

## CHEMICAL COMPOSITION AND SALT LOAD IN RAINWATER OF MOSUL CITY-NINEVEH GOVERNORATE

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### ABSTRACT

The present study reports the chemical composition and atmospheric salt load rainwater of Mosul city/ Nineveh Governorate / Iraq. The sampling were done from October 2012 to March 2013. Twenty six samples were collected and analyzed for pH, ion concentration ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{--}$ ) and electrical conductivity. Total rainwater was 338.55mm. The results show that the volume weighted mean (VWM) pH and electrical conductivity in the rainwater were 6.83 and  $114.22\mu\text{S}\cdot\text{cm}^{-1}$  respectively. Cation and anion concentration took the following order :  $\text{Ca}^{++} > \text{Mg}^{++} > \text{Na}^+ > \text{K}^+$  and  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{--}$ .  $\text{HCO}_3^-$  and  $\text{Ca}^{++}$  contributed 65.3% of the total ions in the rainwater. Equivalent ratios for different ionic components to sodium, revealed higher values in rainwater than that of seawater. This indicates the dominance of non-marine in studied samples. Analyses revealed that loads delivered from the fallen precipitation in the urban city of Mosul was about  $0.1167\text{kg}\text{Cl}^-/\text{m}^3$  of chloride in rainwater which equal numerically to  $395\text{kg}\text{NaCl}\cdot\text{h}^{-1}$  of land.

Keywords: rainwater, conductivity, pH, volume weighted mean, EF.

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### INTRODUCTION

In meteorology, precipitation is any product of the condensation of atmospheric water vapor that falls under gravity (Tolgyessy,1993). The main forms of precipitation include drizzle, rain, sleet, snow, grapple and hail. Precipitation occurs when a local portion of the atmosphere becomes saturated with water vapor, so that the water condenses and precipitates . It is a major component of the water cycle (Nicolae and Cotet,2012) , and it responsible for depositing the fresh water on the planet. Approximately  $505,000\text{ km}^3$  of water falls as precipitation each year;  $398,000\text{ km}^3$  of it over the oceans and  $107,000\text{ km}^3$  over land .The partition of atmospheric water is 0.001% and 0.04% of total and fresh water respectively (Ghassemi,*etal.*,1995). Raindrops have sizes ranging from (0.1-9.0) mm in diameter, above which they tend to break up. The atmospheric water vapor is the most abundant form of pure natural water , however, it becomes polluted when passes through the air layers, and it wash-out considerable quantities of aerosols from air which is the most important sources of continental dust ,salts carried by wind from the surface of seas, surface rivers, volcanic and anthropogenic activities (Radojevic and Bashkin,2006). Apart of these affects on chemical composition of rainfall are varies from region to region, depending on on water content in clouds, quantity and duration of precipitation, size of droplets and intensity of rainfall (Sillapapiromsuk and Chantara,2010). Therefore the processes controlling the composition of rain are complex and influenced by both natural and anthropogenic sources . If the source is influenced by increasing man made activities, the rainwater will become acid because the anthropogenic activities contribute acidic gases like  $\text{SO}_4$  and  $\text{NO}_3$  and basic gases like  $\text{NH}_3$  (Kulshrestha et al.,2003). The aim of this paper is to obtain an initial understanding of rainfall chemistry, including its composition and salt load at an urban locality in the center of Mosul, capital of Nineveh Governorate, due to *non availability* of these data.

## MATERIALS AND METHODS

**Sampling site :** The sampling site located at an urban location in Mosul , the center of Mosul city and provincial capital of Nineveh which lies across the Tigris river on the right side of ancient Nineveh (36°0'N 42°28'E). Mosul has an area of 37,323 square kilometers (14,410 sq mile).

