
R11	Al-Shaab	6.6	118	96	12.7	0.43	7.7	11.22	20.4	15.6	24.4
R12	Al-Adil	6.4	155	137	11.9	0.31	4.85	18.02	34.98	22.1	24.4
R13	Shiekh Maaruf	6.43	129	127	14.2	0.63	3.38	24.43	24.98	18.6	27.45
R14	Yarmmok	6.44	149	130	14.7	0.73	9.7	18.02	34.98	22.8	24.4

Table 2: Basic statistics of chemical contents of 2008-2009 samples.

	pH	Ec	TDS	Na	K	Mg	Ca	Cl	SO_4	HCO_3
No. of values	14	14	14	14	14	14	14	14	14	14
Minimum	5.75	114	95	11.9	0.03	2.2	11.2	17.5	15.6	18.3
Maximum	6.6	190	189	28	0.9	9.7	36.2	39	43	46.9
Mean	6.16	153	135	17	0.5	5.6	20.1	26.9	24.4	29.5
Standard deviation	0.30	26.9	28.9	4.6	0.2	2.2	8	7.1	7.3	9

Table 3: Isotopic contents of 2007-2008 samples.

Sample No.	δ O18± 0.15 ‰ vs smow	δ D ± 1.0 ‰ vs smow	D_{excess}
R1	0.79	18.75	17.96
R4	-2.91	9.68	12.59
R5	-2.37	13.56	15.93
R6	-2.87	8.37	11.24
R7	-2.26	14.3	16.56
R8	-2.72	9.07	11.79
R10	-1.82	2.15	3.97
R12	-3.08	3.67	6.75
R13	-7.25	-48.78	41.53

Table 4: Accuracies of results for 2008-2009 samples.

Sample No.	$TDS_{meas.}$	$TDS_{cal.}$	$(TDS_{meas.}-TDS_{cal.}) / (TDS_{meas.}+TDS_{cal}) * 100$
R1	166	150.46	4.910571
R2	160	155.68	1.368477
R3	150	140.98	3.099871
R4	168	142.64	8.163791
R5	123	110.97	5.141684
R6	120	102.85	7.69576
R7	96	93.2	1.479917
R8	95	97.33	-1.21146
R9	189	170.73	5.078811
R10	134	125.42	3.307379
R11	96	92.45	1.88379
R12	137	116.56	8.06121
R13	127	113.67	5.538705
R14	130	125.33	1.829005

Discussion

A-Chemical content

1-pH variation

Samples indicate a pH variation in range of (5.75 - 6.6) while the mean is (6.16) with standard deviation of about (0.3). Generally, natural pH is wildly acidic [14], the pH in this study reflects the acidity characterization because of dissolved the naturally exist gases just like CO_2, NO_2, and SO_4, in addition to the gases released from consumptions.[15] Fig 2-a shows the variation of pH in the study area.

2-TDS and Ec variations

TDS and Ec are very significant parameters describing the chemical constituents of the water [16]. In the present study, the TDS are in the range of (95-189 mg/l) and the Ec (114-190 μS/cm). The variation of values reflects the amount of dissolved dust in rainwater during storm. Fig 2-b, c shows the variation of TDS and Ec in the study area, the noticeable things from the maps that the increasing direction were from the middle of study towards outside the area, that means the area over Tigris river is the lowest concentration and the values are increasing outside. The TDS concentration reflects that rainwater is classified as fresh water, because it is under the upper limit of fresh water which is 1000 mg/l. The relation coefficient between TDS and EC are represent by liner regression equation as shown in figure 3, which reaches about 90%.

