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Investigating Salt Effect Correction for $\delta^{18}O$ and δ^2H in Saline/Brine Groundwater Samples

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Abstract

This study focuses on the Kashan Plain Aquifer (KPA), an emblematic case in Iran, where overpumping groundwater intensifies salinity. Employing advanced isotopic techniques, specifically analyzing stable water molecule isotopes (δ^{18} O and δ^{2} H) through the Gasbench+DeltaPlusXP method, the current study addresses the intricate nature of saline waters by analyzing geochemistry and isotopes of 15 groundwater samples. It should be noted that the electric conductivity (EC) of the water samples varied from 2210 to 212000, with their mean value being 65499 µS/cm. The study also investigates the impact of salinity on isotopic values, considering ion hydration and salt effects that are crucial for accurate measurements. The results of the study revealed that δ^{18} O values ranged between -8.4 to 6 and -8.38 to 6.48 % before and after salt effect correction, respectively. Moreover, it was found that the average δ^{18} O values varied from -4.58 to -4.49 % before and after salt effect correction. In addition, the disparity between measured and corrected δ^{18} O revealed the impact of MgCl₂, and CaCl₂ salts on δ^{18} O in all collected samples. However, no difference was found between measured and corrected δ^{2} H. Therefore, while the findings indicate the necessity of salinity correction for δ^{18} O, it appears that salinity correction bears less significance for δ^{2} H.

Keywords: Environmental Isotopes, Activity, Saline Groundwater, Brine, Isotope Hydrology. **1. Introduction**

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Salinization is one of the most important factors contributing to the degradation of groundwater quality on a global scale (Mirzavand et al., 2018; Mirzavand and Walter, 2024). Groundwater resources may undergo salinization due to various reasons such as seawater intrusion, waterrock/clay interactions, and ion exchange (Mirzavand, 2018; Walter et al., 2017). As groundwater salinization is a global concern, it is crucially important to devote serious attention to studying and developing new methods for the investigation and management of groundwater resources (Bagheri et al., 2019; Mirzavand and Ghazban, 2022). The issue assumes special significance when it comes to arid and semi-arid regions, where there is high reliance on groundwater resources.

As a country where approximately 65% of its area lies in an arid and semi-arid region, Iran is highly dependent on groundwater resources (Mirzavand and Ghazavi, 2015). However, excessive pumping of groundwater has resulted in a significant decline in the country's aquifers' water table, leading to the intrusion of saltwater into aquifers.

Various methods have been proposed to determine the origin and mechanism of groundwater salinization (Mirzavand et al., 2020a), one of the most recent and accurate of which is the isotopic technique. The literature review on saline groundwater highlights that the utilization of stable water molecule isotopes (deuterium (δ^2 H) and oxygen-18 (δ^{18} O)) constitutes a fundamental aspect of isotopic studies, where the focus is given to saline groundwater (Vengosh 2005; Clark 2015).

The analysis of δ^{18} O and δ^{2} H on the samples collected from saline waters faces much more difficulty than those of the freshwater (Skrzypek and Ford, 2014). On the other hand, high salinity concentration sounds as a fundamental issue in the direct measurement of the isotopic values of δ^{18} O and δ^{2} H, and the obtained results may require correction to increase the accuracy of the analyses (Horita et al., 1993). Moreover, as Ion hydration causes depletion in the isotopic composition of water molecules in saline waters, the crystallization of water and salt deposition exert a greater impact on such a process (Clark, 2015). Furthermore, using the Gasbench+DeltaPlusXP method, ¹⁸O, and ²H can

be measured in CO_2 and H_2 injected into the sample after it has reached equilibrium with the water sample (Mirzavand, 2018). Therefore, under such conditions, the measured isotopic values result from the activity of $\delta^{18}O$ and $\delta^{2}H$.

As for saline waters, the activity of isotopes decreases with an increase in salinity while the concentration remains constant (Clark, 2015). Consequently, the results of stable hydrogen and oxygen isotope analysis of saline water samples can be reported on two scales: 1) the "concentration scale," representing the average stable isotope composition of all water molecules in the sample, and 2) the "activity scale," representing the concentration of isotopes only in the "free" water without water associated with cation hydration bubble. as defined by Sofer and Gat (1972), the correction of "activity" allows for a re-calculation from the activity scale to the concentration scale, serving as the function of the molality of chemical compounds present in the water sample that exert a significant influence on measured stable isotope composition the (Skrzypek and Ford, 2014). Thus, without such a correction, the isotopic data may reflect only the isotopes in the "free" water and exclude those associated with cation hydration bubbles, thus providing an incomplete picture of the groundwater's isotopic composition.