**Sampling and analysis:** Although rainwater analysis may appear to be fairly straightforward, but it is in fact quite problematic because of the low concentrations of ions present . Therefore, great care must be taken during handling, storing and analyzing samples in order to maintain sample integrity from pollution. Rainwater samples were collected continuously after each rainfall from October 2012 to the end of March 2013 using a clean container of 32cm in diameter. The volume of the sample was measured and divided by the cross sectional area of the container to obtain the depth of the atmospheric precipitation. The samples were filtered to remove particulate matter and sediment and rainwater samples were stored in a refrigerator at 4°C until analysis. Each sample was analyzed for pH and conductivity immediately using a conductivity and pH meter (Type : JENWAY 3540 pH & Conductivity meter). Samples were analyzed for cations ( $K^+$ ,  $Mg^{2+}$ ,  $Na^+$  and  $Ca^{2+}$ ) and anions ( $Cl^-$ ,  $HCO_3^-$  and  $SO_4^{2-}$ ) according to methods outlined by (Tandon ,1999). In rainwater surveys, the common practice to calculate the volume weighted mean (VWM) of ionic concentrations rather than the arithmetic average because it takes into account dilution effect by the rainfall amount (Oliveira *et al.*,2012). The VWM can be calculated from:  $VWM\ of\ X = \frac{\sum([X_i] \times R_i)}{\sum R_i}$  . Where  $[X_i]$  is the concentration of substance X ,  $R_i$  is the rainfall amount . To account for rainfall uniformity, precipitation concentration index (PCI) was calculated from:  $PCI = 100 \frac{\sum P_i^2}{P^2}$  , where  $p_i$  = monthly precipitation and  $p$  = annual precipitation. According to Valli *et al.*,(2013),  $PCI < 10$  indicates uniform precipitation and  $PCI > 20$  indicates a strong irregularity (i.e., high precipitation concentration). Enrichment factor (EF) for different ionic components with respect to sodium was also estimated and considered as effective tool to assess the origin of salts in rainwater and was estimated according to (Tiwari *et al.*,2006) by the following equation :

$EF = \frac{[X/Na^+]_{rain\ water}}{[X/Na^+]_{seawater}}$  Where  $[X/Na^+]_{rain}$  and  $[X/Na^+]_{seawater}$  are the mass ratios of ion X relative to sodium in rain and seawater respectively. An EF approaching to unity suggests that the ion is originated from sea-salt (no enriched elements), whereas an EF greater than unity suggests that a significant portion of the ion has origin in a source different than sea-salt (enriched elements).

## RESULTS AND DISCUSSION

**1-Rain quantity :** A total of 26 rainwater samples were collected continuously. The largest number of rainfall along with precipitation depths were observed in January (6) (25, 6.25, 24.38, 37.75, 22.88, 17.75) mm and in February (6) (5.25, 21.88, 7.98, 3.6, 1.5, 18.88)mm followed by November (5) (2.4,5.8,5.9,19, 22.5)mm and December (5) (1.9, 2.9, 10, 13.75, 23.75) mm, March (3) (3.75,22.5 ,4.88)mm and only one rainfall was present in October with a 6.75mm depth. Monthly rainwater during the study period is presented in Figure1. The largest number of monthly events occurred in January with the highest rainfall (134mm) followed by February (59mm), November(55.5mm), December (52.3mm), March (31mm) and October(6.75mm) . The months of April, May, June, July, August and September are considered as dry season. The Precipitation Concentration Index (PCI) value for the urban studied area of Mosul indicate highly irregular distribution of rainfall (24.7%) as outlined by Valli *et al.*,(2013).