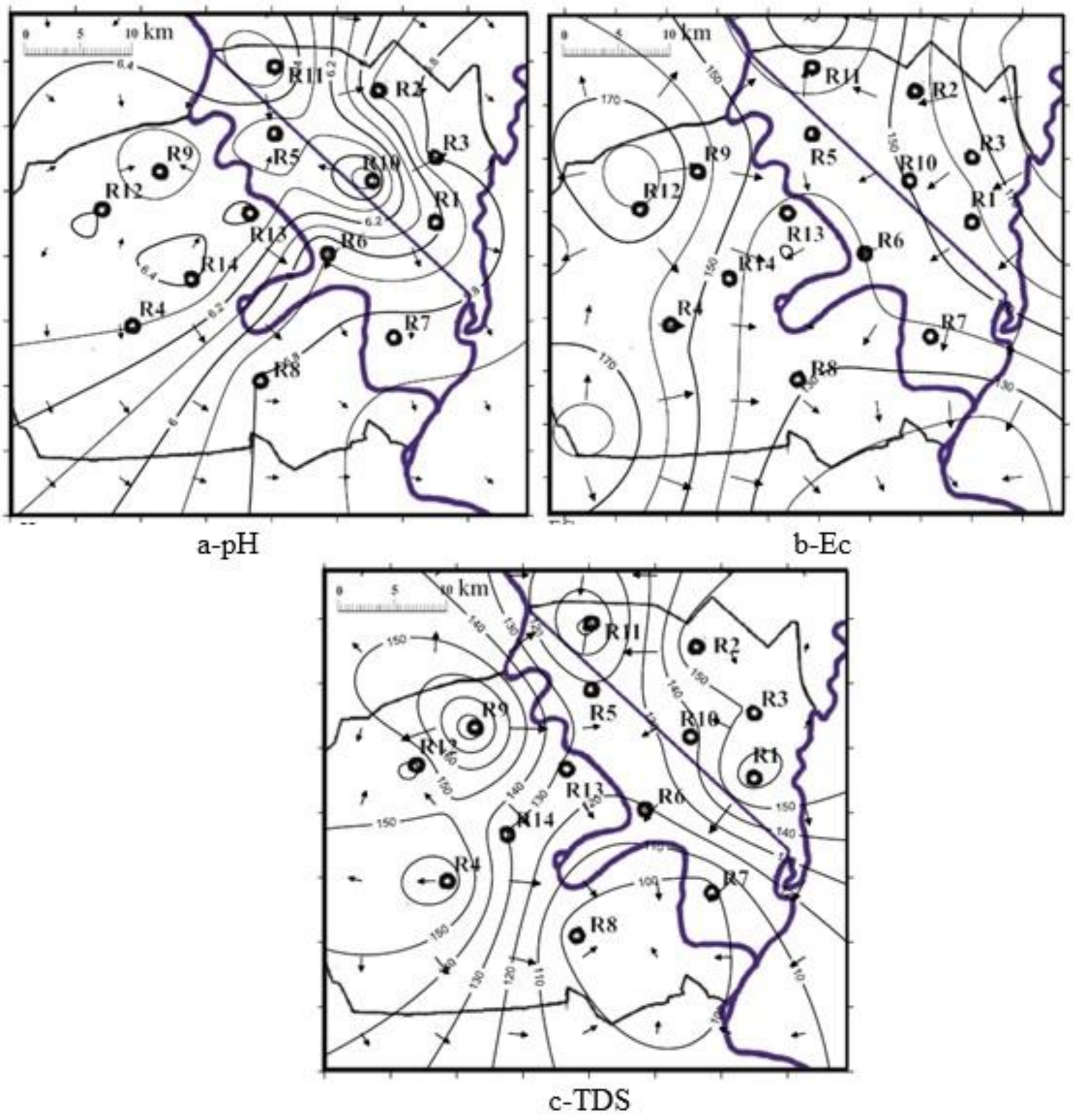


Fig. 2: Physical properties variations of rainwater samples in study area.

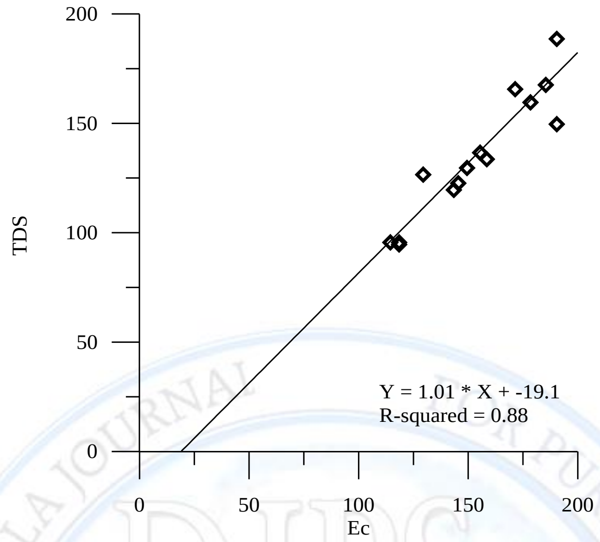


Fig 3: the linear regression relations between TDS (mg/l) and Ec (µS/cm).