Correcting the salt effects is essential for obtaining precise and meaningful data, preparing the grounds for a more accurate interpretation of the hydrological processes and the origins of groundwater salinization. Moreover, such a correction ensures the portrayal of water's true composition by the isotopic values, facilitating better management and conservation strategies. Therefore, this study set out to investigate the effect of salt on the measured isotopic values in the groundwater of the Kashan Plain Aquifer (KPA), compare the effects of salt on the isotopic values of δ^{18} O and δ^{2} H, and determine which of these isotopes in the saline water samples need correction. To the best of our knowledge, the current study is the first of its kind in Iran, and the obtained results can be useful for researchers and specialists in the field of isotope hydrology.

2. Materials and Methods 2.1. Study Area

Located in Isfahan Province, Iran, the KPA (longitude: 51°32' to 51°03'E, latitude: 33°27' to 34°13'N) covers an area of 2403 km² (Figure 1) (Mirzavand and Ghazavi, 2015). The underlying layer of the aquifer comprises evaporitic marl deposits of the Miocene and Upper Red Formation, which is covered by aeolian deposits and alluvial sediments, with an average depth of 250 meters (Mirzavand et al., 2020b).

The alluvial deposits are a mixture of fine silt, coarse silt, clay, sand, gravel, conglomerate, and shale. The water table in the sandy hills is approximately 3 meters (on the east and northeast sides of the aquifer), while in the western and southwest of the plain, it is around 180 meters (Mirzavand and Ghazavi, 2015).

The first exploitation wells in the Kashan Plain were drilled in 1956. Since then, the number of pumping wells has increased to over 2000 due to population growth and increased water demand, leading to an annual one-meter decline in the water table. On the other hand, groundwater resources recharge through the west zone and discharge through the northeast zone into the playa lake. Additionally, groundwater salinity increases from the west and southwest to the northeast of KPA (Mirzavand et al., 2020b).



According to the review of the related literature, the cumulative deficit of the Kashan aquifer is 1065.96 Mm³, and the long-term average volume change is about -35.5 Mm³ (Mirzavand, 2018). Therefore, due to overpumping and low recharge in this region (precipitation = 131 mm/y and potential evapotranspiration of 3000 mm/y), the KPA has

been listed as a critically restricted aquifer in Iran. Furthermore, in addition to the critical condition of the water crisis in the Kashan Plain and land subsidence (3.5 cm/y) (Ghazifard et al., 2016), such limited and valuable water resources are becoming saline and disappearing due to the presence of various saline sources in the plain (such as Nasrabad buried salt dome, Playa Lake, Upper and Lower Red Formations, Qom Formation, and Miocene marls), over-pumping, and the effect of ion exchanges, (Mirzavand et al., 2020b).

2.2. Sampling and Analysis

2.2.1. Hydrogeochemical sampling and analysis

To investigate the salt effect on the isotopic values of deuterium and oxygen-18 in groundwater resources of the Kashan aquifer, a total of fifteen groundwater samples were collected from different locations in the Kashan Plain for hydrogeochemical and isotopic analysis. Moreover, the water samples were collected from various areas to examine different TDS levels (from freshwater in the southwest of the aquifer to brine in the Playa Lake). The samples were collected and analyzed according to sampling standards (Clark, 2015), and parameters such as pH, EC, CO_3^{2-} , and HCO_3^{-} were measured in the field. On the other hand, anionic samples were collected in 250 mL containers. Additionally, cation samples were collected in 250 mL containers, acidified to a pH less than 2 with pure HCl, and transported to the hydrogeochemical laboratory at the University of Ottawa, Canada. Finally, after the dilution process, ion analysis was performed using ion chromatography (IC) for anions and inductively coupled plasma mass spectrometry (ICP-MS) for cations.

2.2.2. ¹⁸O and ²H sampling and analysis

For sampling isotopes of water molecules, 50 mL PVC bottles were utilized. The bottles were rinsed three times with water collected from the same well before sampling and they were completely filled with water, ensuring no bubbles were present. Finally, the samples were transferred to the Ján Veizer Laboratory at the University of Ottawa, Canada, for preparation and isotopic analysis.

