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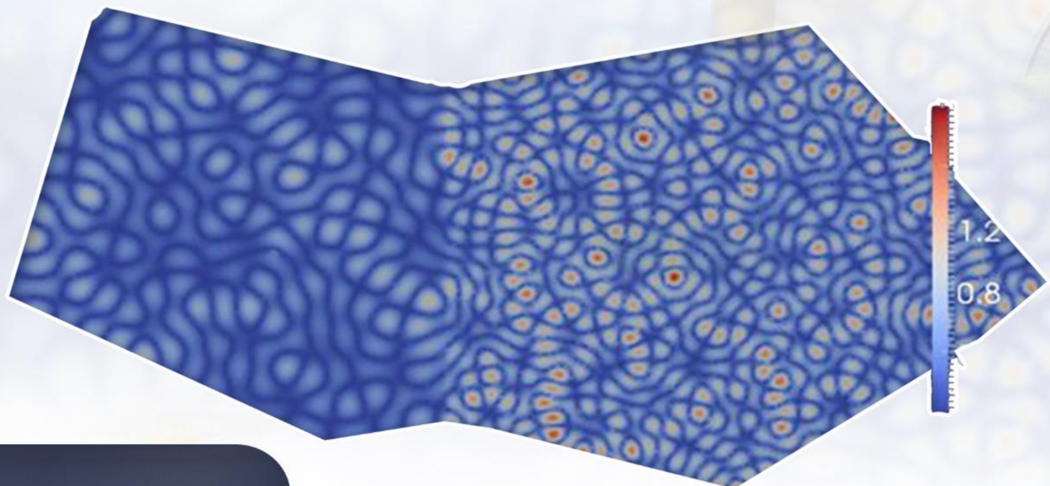

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Some Physico-Chemical Analyses of Groundwater Sources in Al-Marj Region in the North-East of Libya

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A B S T R A C T

The main aims of this study are to evaluate some Physico-chemical quality of groundwater in Al-Marj city in Libya for drinking, domestic and irrigation uses. All results of the measured physical parameters (Temperature, turbidity, and odor) were within the recommended range by Libyan standards, and WHO guideline values but the chloride (Cl) and ammonia (NH3) concentrations in some sites are exceeded the recommended values by Libyan standard. This is indicating that the potential contamination by municipal sewage or agricultural activity.

Most of the groundwater samples were within the recommended value by Libyan standards and WHO guidelines, except one groundwater sample, which was collected from site 6W (sample No.10), in the west direction of Al-Marj city. This groundwater sample recorded the turbidity values 5.85 NTU, and this value was higher than the permissible value by Libyan.

The average results for the physical parameters the average of turbidity results was higher than 3.0 NTU at site 6W (sample No.10), and the rest of the physical parameters of the other sectors, were within the recommended range by the Libyan standards in all other sites.

The results of the chemical parameters were within the Libyan permissible limits, except the Cl^- average levels were higher than the Libyan standard, which were ranged from 256.8 to 372 mg/l in the Eastern and western sectors in the study area. Also, the ammonia was elevated to the Libyan standard in eastern sites which was ranged from 1.66 to 9.72 mg/l.

1 Introduction

For all living creatures including the human being, water is considered as one of their basic needs., Therefore, water is one of the most important and valuable substances on the earth (WHO.,2014; WHO.,2011). Recently, there has been a great increase in the demand for safe drinking water. Although water plays an important role in life due to its essential for human survival, many are denied access to sufficient potable drinking water supply and sufficient water to maintain basic hygiene (WHO., 2011). However, around 71% of the earth's surface is covered by water (B.Nirmala et al ., 2012). The freshest water is available as groundwater in aquifers. Several water resources such as oceans, ice caps, glaciers, groundwater, and lakes, and rivers contained 98.93%, 1.05%, 0.009%, and 0.0001%, respectively (R. M. Harrison, 1995).

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This underground freshwater has been considered as one of the purest forms available in nature to meet the overall demand of household, industrial, recreational, agricultural, and environmental activities (S.C.Izah et al .,2015 ; R.D.Pratima et al ., 2014).