3-Major Cations variations (Na, K, Ca, Mg)

The concentrations of sodium were in range of (11.9 to 28 mg/l). The concentrations are within the normal values, and the sources of this cation is from seawater and non-seawater. The concentration of potassium was in range of (0.03 to 0.9 mg/l). The source of the potassium is derived from erosion and geological processes for clay which allow fine grains to be suspended in high layer of air. Fig 4-a, b shows the variation pattern of sodium and potassium.

The concentrations of Mg cations were in range of (2.2 to 9.7 mg/l) and for Ca (11.2 to 36.2 mg/l), the source for these cations comes from geological processes and from human activity such as mining. Fig. 4-c, d shows the variation of Ca and Mg, which refers to be the opposite of sodium and potassium behaviors that the increasing of Mg and Ca cations concentration is to be found in the middle of study area.

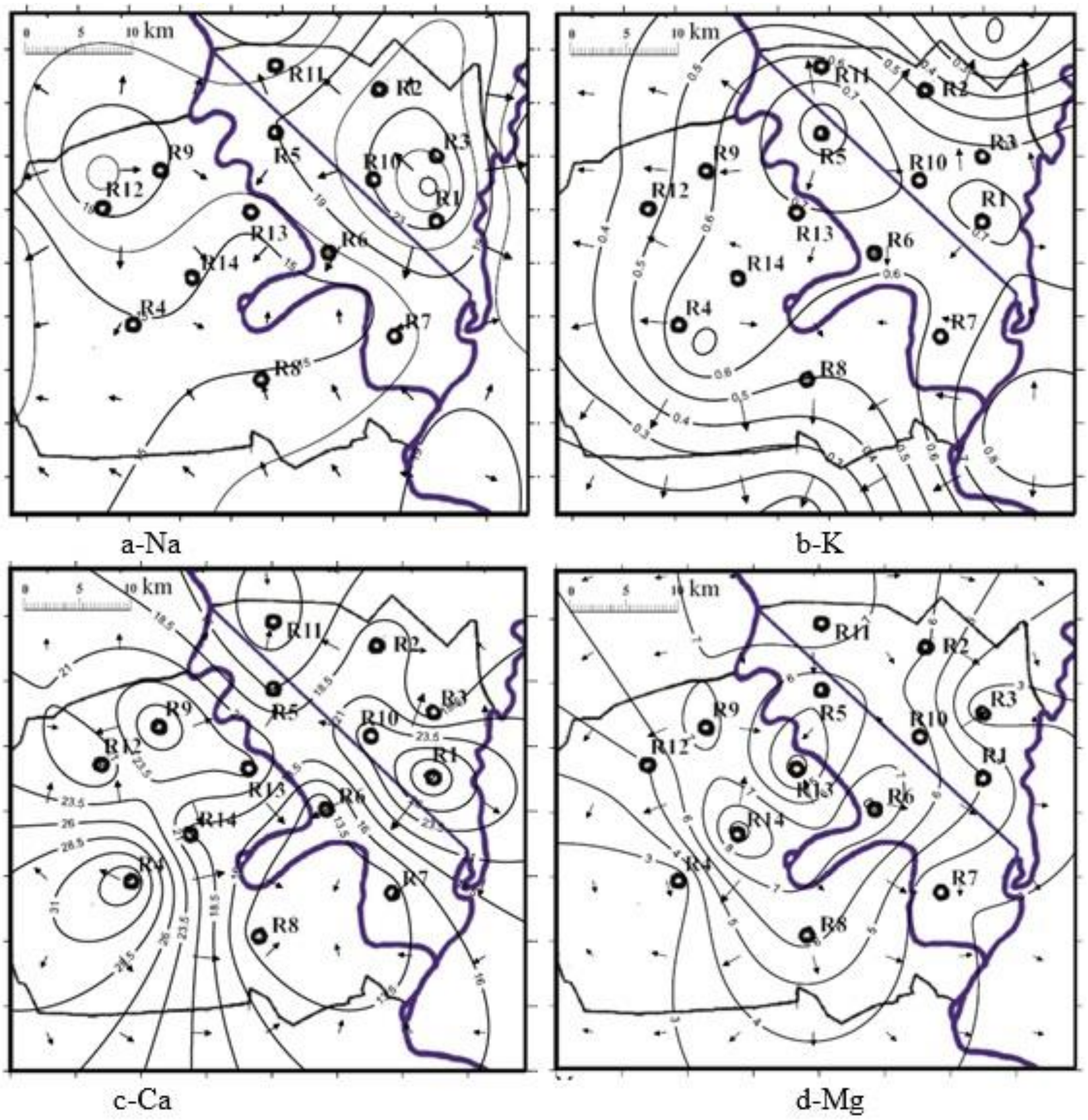
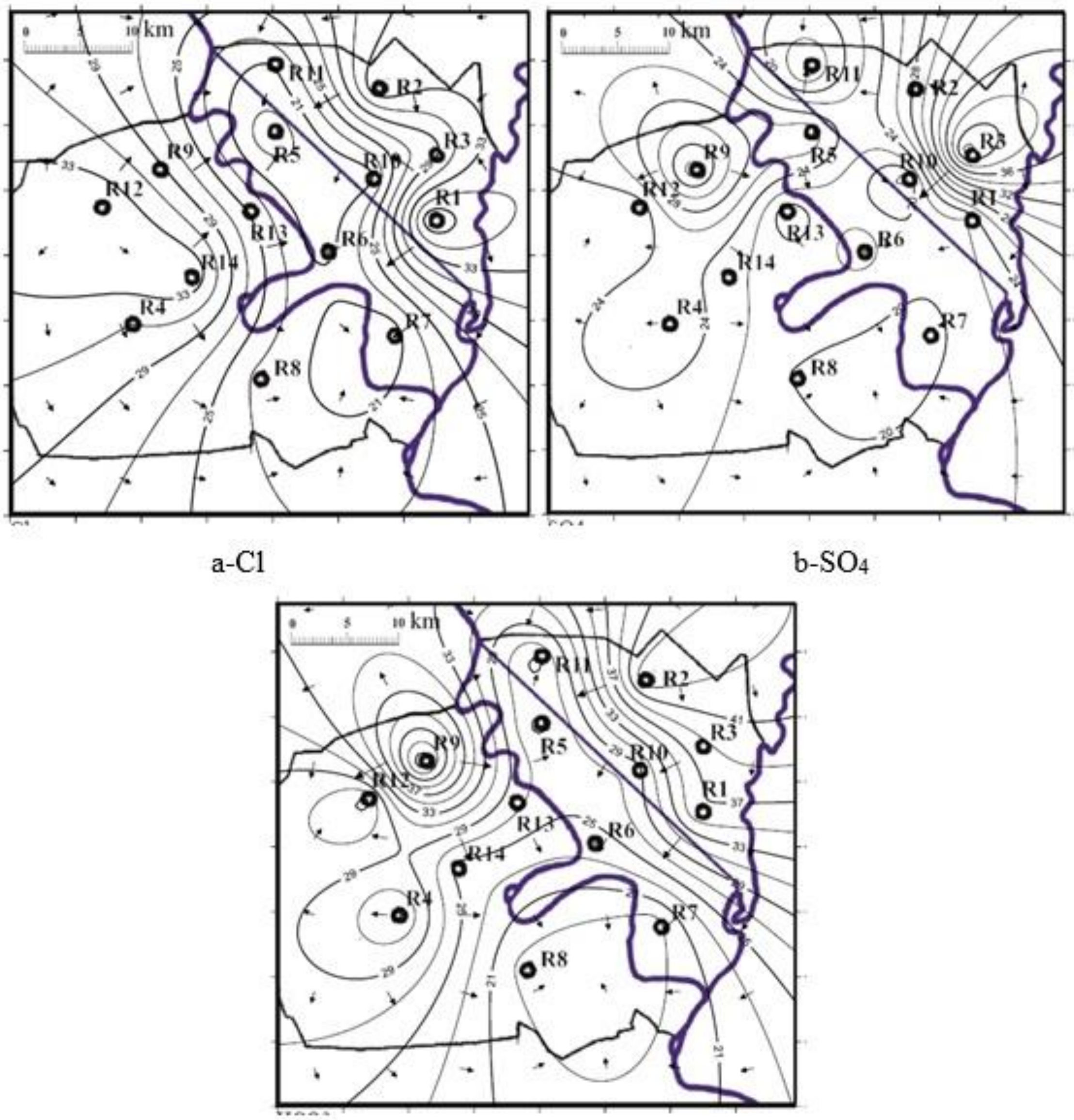


Fig. 4: Cations variations of rainwater samples in study area.

