



Research article

Chemical composition of Zamzam water: A comparative study with international standards of drinking water



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ABSTRACT

Studies conducted on the chemical composition of Zamzam water are conflicting especially for arsenic. Therefore, the aim of our study is to study the composition of tap and bottled Zamzam water and to compare its quality according to international guidelines of drinking water. Six Zamzam tap water samples as well as one bottled sample were analyzed according to standard methods (APHA) for their chemical constituents (pH, TDS, Na, K, Mg, Ca, Fe, Cu, Zn, Cd, Pb, Mn, Al, As, Cl⁻, SO₄²⁻, HCO₃⁻ and PO₄³⁻). The results were compared to guidelines of WHO and EPA for quality of drinking water. All analyzed parameters were below the maximum allowable limits (MAL) of WHO and EPA ($p < 0.05$), with the exception of TDS. The average values of TDS (814 mg L⁻¹ in tap zamzam water samples and 812 mg L⁻¹ in bottled sample) were below the MAL of WHO (1000 mg L⁻¹) but exceeded the limit that defined by EPA as a non-enforceable guidelines (500 mg L⁻¹) ($p < 0.05$). Compared to the collected tap zamzam water samples, bottled sample had significantly lower levels of Na, PO₄³⁻ ($p < 0.05$) and Cu ($p < 0.01$). The study concluded that Zamzam water has acceptable chemical composition including arsenic, except for TDS that exceeds the high non-enforceable accepted limit according to EPA.

1. Introduction

The assessment of existing drinking water resources is interesting topic due to their potential health effects [1, 2]. Zamzam water is a holy water that Muslims use for religious and medicinal purposes. Millions of pilgrims drink it and bring it as a gift for their relatives and friends when they return home. Zamzam water, supplied by the well of Zamzam (Figure 1), is available through taps and containers that are distributed in the Masjid Al Haram in Mecca. Zamzam water is also available in bottled form to facilitate air transportation for pilgrims who want to, as the Saudi government has banned the commercial export of Zamzam water [3, 4, 5].

The Zamzam well is about 30.5 m deep with diameter ranges from 1.08 to 2.66 m. The well is now located in ground floor surrounded by glass plates permitting a clear vision of the inside. The water is withdrawn by electrical pumps to become available in the taps distributed in specific areas in the mosque [6].

In 1976, the American Water Resource Association published the first international article about the chemical composition of Zamzam Water. Other studies were also conducted on this topic, and the results were conflicting, especially with regard to arsenic [7, 8, 9, 10]. Shomar found

elevated levels of As, NO₃, Ca and K in Zamzam water samples collected by pilgrims after their return from Mecca [8]. In 2011, BBC news interestingly announced illegal sale of Zamzam drinking water contaminated with arsenic in the UK shops [11]. Conversely, the Saudi geographical survey states that it has a dedicated center (Zamzam Studies and Research Centre) which analyses and monitors the properties of Zamzam well [3]. Alfadul and Khan [9] confirmed that As concentration was within the acceptable range endorsed by different committees. Al-Barakah et al [10] recorded accepted levels of As and NO₃ in Zamzam water samples regarding local and international standards. Nevertheless, scientific studies on Zamzam water are scarce [6]. Therefore, we conducted this study to explore the chemical composition of Zamzam water. chemical constituent. We analyzed Zamzam water samples for their chemical composition (pH, TDS, Na, K, Mg, Ca, Fe, Cu, Zn, Cd, Pb, Mn, Al, As, Cl⁻, SO₄²⁻, HCO₃⁻ and PO₄³⁻) by the American Public Health Association (APHA) standard methods and compared these levels with the maximum allowable levels (MAL) defined by World Health Organization (WHO) and Environmental Protection Agency (EPA). This study might add more evidences about safety of Zamzam water which is consumed by millions of Muslims around the world.