Various methods and devices have been developed for measuring water isotopes, taking

into account the differences in samples and the required precision. Nowadays, many isotopes of the periodic table can be measured with a device called AMS (Accelerator Mass Spectrometry). However, as analysis with the AMS device is expensive and sample preparation is timeconsuming, there are two alternative, more costeffective, and faster methods for analyzing isotopes: LGR-TWVIA (Liquid-Gas Ratio -Triple Water Vapor Isotope Analyzer) and Gasbench+DeltaPlusXP methods (Mirzavand, 2018). In the LGR-TWVIA method, the water samples should not contain a salinity higher than 4 PSU (Practical Salinity Unit). Therefore, it is preferable to analyze the isotopes of ¹⁸O and ²H in brackish to brine water using the Gasbench+DeltaPlusXP method (Sadatinejad and Mirzavand, 2023). Therefore, this study used the Gasbench+DeltaPlusXP method to analyze the isotopes existing in the groundwater samples of the Kashan aquifer. In this regard, to prepare samples for the analysis of ¹⁸O and ²H isotopes Gasbench+DeltaPlusXP with the method. parameters such as chloride and organic matter present in the samples need to be precipitated. Therefore, first, 3 ml of each sample was transferred to a new vial. Then, approximately 1 gr of pure copper was added to the sample for chloride sedimentation. Moreover, for the sedimentation of potential organic matter in the sample, about 1 gr of activated charcoal was added to the sample (Mirzavand, 2018). After gently shaking the vials by hand, the samples were stored in the laboratory environment for one week, after which 6.0 ml were extracted from each vial using a digital pipette, which was then transferred to a new vial. On the other hand, in addition to obtaining a new 6.0 ml sample from each of the original samples, duplicates were prepared from two of the samples to assess measurement accuracy. Furthermore, four standard samples were also prepared in the amount of 6.0 ml in each vial. To do so, one sample was selected as the standard one for analysis. Then, the standard samples including the light water sample, distilled water sample, heavy water sample, and the EDT standard were prepared and made ready in vials similar to those used for the experimental samples. Table (1) shows the arrangement of samples and standards for the analysis of 15 isotopic samples.

84	

for the analysis of deuterium and oxygen-18 using the Gasbench+DeltaPlusXP method.							
Samples analysis for ¹⁸ O Samples analysis for D							
J-2	Sample 8b	J-2+Pt	Sample 8b+Pt				
W-7	Sample 9	W-7+Pt	Sample 9+Pt				
W-10	Sample 10	W-9+Pt	Sample 10+Pt				
W-9	Sample 11	W-20+Pt	Sample11+Pt				
W-20	Sample 12	W-10+Pt	Sample 12+Pt				
Sample 1	Sample 13	Sample	Sample 13+Pt				
Sample 2	Sample 14	Sample	Sample 14+Pt				
Sample 3	Sample 15a	Sample	Sample 15a+Pt				
Sample 4	Sample 15b	Sample	Sample 15b+Pt				
Sample 5	W-7	Sample	W-7+Pt				
Sample 6	W-10	Sample	W-10+Pt				
Sample 7	W-9	Sample	W-9+Pt				
Sample 8a	W-20	Sample 8a+Pt	W-20+Pt				

 Table (1): The arrangement of samples and standards

Note: In the samples presented in the above table, samples 8 and 15 were analyzed twice to examine the accuracy of the analysis. In this table, samples containing platinum catalysts are also arranged.

2.2.2.1. preparation of the Samples for ¹⁸O analysis

To inject 2% CO₂ and He, vials containing samples and standards were arranged on a holder. The cover of the holder was then securely closed. Then, eight syringe needles, numbered from 1 to 8, were inserted into the left part of the vial cap at a 45-degree angle to extract oxygen from inside the samples. Moreover, the gas valve was set to 2%, and the 2% gas was released, with the pressure gauge being adjusted to 3 to 3.5 atmospheres. Then, a series of needles connected to the 2% oxygen and helium gases were inserted into the vials from the right side of the vial caps, numbered from 1 to 8 at a 45-degree angle, followed by checking the oxygen output from the vials to ensure the proper functioning of the system. To do so, the flowmeter was turned on and connected to the exit needles numbered from 1 to 8 (A flow rate between 70 to 80 ml indicated the correct performance of the system). After installing the needles and checking the output flow, the timer was set to four minutes to inject 2% O₂ and He into the vials and remove the oxygen for a duration of four minutes. Once the four minutes elapsed, the output needles were removed (if this step is not taken, damage may occur to the Gasbench+DeltaPlusXP device). The process was repeated for the subsequent samples until oxygen was removed, and 2% O₂ and He were injected into all samples. Finally, after completing the process for all samples, the needles were removed, and the input gas and pressure gauge were closed.