4-Major Anion variations (Cl, SO4, HCO3)

The concentrations of Cl, SO_4, and HCO_3 are in range of (17.5 to 39.82 mg/l), (12.47 to 45.58 mg/l) and (18.3 to 49.57 mg/l) respectively. The source of chloride comes from seawater and non-seawater origin. As for SO_4 and HCO_3, they come from gases released from human activities such as refinery and electricity generators, and natural geological processes. Fig. 5 shows the variation of these anions in the study area.



a-Cl b-SO_4

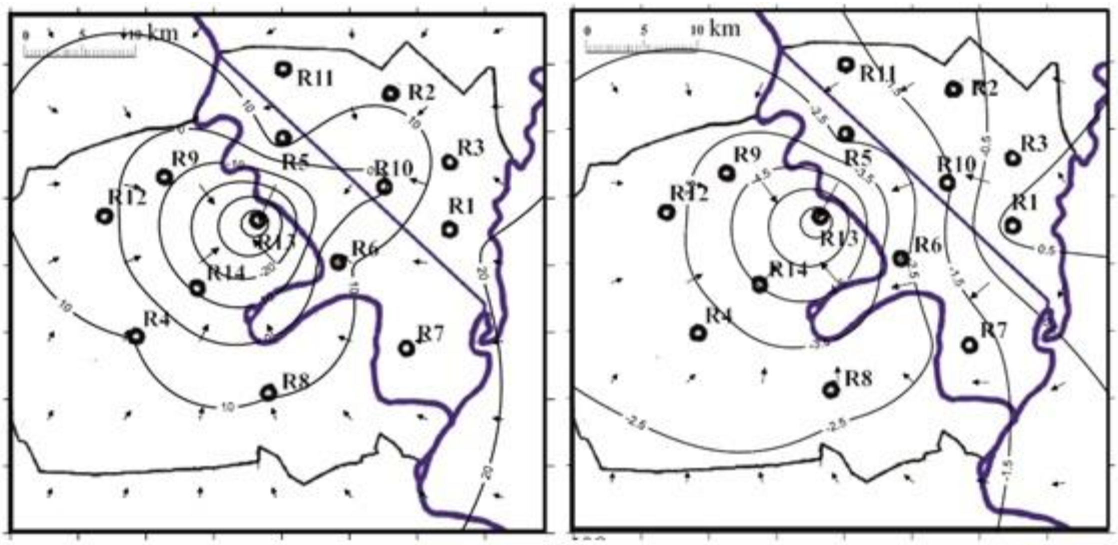
c-HCO_3

Fig. 5: Anions variations of rainwater samples in study area.

B-Isotopes contents

1-Deuterium (^{2}H) and Oxygen-18 (^{18}O) variations:

These elements represent the stable isotopes of Hydrogen and Oxygen respectively. They are in range of (-7.25‰ to 0.79‰) for Deuterium and (-48.7‰ to 18.75‰) for Oxygen-18. Fig. 6-a, b shows the variation of Deuterium and Oxygen-18 in the study area.



a-^{2}H b-^{18}O

Fig. 6: Isotopes contents variations of rainwater samples in study area.

2-Local Meteoric Water Line (LMWL)

Table 4 shows the values of deuterium and oxygen-18, the values of ^{2}H and ^{18}O reflect the all process and fractionation on its content happen from the sources until it rains in Baghdad. The deuterium access is represented by linear regression which is known as meteoric water line (MWL). Craig, 1961 carried out the global meteoric water line. The global Deuterium access was 10, according to the equation ($\delta^{2}H = 8 * \delta^{18}O + 10$) [17]. Dansgrad, 1972 give the Mediterranean meteoric water line in the equation ($\delta^{2}H=8* \delta^{18}O + 22$) [18]. Fig. 7 shows the linear regression of stable isotopes data (^{2}H and ^{18}O) in present study.

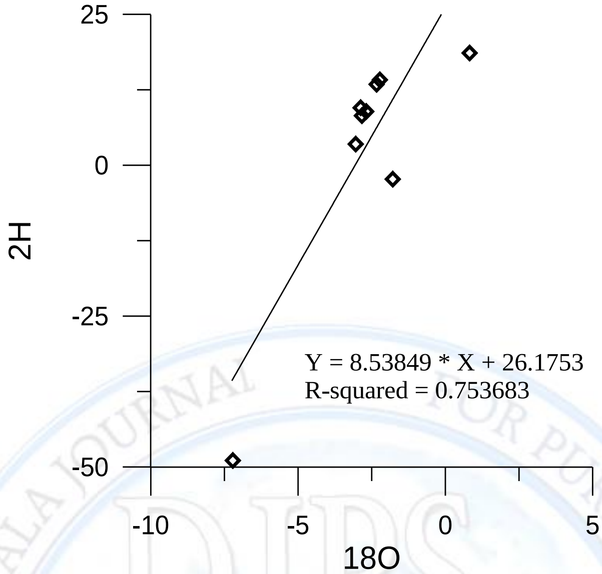


Fig. 7: Linear regression of ^{2}H and ^{18}O (LMWL) for Baghdad in this study.