Around the world, 1.5 million people mostly are children, die annually from diarrheal diseases regarding water-related diseases (WHO., 2006). However, approximately 1.1 billion people in

The world relies on unsafe drinking water sources from lakes, rivers, and open wells (An R Lawrence et al., 2001). About 22 African countries, including Malawi, are failed to provide safe and clean drinking water to 50% of their population (T.Kanyerere et al., 2012). This is caused by the drinking and using of water contaminated by faucal matter. In addition, by inadequate sanitation. Naturally occurring chloride ion in water is caused by the dissolving of minerals containing chloride, also, chloride ion comes from sewage and industrial effluents, and fertilizers. (Hale, R.L.,2006)

2 Materials and Methods

2.1 Study Area

The study area was in the Al-Marj region, which is located at Al-Akhder in the eastern north part of Libya, at 32.50 ^{0}N –20.82 ^{0}E; (The General People's Committee, the General Information Authority;2006). It can be seen from Fig (1) and (2) that the huge area of municipal sewage discharge in two side-lakes is as random damping sites in Al-Marj city. These lakes are the main contamination sources in the Eastern sector of this city, and the secondary contamination source in the western sector of this city.

In the study area, groundwater is the main source of water supply for all water uses, therefore, this excessive demand became too much load on the groundwater of this area, and the pure water that comes from the Al-Marj Region desalination plant is not enough for Al-Marj city, and its surrounding area. Therefore, the quantity and quality of this source of groundwater might be changed without a propel control or protection.

A **B**

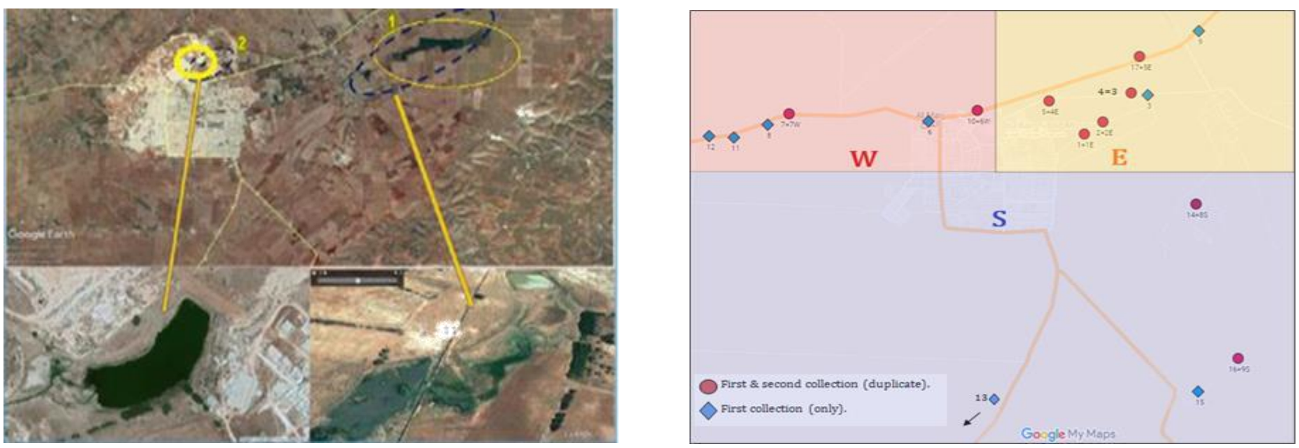


Figure (1) . (A): The huge areas of municipal sewage in the study area. (1) Is the main contamination source, and No (2) is the secondary contamination source. (B): Groundwater sampling locations of the study area. The studied area was divided into three sectors: Eastern(E), Western(W), and Southern(S).

2.2 Groundwater Sampling

Samples of groundwater from the study area were selected to represent the condition of groundwater quality, and ground surface contaminants, especially, municipal sewage effluent. All sampling wells are boreholes with electrical pumps, and the samples were collected twice (Fig.2) from nine sites. The first collection was collected during the dry season (fall 2017), and the second collection (nine samples) was collected from the same wells to assess the wet season in summer 2018. All samples were collected in clean and autoclaved glass bottles and carried over from samples locations to the lab before 24 hours of sampling time.