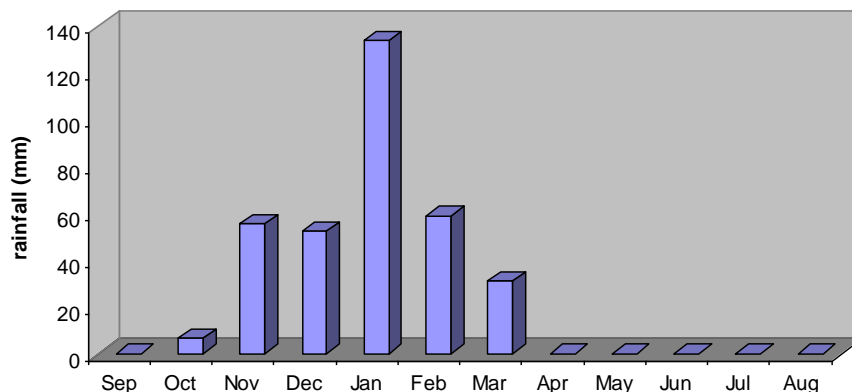


Fig.(1): Monthly variation of rainfall occurrence during the studied period

**2- Variation of pH :** The pH of natural rainwater is controlled by dissolved CO<sub>2</sub> due to the interaction between water droplets and carbon dioxide. It varies between 3 and 9, but generally having ranged between 4 and 6. Rainwater pH is modified by addition of both acidic and alkaline components (Topcu and Atimtay, 2002; Singh and Mondal,2008). Fig.2 shows the temporal variation of volume weighted pH with a mean of 6.5 for the urban city of Mosul which is greater than the pH value of unpolluted rainwater at equilibrium with atmospheric CO<sub>2</sub>. It seems that in the dry month , high amounts of alkaline dust accumulated in the atmosphere due to human activities and low levels of precipitation, accordingly, rain samples collected contain high ionic concentrations, which presented low pH values . Monthly VWM pH were lowest in January (6.21) and highest in March (7.66). Alkaline rainwater has been reported in different parts of the world . In India ,Chandra *et al.*, (2005) reported an alkaline VWM pH (6.78).In another study, in the urban area of Ankara, Turkey, reported alkaline pH values due to high calcium carbonate loading from soil (Topcu *et al.*,2002).

**3- Electrical conductivity measurements:** The EC of rainwater is mainly attributed to the total soluble ionic components present in the rainwater samples which reflect the impact of atmospheric particulate matter on the rainwater chemistry. The mean of electrical conductivity values were  $152.1 \pm 126.4 \mu\text{S} \cdot \text{cm}^{-1}$ . The results showed higher dispersion around their mean values according to the standard deviation. Depending on rain event basis, EC values ranged from  $5.16\text{-}600 \mu\text{S} \cdot \text{cm}^{-1}$  for all the rainwater samples and from  $91.3\text{-}300 \mu\text{S} \cdot \text{m}^{-1}$  on a monthly basis. For calculating VWM of the EC values, it must first converted to concentration (TDS), it was found to be  $114.22 \text{mg} \cdot \text{l}^{-1}$ . Irrespective of rain quantity, March recorded the highest mean EC values whereas the month with the lowest value was October (Fig.3), .In January relying on EC with rain quantity, based on the dilution effect, the amount of precipitation is inversely related to the EC values.

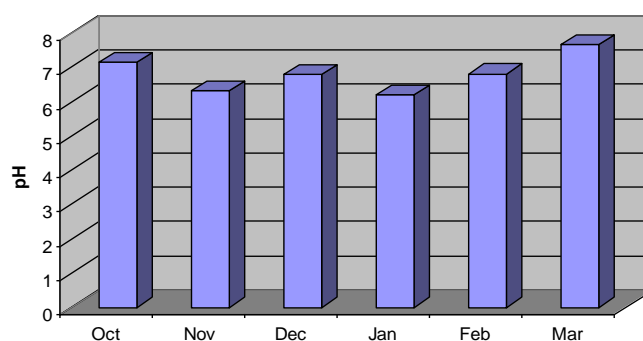


Fig.(2): Monthly volume weighted mean of pH

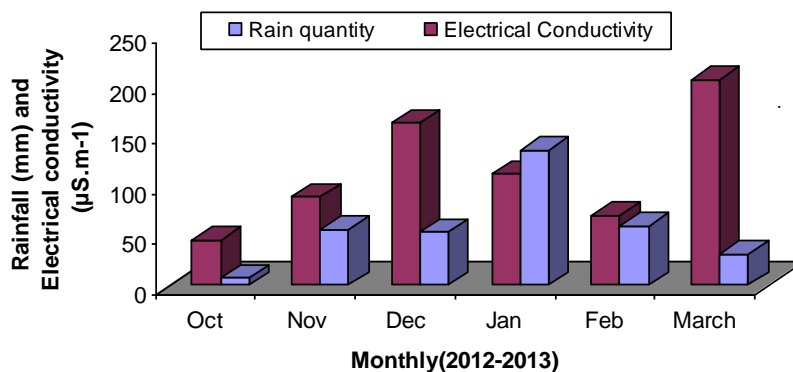


Fig.(3):Variation in monthly precipitation amount and VWM of electrical conductivity