The previous studies to identified the meteoric water line in Iraq have only been started recently, Mawlood, 2003 [19] studied the Erbil-Hajji Omaran meteoric line in the northern part of Iraq which was represented by **(δ^{2}H= 8 δ^{18}O + 20).** Ali, in 2012 [7] studied the local meteoric water line in Baghdad and was represented by (**δ^{2}H = 8.6 δ^{18}O + 17.48)**, and Al-Barwany, in 2013 [20] described the rainwater sampling collected from 18 station which covered Iraq areas and presented the following equation **(δ^{2}H =7.573δ^{18}O+13.82)** .

All these equations have slope value of about 8 and different intercept values. The intercept values refer to the depletion in deuterium access due to variation in environmental factors that affect the value of deuterium access. In Ali's work, 2012, sampling of rainwater depended only on one station in Baghdad at deferent times, so it refers to temporal variation. Whereas in this work the method of sampling depended on several stations distributed in Baghdad and have samples at the same time so the study concerns with the spatial variations in deuterium access.

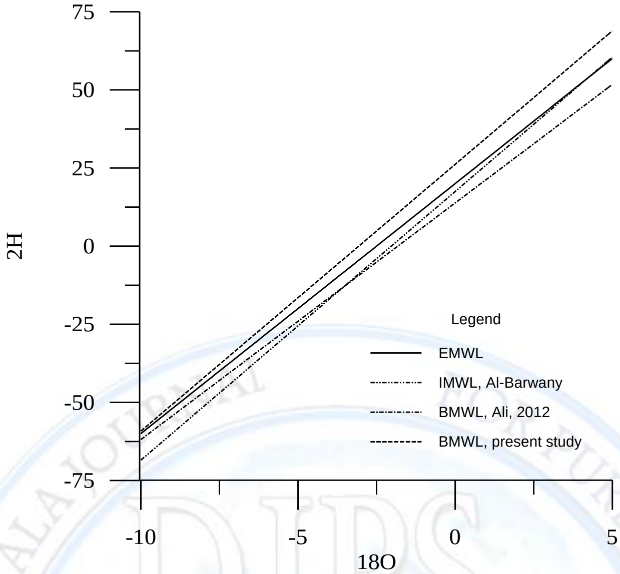


Fig. 8: comparison of baghdad LMWL in this study with the previous study

The equation for deuterium access for Baghdad in this study is described as ($\delta^2H = 8.538 * \delta^{18}O + 26.175$) which reflects the high deuterium access. The value of deuterium access reflects the effect of rising air temperature parameter.

The variation between local meteoric water line in Baghdad with global and local lines in surrounding regions shown in table 5. which clearifies that the local meteoric line of Baghdad is close to the Meditrrranean line, that refers to the same origin of vapor but that variation in distance from the source point which is the Mediterranean Sea, the fractionation of oxygen isotopes are reflecting the evaporation process due to rise of temperture degrees in baghdad.

Table 5: Meteoric water lines for global and local surrounding areas.

Meteoric water line	Correlation equation	Reference
Global meteoric water	$^2H = 8.13 * {}^{18}O + 10.8$	Craig, 1961 [17]
Mediterranean meteoric water	$^2H = 8 * {}^{18}O + 22$	Dansgrad, 1971 [18]
Baghdad meteoric water	$^2H = 8.538 * {}^{18}O + 26.175$	Present study
Tehran meteoric water	$^2H = 6.46 * {}^{18}O + 0.24$	IAEA data base
Lebanese Meteoric water	$^2H = 7.13 * {}^{18}O + 15.98$	Saad, et al., 2005 [21]

Conclusion

Rainwater chemical content and its variation in Baghdad city have been identified for 2008-2009 rainy season in addition to isotopic content for 2007-2008 rainy season. The study includes the pH, Ec and TDS in addition to major ions concentrations as described in tables 1,2. All the chemical cationes and aniones are in the limites of fresh water and the variations depend on the amount of areosoles dissolving and gases in the air from natural and humman acitivities.