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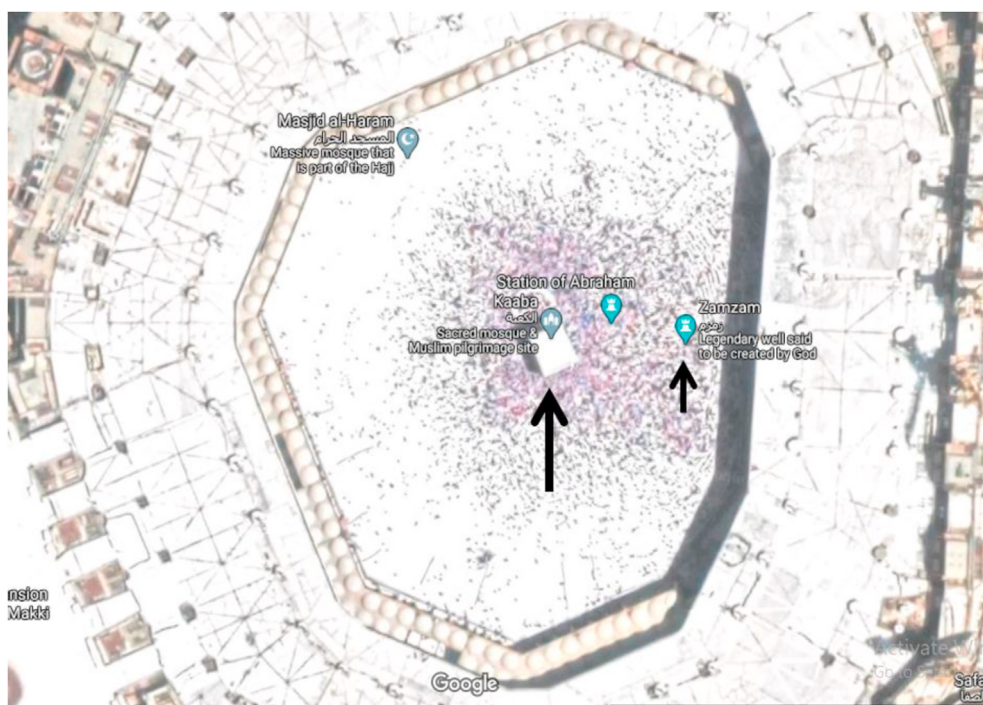


Figure 1. A Google-map view of the Holy Mosque “Masjid al-Haram” showing “Kaaba” (long arrow) and Zamzam well (short arrow).

2. Materials and methods

2.1. Study design

Six Zamzam water samples from taps of Zamzam well in addition to a bottled Zamzam water sample were analyzed for their chemical composition (pH, TDS, Na, K, Mg, Ca, Fe, Cu, Zn, Cd, Pb, Mn, Al, As, Cl^- , SO_4^{2-} , HCO_3^- and PO_4^{3-}). The results were compared to the international standards (WHO and EPA) for drinking water.

2.2. Reagents

Ultrapure deionized water (Millipore S.A., France) was used for preparation of reagents and dilution throughout the work. Chemicals used were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (St. Louis, MO, USA). Before use, glassware was soaked in 5% HNO_3 . It was then washed by tap water followed by deionized water.

2.3. Study area

“Zamzam” a water well in the valley of Abraham, Mecca city, Saudi Arabia, the Arabian Peninsula, Asia. Mecca city is located in the western region of Saudi Arabia and is known by “Masjid al-Haram” which is the sacred Mosque of Muslims. Inside the mosque are “Kaaba” (the holiest place in Islam) and Zamzam well. The latitude and longitude of Zamzam well are $21^\circ 25' 21.5''\text{N}$ and $39^\circ 49' 35.5''\text{E}$, respectively [12] and the well is 310 m above the sea level [13]. Zamzam well is the destination of millions of Muslims every year for its water which is said to be blessed according to the Islamic belief. They drink Zamzam water and bring it to their relatives in their country.