2.3 Analytical Methods

For Physico-chemicals and, all groundwater samples were collected in cleaned and autoclaved glass bottles, and stored in a cold box, and carried over to the laboratory of the Environmental and Biological Chemistry Research Center (EBCRC). However, ((pH, Electrical Conductivity (EC), Dissolved Oxygen(DO), Total Dissolved Solids(TDS), Ammonia (NH3), Total Hardness(T.H), Alkalinity (Alk), Chloride (Cl^-), Odour and Colour Temperature, and Turbidity) parameters were measured and recorded at the sample point. The quality of groundwater wells is determined by measuring some Physico-chemical parameters of collected samples, by using standard analytical methods for water quality as follow.

2.3.1 Physical Analyses and Chemical Analyses

For physical parameter analyses of groundwater samples, the physical parameters (odor, color, temperature, and turbidity) were measured by using the methods as shown in Table (1). For chemical analysis Table (1) includes the chemical parameters and the methods, which are used to determine the chemical quality of groundwater in this research, and the mathematical calculation for some chemical parameters.

2.3.2 Principals of Used Analytical Methods in this Study:

1. Volumetric Titration, the titration end-point is identified by the development of color resulting from the reaction with an indicator (A Malik et al., 2012; Health Association., 1999).

2. Colorimetric Methods: these are based on measuring the intensity of the color of a colored target chemical or reaction product. The optical absorbance is measured by using light of a suitable wavelength (WHO 2001 Health Association, 1999). Electrometric Methods: Also, the voltages are produced when the electrodes are immersed in a solution or water sample (Health Association., 1999). Nephelometric Method: This method is based on a comparison of the intensity of scattered light by the sample under defined conditions, with the intensity of scattered light by a standard reference suspension under the same conditions. The higher the intensity of scattered light is thehigher in turbidity.

Table (1). A used method for chemical tests of groundwater samples.

Parameter	Method	Instruments apparatus	UNIT
pH	Electrometric	Multi-parameter	-
Total Dissolved Solids (TDS)	Electrometric	Multi-parameter	mg/l
Electrical Conductivity (EC)	Electrometric	Multi-parameter	µS/cm
Dissolved Oxygen (DO)	Electrometric	DO-meter	mg/l
Ammonia (NH3)	Colorimetric	Spectrophotometer DR 2800	mg/l
Total Hardness (T.H)	Titration	Titration by EDTA	mg/l
Alkalinity (Alk)	Titration	Titration by sulphric acid	mg/l
Chloride (Cl-)	Titration	Mohr titration by AgNO3	mg/l
Temperature	Electrometric	Multi-parameter	Celsius (°C)
Turbidity	Dispersion (Nephelometric)	Turbid meter	Nephelo metric Turbidity Unit (NTU)
Odor and Colour	Personal Observation	Look and smell	Good or acceptable/ Bad or unacceptable

3 Results and Discussion

The analytical results for groundwater samples that were collected from the study area in Al-Marj city in two collections are described in this study. For the first collection, nine groundwater samples were collected for analytical purposes, and the results are shown in the following section. The list of nine duplicated (First collection (dry) and Second collection (wet) groundwater samples, which were collected from the study area are shown in Table (2).

Table (2). Numbers of duplicated sampling sites in both collections.

The first collection (dry)	1	2	4	5	17	10	7	14	16
Location of the samples collections	1E*	2E	3E	4E	5E	6W*	7W	8S	9S
The second collection (wet)	1	2	4	5	17	10	7	14	16

E*, East, W*, West and S*, South (Sample locations).

The analytical results for physical, chemical parameters indicators of both (First collection (dry) and Second collection (wet)) collections are described in the following sections.

3.1 First Collection Result

The analytical results for physical, chemical parameters indicators for the collected nine groundwater samples (n=9) are shown in Tables (3).

From the analytical results of physical parameters as shown in Table (3), it can be seen that all results of the measured physical parameters (Temperature, turbidity, and odor), were within the recommended range by Libyan standards, and WHO guideline values (WHO., 2011; Health Association., 1999). Also, the color of all groundwater samples was colorless.

3.1.1 Chemical parameters' Results for the First Collection. (Chloride and Ammonia):

For the chemical parameters the analytical results of the same samples, are shown in Table (3). However, it can be seen that the most results of the measured chemical parameters, were within the permissible limits recommended by Libyan standards (WHO ., 2011 ; Health Association ., 1999). Nevertheless, as shown in Table (3), the chloride and ammonia concentrations in some sites are exceeded the recommended values by Libyan standard. This is indicating that the potential contamination by municipal sewage or agricultural activity.