2.2.2. 2. samples preparation for ²H analysis

the ²H isotope To analyze with the Gasbench+DeltaPlusXP method, it is necessary to inject 2% H₂ and He into the samples, so that the injected hydrogen can be exchanged with the hydrogen molecules in the samples and standards and the hydrogen molecules in water be released for analysis. Since such an exchange occurs slowly, a catalyst is needed to accelerate the process. The catalyst used in this method is platinum (Pt). Therefore, from each sample (those containing pure copper and activated charcoal), 6.0 ml were taken using a digital pipette, which was then placed in each vial with a Pt catalyst holder (it should be noted that the catalyst should not come into contact with water). The process is also conducted for standards. Then, the samples containing the catalyst were transferred to the injection site of 2% H₂ and He, similar to the previous process where 2% CO₂ and He were injected into the samples.

After the completion of the process, there remained two samples from each sample and standard (except for two additional samples used for the purpose of measurement repetition and accuracy assessment). These samples were stored in the laboratory temperature for five days to be prepared for analysis with the Gasbench+DeltaPlusXP technique (Mirzavand, 2018). At the sample injection site, the samples were placed on a heated plate (it should be noted that water samples do not need to be heated, but samples requiring isotopic carbon analysis up to 50° C need to be heated). Then, the samples were sequentially withdrawn using a syringe-like device (automatically programmed to extract samples from each vial). The device was connected to two very thin tubes, one of which connected to the helium reservoir. was Simultaneously with sample extraction, the helium enters, and the water sample is pushed into the device for isotopic measurement.

When the sample enters the Gasbench+DeltaPlusXP device, there is no need for the water sample part, and only the gas (H₂ or

 CO_2) needs to be injected into the sample. This is key difference between the a Gasbench+DeltaPlusXP and LGR analysis methods. The desired gas was then dried using liquid nitrogen. After this process, the two gases were separated from each other, and each gas was individually sent into the Mass Spectrometer. Each isotope was measured six times, and the final accurate value for each isotope was obtained by averaging such readings. In the computergenerated graphs, the first peak corresponds to nitrogen, and the second peak corresponds to CO₂ or H₂ gas. It should be noted that the obtained values for each isotope were calibrated using the equation to determine Craig the actual concentration of each isotope (Sadatinejad and Mirzavand, 2023).

2.2.2.3. Salt effect correction for $\delta^{18}O$ and $\delta^{2}H$ isotopes

Hydration of ions causes discrepancies in the measurement of ¹⁸O and ²H in saline/brine water (Clark and Fritz, 1997). Gasbench+DeltaPlusXP technology measures ²H from H₂ in equilibrium with water. This is a measure of ²H activity. Additionally, ¹⁸O is measured by CO₂ in equilibrium with water. Thus, it is a measure of ¹⁸O activity (Sofer and Gat, 1972). The isotopic activity of saline/brine decreases with salinity concentration even though the remains unchanged. For consistency, measurements of δ^{18} O and δ^{2} H activities should be corrected and expressed as concentrations before comparison. Sofer and Gat (1972) developed the following equations (1 and 2) to correct the measured values of salinity δ^{18} O and δ^{2} H.

$$\delta^{18}O_{\text{corrected}} = \frac{(1.11m_{\text{MgCl}_2} + 0.47m_{\text{CaCl}_2} - 0.16m_{\text{KCl}})}{1000}$$
(1)
× $(\delta^{18}O_{\text{measured}} + 1000) + \delta^{18}O_{\text{measured}}$

$$\delta^{2} H_{\text{corrected}} = \frac{-0.4 m_{\text{NaCl}} - 5.1 m_{\text{CaCl}_{2}} - 2.4 m_{\text{KCl}}}{1000}) \qquad (2)$$
$$\times (\delta^{2} H_{\text{measured}} + 1000) + \delta^{2} H_{\text{measured}}$$

Where $\delta^{18}O$ stands per mil, and ions concentration stands per molality.