2.4. Sample collection

An authorized 5-liter package of bottled Zamzam water (Figure 2) officially prepared for avian freight was purchased by one of the authors from the authenticated outlet and transported as a separate luggage from Saudi Arabia to Egypt (purchase date: 28/2/2019; batch number: L1 P:



Figure 2. An authorized 5-liter package of bottled Zamzam water.

22/01/19 18:37 B022). In addition, six samples of Zamzam water were directly collected in polyethylene containers during May 2019, from taps of Zamzam well available for pilgrim's drinking at the location of the well (Figure 3). These six samples were collected with responsibility of the other author.



Figure 3. One of the taps at the location of Zamzam well (part of a photo on Google maps website). <https://www.google.com.eg/maps/place/%D8%B2%D9%85%D8%B2%D9%85%E2%80%AD/@21.4225687,39.8265271,3a,84.6y,90t/data=!3m8!1e2!3m6!1sAF1QipOqD1qYPysCyPXTZTmc7Rzkenrn7RZ2T7BBotvK!2e10!3e12!6shttps://2F%2Fh5.googleusercontent.com/2Fp%2FAF1QipOqD1qYPysCyPXTZTmc7Rzkenrn7RZ2T7BBotvK%3Dw203-h114-k-no!7i1280!8i721!4m5!3m4!1s0x15c204b74f16c8cd:0xb70d537a6368b148!8m2!3d21.4225687!4d39.8265271>.

2.5. Sample preparation

After collection, each water sample was filtered through 0.45 μm cellulose acetate membrane and divided into two portions. The first was used for determination of pH, total dissolved salts (TDS) and levels of Cl^- , HCO_3^- , SO_4^{2-} and PO_4^{3-} . The second part was processed for metal ion analysis according to APHA 3005A. Briefly, 200 mL was mixed with 10.0 mL of 5.0 % HNO_3 in a 500 mL conical flask and was gradually heated on a hot plate to near dryness. The residue was diluted and its volume was made up to 10.0 mL by deionized water. All analyses were carried out within a week of collection.

2.6. Sample analysis

All samples were analyzed at the central laboratories of the Egyptian Mineral Resources Authority (EMRA); a subsidiary of the Egyptian

ministry of petroleum and mineral resources. The choice of conducting analysis at these Governmental laboratories was based on their nationally-accredited standards especially in the field of water analysis (equipment-staff). Staff of the analyzing laboratories was blind of the nature of water samples. Therefore, the analyzing laboratories don't bear any legal or ethical consequences due to analysis of water samples in this study.

All measurements were performed according to APHA protocols [14]. The pH was measured by using Metrohm 632 digital pH meter (Metrohm Autolab, Herisau, Switzerland). Total dissolved solid (TDS) was determined by gravimetric method (APHA 2540 C). Major cations (Na, K, Mg and Ca) and trace elements (Fe, Cu, Zn, Cd, Pb, Mn, Al, and As) were determined according to the standard method (APHA 3120) by Inductively Coupled Plasma-Optical Emission Spectrometry (Agilent technologies 720 ICP-OES Series, Santa Clara, CA, USA). Table S1 summarizes the ICP-OES operating parameters along with the instrumental limit of detections (LODs) for the metal ions. ICS-2000 ion chromatograph (Thermo Scientific, Waltham, MA, USA) equipped with Dionex Ion Pac AS 14 column was used for determination of Cl^- and SO_4^{2-} . HCO_3^- was determined by titration procedure according to APHA standard method 2320. Ascorbic acid method (APHA 4500 P-E) was used for determination of PO_4^{3-} . Analysis of standard solutions and samples was performed in triplicate. Data were expressed as Mean $\pm$ standard deviation (SD). ANOVA test was performed to statistically compare data. p value < 0.05 was considered significant.

2.7. Quality control program

The precision of analysis was assessed by calculation of relative standard deviations (RSD). The within run and between run RSD didn't exceed 5.0% for all analyses. Recovery of the analyte from spiked samples was used to evaluate accuracy of the procedure. The recoveries of analytes were in the range of 96.0–102.0%.