3.2 Second Collection Results:

The results of the duplicated (First collection (dry) and Second collection (wet) groundwater samples, for physical and chemical parameters of the second collection, are shown respectively in Table (3).

3.2.1 Physical parameters' Results of the Second Collection:

Form physical parameter results as shown in Table (3), it can be seen that most groundwater samples were within the recommended value by Libyan standards and WHO guidelines, except one groundwater sample, which was collected from site 6W (sample No.10), in the west direction of Al-Marj city. This groundwater sample recorded the turbidity value is 5.85 NTU, and this value was higher than the permissible value by Libyan standard, and however, this is related to the presence of microorganisms, which may threaten human health and life. As well, the watercolor of all groundwater samples was colorless.

3.2.2 Chemical parameters' results of the Second Collection:

The results of chemical parameters for the duplicated (First collection (dry) and Second collection (wet)) nine groundwater samples are shown in Table (2). However, the most values of measured chemical parameters value were in the recommended value by Libyan standards, except the chloride concentration levels in groundwater samples numbers (5, 10, and 17) (4E,6W, and 5E) were recorded values of 284, 372 and 265.9 mg/l, respectively, which were higher than the recommended value by Libyan Standards. These three groundwater samples are located in the west and east sections of Al-Marj city near the municipal sewage water damping sites, and these recorded higher concentrations of chloride indicate the influence of municipal sewage water on the groundwater in these sections. Nonetheless, as shown in Table (3) it can be seen that the other chemical parameters' results were within the permitted limit by Libyan standards. This is maybe due to the consequence of dilution of groundwater by rainwater in the wet season, and therefore, this is not meaning these groundwater sources are safe for drinking purposes.In this study, the results of duplicated (First collection (dry) and Second collection (wet)) samples were correlated with each other in order, to give clear data about the contaminated locations of the groundwater sources in Al-Marj city.

Correlation between Physical Parameters' Results of Both Collections

It can be seen from Table (3) that the average temperature and turbidity results were within the permissible range by Libyan standards. But, according to WHO guidelines the most turbidity values go above the permissible limit at <1 NTU.

Correlation bChemical Parameters' Results of both Collections.

The results' averages (mg/l ± SD) for all chemical parameters of the collected groundwater samples for both collections are shown in Table (3) and therefore the correlation of the results between each chemical parameter are as follow:

pH Results Correlation (pH ± SD) between both Collections.

From the correlation results of pH values in groundwater samples of both collections Table (2) that the pH average values in most sites gave a. However, the average pH results were within the acceptable limits recommended by Libyan standard and, it is ranged between 7.0 ± 0.21 to 7.6 ± 0.35.

3.6 TDS Results Correlation (mg/l ± SD) between both Collections.

The total dissolved solids (TDS) generally comprise chloride, consequently, it arises from municipal sewage water contamination and agricultural activities. However, as shown in Figure (2. a) and from Table (3) the TDS results average were ranged between 400 ± 7.07 to 920 ± 41.72 mg/l. However, the groundwater samples from the East and the west sites of Al-Marj city have the higher values of TDS, and however, the average TDS results were giving a strong correlation between both collections. This indicates that the groundwater sources in the east and west of Al-Marj city are contaminated by sewage water, which comes from the damping sites of municipal wastewater in these directions.

The Electric Conductivity of Water Results in Correlation (µs/cm ± SD) between both Collections