**4- Ionic composition of rainwater:** Table(1) shows the mean, minimum and maximum values, standard deviation of measured ions and volume weighted mean(VWM) concentration ( $\mu\text{eq/l}$ ) of various chemical constituents of rainwater collected along the studied period. Cation and anion concentration decreased respectively, according to the following sequences:  $\text{Ca}^{++} > \text{Mg}^{++} > \text{Na}^+ > \text{K}^+$  and  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{--}$ . Volume weighted mean concentration of ions take the same order with values ranging from 2800 to 82.5  $\mu\text{eq/l}$  for cations, and from 2800 to 400  $\mu\text{eq/l}$  for anions. Although the study revealed greater variation in monthly mean concentration of major ions in rainwater, but the higher concentration of chemical species especially calcium, chloride and bicarbonate were associated with small volume of rainwater and vice versa (Chandra et al., 2005). Figure(4) describes the percentage contribution of each ionic constituent to total ionic mass. Among the anions the dominant species was bicarbonate contributing 70% and 37.7% to the total ionic composition. This was followed by  $\text{Cl}^-$  (8.1%) and sulphate (7.7%). In cation category  $\text{Ca}^{++}$  was dominant contributing 59% of the total cations and 27.6% of the total ionic content in the rainwater samples. This was followed by  $\text{Mg}^{++}$ (16.1%), sodium (2.2%) with very low contribution of  $\text{K}^+$  (0.6%) to the total ionic mass. The alkaline components measured in rainwater were,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$  and  $\text{K}^+$  contribute about 46.6% of the total concentration, where the acidic components comprising of  $\text{SO}_4^{--}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  make up 53.4%. As the soils in Iraq are calcareous and contain between 15-35% calcium carbonate (Anonymous,1977), therefore, the presence of both  $\text{HCO}_3^-$  and  $\text{Ca}^{++}$  in the precipitation are natural and act as sources of carbonate-rich soil/dust particles and were responsible for 65.3% of the total ions in the rainwater. The elevated levels of dust storms in Mosul in recent years due to desertification caused by shortage of precipitation led to re-suspending dust from soil into the atmosphere and the intensive building activities involving the use of cement within the urban city of Mosul.

Table (1): pH and major ion chemistry( $\mu\text{eq/L}$ ) (volume weighted) of rainwater over

Parameter	Min	Max	Mean $\pm$ SD	VWM
pH	6.21	7.66	7.01 $\pm$ 0.53	6.83
$\text{Na}^+$	9.5	188.05	100.6 $\pm$ 61.01	90.9
$\text{K}^+$	5.8	82.50	33.6 $\pm$ 29.43	26.1
$\text{Ca}^{++}$	499.4	2800	1390 $\pm$ 794.0	1132.5
$\text{Mg}^{++}$	229.8	1486.3	673.2 $\pm$ 448.7	659.4
$\text{Cl}^-$	285.6	400	332.3 $\pm$ 319.1	333.0
$\text{SO}_4^{--}$	42.7	904.8	350.6 $\pm$ 337.7	316.6
$\text{HCO}_3^-$	907	2800	1689 $\pm$ 670.0	1545.1