3. Results

The concentrations of all analytes along with drinking water standards of WHO and EPA are presented in Table 1. All parameters were within the accepted limits of the international institutions except for TDS that only affect taste of water and has no significant health impacts [15]. The mean values of T.D.S. were 814 and 812 mg L^{-1} in the collected and bottled samples, respectively. These levels exceed the MAL defined by EPA (500 mg L^{-1}) and lower than that assigned by the WHO (1000 mg L^{-1}). On the other hand, As and Cd concentrations in all samples were below the LOD of ICP-OES (3.3 and 0.2 $\mu\text{g L}^{-1}$ for As and Cd, respectively) that are lower than the WHO and EPA standards. This indicates that the concentrations of As and Cd in all analyzed samples are also below MALs of WHO and EPA.

Both collected and bottled Zamzam water samples were compared relative to their chemical analysis. No significant differences were observed ($p > 0.05$) except for Na^+ , Cu^{2+} and PO_4^{3-} . Bottled Zamzam water sample had significantly lower levels of Na^+ , PO_4^{3-} ($p < 0.05$) and Cu^{2+} ($p < 0.01$) compared to the collected samples.

4. Discussion

The study was designed to resolve conflicts about the safety of Zamzam water and give reassurance to millions of Muslims who drink little of it in honor and blessings. The results of the present study pointed that chemical composition of Zamzam water is acceptable according to guidelines of WHO and EPA for drinking water, except for TDS.

Our study showed that arsenic concentrations were below the instrumental detection limit in all Zamzam water samples (bottled and tap-collected samples). Arsenic concentration in Zamzam water had conflicting results in the literature. In his well-designed study, Shomar [8] reported high arsenic levels (average concentration = 27 $\mu\text{g L}^{-1}$) in

Table 1. Chemical analysis of directly-collected and bottled Zamzam water samples compared to WHO and EPA drinking-water standards.

Parameter	Unit	Directly-collected Zamzam water	Bottled Zamzam water	Maximum allowable limits	
				WHO ¹	EPA ²
pH	-	7.65 ± 0.1	7.6 ± 0.1	6.5–9.5	6.5–8.5
T.D.S.	mg L ⁻¹	814.0 ± 13.2	812 ± 14	1000	500
Na	mg L ⁻¹	119.6 ± 17.3	72.5 ± 6.8**	-	-
K	mg L ⁻¹	37.5 ± 4.0	30.8 ± 3.3	-	-
Mg	mg L ⁻¹	20.5 ± 1.7	18.5 ± 1.4	-	-
Ca	mg L ⁻¹	71.5 ± 6.0	74.0 ± 7.3	-	-
Fe	µg L ⁻¹	80.8 ± 5.9	86.5 ± 6.3	300	300
Cu	µg L ⁻¹	1.8 ± 0.4	1.1 ± 0.3*	1000	1300
Zn	µg L ⁻¹	13.7 ± 2.9	10.5 ± 2.1	5000	5000
Cd	µg L ⁻¹	BDL	BDL	3	5
Pb	µg L ⁻¹	0.65 ± 0.11	0.54 ± 0.08	50	15
Mn	µg L ⁻¹	1.70 ± 0.22	1.71 ± 0.24	100	50
Al	µg L ⁻¹	28.4 ± 3.3	20.1 ± 2.8	200	200
As	µg L ⁻¹	BDL	BDL	10	10
Cl ⁻	mg L ⁻¹	158.7 ± 7.1	149.5 ± 6.5	250	250
SO ₄ ²⁻	mg L ⁻¹	110.8 ± 15.8	96.5 ± 13.0	-	250
HCO ₃ ⁻	mg L ⁻¹	177.2 ± 10.8	184.0 ± 11.6	-	-
PO ₄ ³⁻	mg L ⁻¹	0.11 ± 0.02	0.06 ± 0.01*	-	-

p* < 0.05.*p* < 0.01.¹ WHO guidelines for drinking-water quality (4th edition, World Health Organization, 2011, Geneva).² U.S. Environmental Protection Agency (US EPA) National Primary drinking Water Regulations 2011 (<http://www.epa.gov/safewater/mcl.html>).