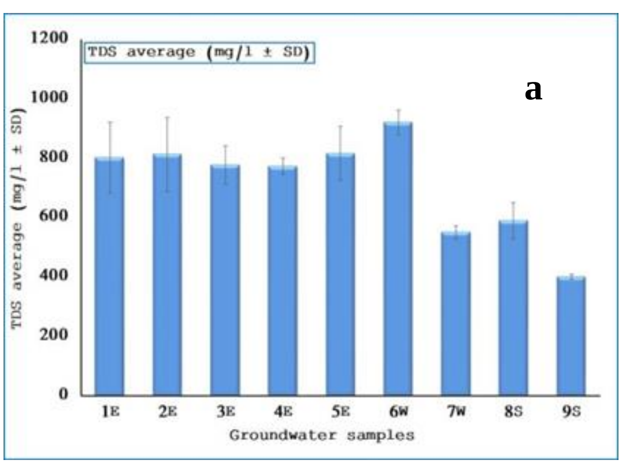
The electric current is conducted through the movement of ions in water, whereas the ions in water are originating from dissolved inorganic matters, hence, are contribute to conductance, and therefore, the EC gives an indication of the concentration of the ions, or the dissolved salts (TDS) in the water, mainly chloride ion. In this study, the average of EC results is shown in Figure (2. a) and from Table (3). The EC averages were ranged between 848 ± 52.8 to 1870 ± 126.1 µs/cm, whereas the values of sites which are located around the municipal wastewater damping sites are higher than other sites. Moreover, the EC concentrations' averages in groundwater gave a very strong correlation between both collections. Therefore, these EC and TDS results are indicating that the contaminated sites in the east and west of Al-Marj city are due to the municipal wastewater damping sites.

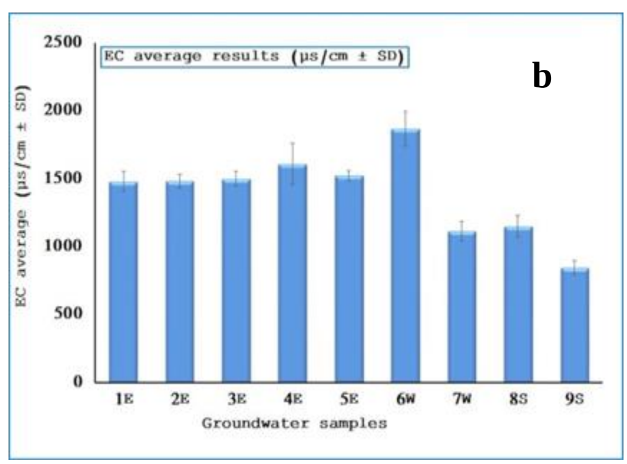
Chloride Ion Results Correlation (mg/l ± SD) between both Collections

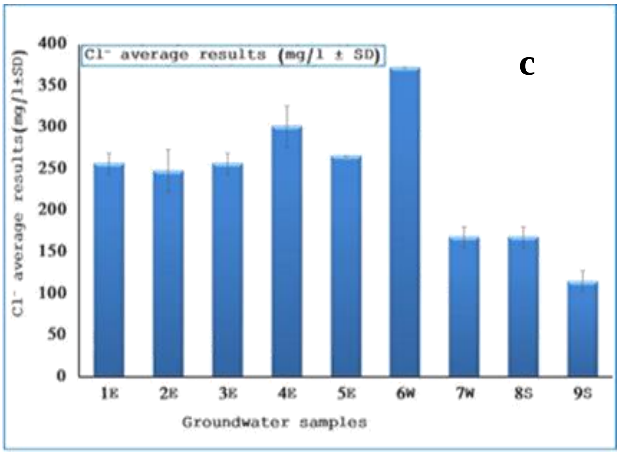
chloride is a significant indicator of water contamination by sewage, consequently, to microbiological [25] contaminations. However, it can be concluded from Figure (2. c), and Table (3) the averages of Cl- ion concentrations in groundwater samples in five duplicated samples from east and west sites near the municipal sewage damping zones, were exceeded the Libyan standard limit of chloride (250 mg/l) and between 115 ± 12.5 to 372 ± 0.4 mg/l. These levels of Cl- concentrations gave a strong correlation in both seasons. Furthermore, the higher averages of Cl- ion concentrations were recorded in groundwater sample sites near the contaminated areas in the east and west directions. This result is indicating to reaching of municipal sewage to the groundwater in the vicinity areas of the contamination sources.