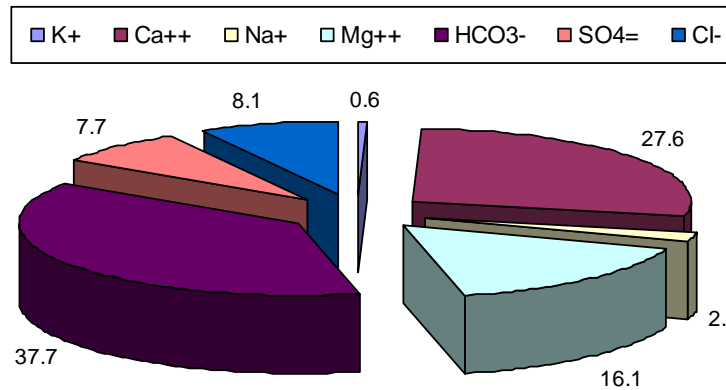


Fig.(4): Percentage contribution of each ion to total ionic mass

**5- Marine contribution and salt load:** Equivalents ratios for different ionic components like Cl<sup>-</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>=</sup> were calculated with respect to sodium by considering sodium completely from marine origin and shown in Table (2). Ratios of major sea salt components are almost constant in the seawater (Keene et al., 1986). Comparison among them reveals that ratio in rainwater are found to be higher than that of seawater values which indicates the dominance of non-marine contribution to the studied components. Results for EF shown in Table(2) revealed that all ion species were enriched which confirmed that other sources than marine mainly anthropogenic sources contributed to their levels in rainwater . As for salt load, it is possible to calculate the loads of chloride ions which reaches the land and falls on any particular area by assessing the concentration of Cl<sup>-</sup>(mg/l) in any particular sample and the amount of rainfall (mm). Analyses of the present data shows that loads delivered from the fallen precipitation in the urban city of Mosul was about 0.1167kg Cl<sup>-</sup>.m<sup>-3</sup> in rainwater delivered which equal numerically to 395kg NaCl.h<sup>-1</sup> of land .

Table (2): Equivalent concentration of ionic components with respect to sodium

Water type	Concentration ratio					
	Cl <sup>-</sup> /Na <sup>+</sup>	Ca <sup>++</sup> /Na <sup>+</sup>	Mg <sup>++</sup> /Na <sup>+</sup>	K <sup>+</sup> /Na <sup>+</sup>	SO <sub>4</sub> <sup>=</sup> /Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup> /Na <sup>+</sup>
Rainwater	3.700	12.500	7.300	0.300	3.500	16.900
Seawater	1.160	0.044	0.227	0.021	0.120	0.005
EF*	3.190	284.100	32.160	14.290	29.170	3380.000

\* Enrichment Factor .

### التركيب الكيميائي والحمل الملحي لمياه الأمطار في مدينة الموصل / محافظة نينوى / العراق

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### الخلاصة

الدراسة الحالية تبين التركيب الكيميائي والحمل الملحي لمياه الأمطار في محافظة نينوى. تم جمع النماذج خلال الفترة من شهر تشرين الأول 2012 ولغاية آذار 2013 وبواقع 26 نموذج وحللت بقصد التعرف على رقم التفاعل وتركيز الايونات الذائبة الرئيسية (SO<sub>4</sub><sup>=</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>) والايصالية الكهربائية الكلية للأمطار الساقطة في مركز المحافظة كان 338.55 ملم. بينت النتائج أن معدل الوزن الحجمي (VWM) لكل من درجة

التفاعل والتوصيل الكهربائي كانت 6.83 و 114.22 مايكروسيمنز/سم بالتعاقب. تركيز الكاتيونات والانيونات انخفضت حسب التدرج التالي: الكالسيوم < المغنيسيوم < الصوديوم < البوتاسيوم والبيكاربونات < الكلوريد < الكبريتات وساهم كل من البيكاربونات والكالسيوم بما مجموعه 65.3% من مجموع الايونات في مياه الأمطار. أظهر حساب النسب المكافئة للايونات الداخلة في تركيب مياه الأمطار نسبة إلى الصوديوم قيم مرتفعة في مياه الأمطار مقارنة مع تركيبة مياه البحر والذي يبين سيادة المكونات غير البحرية في النماذج المدروسة. نتائج حساب الحمل الملحي بينت أن مركز محافظة نينوى يستلم من مياه الأمطار الساقطة حوالي 0.1167 كغم كلوريد.م<sup>3</sup> والذي يعادل 395 كغم كلوريد الصوديوم. هكتار<sup>-1</sup>.

الكلمات الدالة: مياه المطر، الايصالية، رقم التفاعل، معدل الوزن الحجمي، عامل الاغتناء.

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