The isotopic content reflects the depleted ^{18}O, because of many factors, such as the far away form sources and evaporation due to high temperature of air. The local meteoric water line for Baghdad city indicate the effect of rising air temperature. The compareson between LMWL with other results such as Ali, 2012 reflected the difference in sampling pattern.

Finally, a sampling network is recommended to be established for Iraq to set up a database to be used in diffirent studies of environmental effecs on rainwater composition and to identify the changing pattern with high accuracy.

References

1. Lev S. Kuchment, (2004), “The hydrological cycle and human impact on it, in water resources management”, [Eds. Arjen Y. Hoekstra, and Hubert H.G. Savenije], in Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net].

2. Frenken, K., 2009, “Irrigation in the Middle East region in figures AQUASTAT Survey – 2008”, Food and Agriculture Organization of United Nations (FAO), Rome, Italy,

3. Berner, E.K., and Berner, R.A., (1987), “The Global Water Cycle. Geochemistry and Environment”, Prentice-Hall, New York.

4. Clark, I.D. and Fretz, P., (1997), “Environmental Isotopes in hydrogeology”, Lewis publishers, p. 329.

5. Mouli, P.C., Mohan, S.V. and Reddy, S.J., 2005, “Rainwater Chemistry at a Regional Representative Urban Site: Influence of Terrestrial Sources on Ionic Composition”, Atmospheric Environment, 39, 999-1008.

6. Negrel, P., Guerrot, C., and Mellot, R., 2007, “Chemical and strontium isotope characterization of rainwater in france: influence and sources and hydrogeochemical implications”, Isotope and health studies, 43, 179-196.

7. Ali, S.M., 2012, “Hydrogeological environmental assessment of Baghdad area”, unpublished Ph.D. thesis, geology department, science college, Baghdad university, 230p.

8. Al-Basrawi, N.H., Awad, J. H., and Hussain, T. A., 2015, “Evaluation of the Ground Water in Baghdad Governorate / Iraq”, Iraqi Journal of Science, 2015, Vol 56, No.2C, pp: 1708-1718.

9. APHA, 1999, American Public health Association Standard methods of water and Waste water.

10. WHO, 1999, World health organization, Guide Line for drinking water Quality.

11. Geyh, M.A., 2000, “Environmental Isotopes in the Hydrological Cycle Principles and Applications”, Water Resources Programme, Vol. 4 groundwater saturated and unsaturated zone, International Atomic Energy Agency and United Nations Educational, Scientific and Cultural Organization (reprinted with minor corrections), pp. 311-424.

12. Toran, and Laura, 1982, “Isotopes in ground-water investigations”, Ground Water Journal, Vol. 20, No. 6, p. 740–745.

13. Fetter, W.T., 1980, Applied hydrogeology, ed. Chanels, E. Merrill Pub. Co., A Bell and Howell Co., pp. 488.

14. Galloway, J.N., Savoie, D.L., Keene, W.C., and Prospero, J.M., 1993. “The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean”, Atmospheric Environment 27A, 235–250.

15. Charlson, R.J., and Rodhe, H., 1982. Factors controlling the acidity of natural rainwater. Nature 295, 683–685. In Galloway, J.N., Savoie, D.L., Keene, W.C., and Prospero, J.M., 1993. “The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean", Atmospheric Environment 27A, 235–250.

16. Goher, M.E.M., 2002, "Chemical Studies on the Precipitation and Dissolution of Some Chemical Element in Lake Qarun", Ph.D. Thesis, Al-Azhar University, Egypt.

17. Craig, H., 1961, "Isotope variation in meteoric water", Science, 133: 1702-1703.

18. Dansgaard, W., 1964, "Stable isotopes in precipitation", Tellus, 16: 436-468.

19. Al-Manmi, D.A., 2008;Water resources management in Rania area Sulaimaniyah NE- Iraq, Ph.D. thesis, College of Science, University of Baghdad, p225.

20. Al-Barwany, K.B., 2013, , unpublished thesis, Science college, Baghdad University

21. Saad, z., Kazpard, V., El-Samrani, A.G.,and Slim, K., 2005, "Chemical and Isotopic Content of Rainwater in Coastal and Highland Regions in Lebanon", Journal of Environmental Hydrology, Vol. 13, paper 29, p. 11.