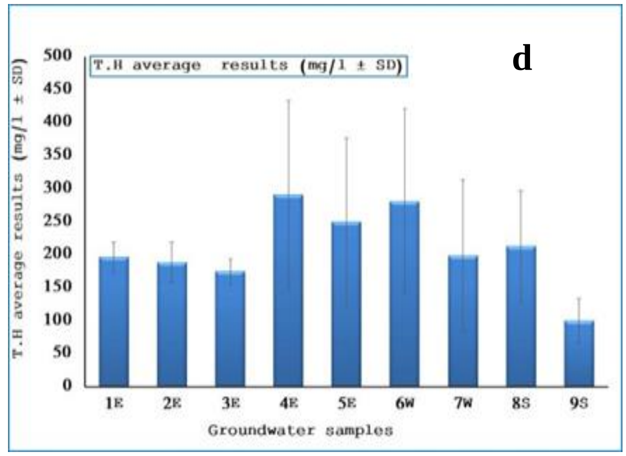
Ammonia Results Correlation (NH_3-N mg/l ± SD) between both Collections

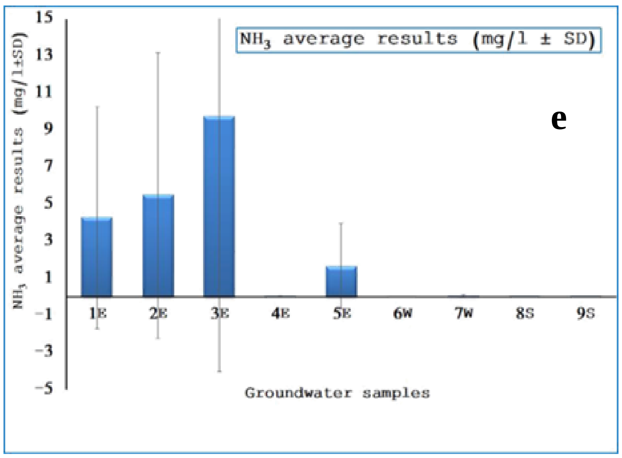
The high concentrations of ammonia are rarely in groundwater in nature, and if it is found at concentrations above 0.1 mg/l as N that indicates an unnatural source of ammonia such as sewage or industrial contamination [24]. As shown in Figure (4. e) and Table (3) it can be seen that the NH_3 levels are exceeded the recommended limit value by Libyan standard in most groundwater sampling sites in the study area, especially which are located in the east direction of Al-Marj city (at Al-Marj old city) around the municipal sewage damping site. Also, ammonia averages were ranged between 0.0 ± 0.002 to 9.72 ± 13.8 mg/l, in addition, there is no correlation between both collections. Therefore, the presence of ammonia is a very strong indication of the presence of ammonia in groundwater in the study area is introduced by sewage leaching, consequently, pathogenic microorganisms are expected to be existent.











All Figures (4). (a), (b), (c), (d) and (e) Correlation of results (mg/l ± SD) between both collections. Figures (4). (a): TDS (b): EC, (c): Cl, T.H: (d) and (e): NH3, results (µs/cm ± SD) between both collections.

Table (3). Comparing Chemical parameters' results of the First collection (F) and second collection (S) with Libyan standards and WHO guidelines.

Samples	pH F	pH S	TDS F	TDS S	EC F	EC S	DO F	DO S	Cl F	Cl S	ALK F	ALK S	TH F	TH S	NH3 F	NH3 S
1	7.2	7.3	884	715	1535	1429	1.8	6.4	266	248	115	110	212	180	8.5	0.06
2	7.2	7.3	900	725	1520	1450	2.9	3.2	266	230	154	110	210	166	10.9	0.05
4	6.8	7.1	822	731	1542	1463	1.2	5.2	266	248	120	111	188	161	19.5	0
5	7.1	7.3	791	752	1719	1502	6.4	5.6	319	284	86	118	392	190	0.0	0.05
17	7	7.4	879	750	1553	1500	6.2	1.2	266	266	103	100	340	160	3.3	0.04
10	7.2	7.1	949	890	1959	1781	6.2	5.8	372	372	100	128	380	181	0.0	0
7	7.3	7.4	566	533	1169	1068	6.7	7.1	177	160	94	100	280	118	0.0	0.11
14	7.5	7.6	632	547	1212	1094	6.2	4.2	177	160	75	82	272	154	0.0	0
16	7.3	7.8	395	405	885	811	6.7	5.1	106	124	96	90	76	124	0.0	0.02
Libyan's	8.5-6.5		1000		-		-		250		-		500		1.5	

Conflict of Interest: The authors declare that there are no conflicts of interest.

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