Zamzam water samples that were either brought to or sold in Germany. On the other hand, Al-Barakah et al [10] reported on arsenic levels that are within permissible limits [0.006–7.728] in Zamzam water collected and analyzed in Saudi Arabia. Differences among studies could be explained by many factors including differences in the laboratory methods used for water analysis as well as in the material used due to variable water samples and ways of collection. In addition, it is possible that arsenic concentration in Zamzam water is dynamic being affected by civil activities at the vicinity of the well. Except for long-term inhabitants and citizens of the country of Saudi Arabia, Zamzam water consumption is expected to be a temporary behavior being limited by the relatively short period of pilgrimage (days-weeks), the relative unavailability of Zamzam water outside ritual areas, the relatively small volume of water that is allowable for pilgrims on returning to their countries (only one authorized 5-liter package of bottled Zamzam water is freely permissible for every returnee) and the possible division of carried water on relatives and friends. As per WHO report on chemical aspects of drinking-water, most chemicals arising in drinking water are of health concern only after extended exposure of years, rather than months [15]. Nevertheless, arsenic content of Zamzam water has gained an increased attention [16], perhaps because the WHO declares inorganic arsenic as a confirmed carcinogen and the most significant chemical contaminant in drinking-water globally. Intake of inorganic arsenic over a long period can lead to chronic arsenic poisoning (arsenicosis) [17]. Effects, which can take years to develop depending on the level and route of exposure, include skin lesions, peripheral neuropathy, gastrointestinal symptoms, diabetes, cardiovascular disease, developmental toxicity, and cancer of the skin and internal organs [18]. Therefore, official, periodically-updated reports on Zamzam water analysis issued by the local authority are needed (including water of the well and at different distribution points).

Similar to arsenic, Cd was below detection limit in all Zamzam water samples included in our study. In addition, the concentrations of all other tested threshold analytes (chemicals which have maximum allowable

limits) were well below the maximum allowable limits stated by WHO and EPA.

The mean values of TDS in the directly-collected as well as the bottled Zamzam water samples were 814 and 812 mg L⁻¹, respectively. TDS comprises inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates) and small amounts of organic matter that are dissolved in water. Generally, TDS in drinking-water originates from natural sources, sewage, urban runoff and industrial wastewater. Concentrations of TDS in water vary considerably according to geological regions owing to differences in the solubility of minerals. WHO doesn't suggest a guideline value for TDS as it is not of health concern at levels found in drinking-water. Nevertheless, drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg L⁻¹ [15].

Bottled Zamzam water sample had significantly lower levels of Na⁺, PO₄³⁻ and Cu²⁺ compared to the collected samples. Treatment of bottled water could be responsible for such differences. Al-Ansy et al [7] reported that bottled Zamzam are ozonated. Nevertheless, this method, up to our knowledge, has not been reported by neither by the official websites nor by other authors. The detailed method of bottling needs to be clarified.

5. Conclusion

Our study shows that Zamzam water has acceptable chemical profile. Nevertheless, larger blind studies are needed. Apart from bias that would affect studying such a religious and spiritual subject, other factors may also affect the results of Zamzam water studies. These include multiplicity of destinations of Zamzam water, different assay methods and enormous civilizational activities around the well. Therefore, periodic announcement of Zamzam water analysis results by the local authority are expected to be the most accurate way to explore the nature of Zamzam water. Efforts are made by the local authorities to maintain Zamzam well [3, 4, 19]. Up to our knowledge, no official analysis results were periodically published. Nevertheless, official reports would reassure consumers of Zamzam water.

Declarations

Author contribution statement

W. Mortada and A.F. Donia: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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