So, in this study, δ^{18} O and δ^{2} H measurements were corrected for salt effect removal using equations 1 and 2, respectively.

3. Results and discussion

Tables 1 and 2 show the results of physio-chemical and isotopic analysis in KPA, respectively.

3.1. General hydro-geochemistry of KPA

Table 1 shows the geochemistry of groundwater samples in KPA. Hydrogeochemical facies show an evolution from Ca-HCO₃ (recharge zone in the west of KPA) to Na-Cl (Discharge zone in the northeast of KPA). The electric conductivity (EC) of the water samples varied from 2210 (GW8) to 212000 (GW10) μ S/cm. On the other hand, the

mean value of EC for investigated areas of KPA was reported to be about 65499 µS/cm. Moreover, the pH ranged between 4.17 and 7.87 with an average of 6.91. The dominant cations and anions in the investigated samples were Na⁺ and Ca²⁺ and Cl⁻ and SO₄²⁻, respectively. The Na⁺, Ca²⁺, Mg²⁺, K, Cl⁻, and SO₄²⁻ concentrations varied from 368 to 83597, 167 to 33873, 49.54 to 14580, 0 to 1.89, 177 to 204800, and 151 to 10080 mg/L, respectively. The average concentration of HCO_3^- in the investigated samples was reported as 8.40 mg/L. Based on the results, the concentration of Na⁺, Cl⁻, and SO₄²⁻ increased and the concentration of Ca²⁺, and HCO₃⁻ decreased by moving from the southwest to the northeast of KPA.

Ta	ble (1): l	Result of	physic	o-chem	ical (pe	r mg/l) paran	ieter an	d Densit	y(d) (K	g/l) anal	lysis in K	PA
ID	UTM-X	UTM-Y	pH	T(⁰ C)	Na	K	Ca	Mg	Cl	HCO ₃	SO_4	EC (µS/cm)	d
W1	527211	3794924	7.16	24	1775	0.01	721	69.07	4047	13.05	770	13000	1.19
W2	525712	3789332	7.12	23	2408	0.01	879	123	4473	30.85	848	4330	1.19
W8	553055	3744880	7.87	25	368	0.00	167	59.70	177.5	16.22	726	2210	1.17
W10	571622	3803128	6.99	31	83597	1.89	667	14580	185023	4.02	7657	212000	1.41
W13	550767	3793764	6.88	31.5	35472	0.17	10694	2655	87935	1.46	890	150200	1.27
W17	523538	3809807	7.25	26	1042	0.00	623	56.93	2026	3.17	1129	7500	1.17
W20	543618	3781795	7.41	32	2383	0.02	847	337	4592	13.29	2035	13510	1.18
W21	546478	3767215	7.36	25.9	1400	0.01	1079	325	4810	6.46	773	13290	1.18
W28	529007	3798177	7.43	25.1	2897	0.02	1565	49.54	5680	6.34	1390	14470	1.18
W29	516837	3810692	7.58	24.6	1030	0.00	481	102	1474.8	6.22	1841	6560	1.17
W31	524052	3803221	7.19	25	1944	0.00	532	63.37	2867	10.24	1220	10420	1.19
W35	530225	3811130	6.18	30	60553	0.19	33873	4844	197309	0	151	200000	1.41
W37	540169	3803080	5.76	30	74223	0.86	960	2438	204800	1.70	10080	204000	1.36
W40	533052	3791659	4.17	25.3	3686	0.13	2842	677	11999	0	1110	28800	1.18
W42	580600	3744492	7.37	23	2226	0.01	426	313	2291	13.05	1385	7660	1.15

Table (2): Result of 518O and 52H (‰) analysis in KPA							
ID	UTM-X	UTM-Y	$\delta^2 H_{measured}$ (VSMOW)	$\delta^{18}O_{measured}$ (VSMOW)			
W1	527211	3794924	-55.9	-8.00			
W2	525712	3789332	-52.3	-7.6			
W8	553055	3744880	-54.7	-8.2			
W10	571622	3803128	25.5	6.00			
W13	550767	3793764	-28.2	0.2			
W17	523538	3809807	-57	-8.3			
W20	543618	3781795	-55.2	-7.7			
W21	546478	3767215	-56.4	-8.3			
W28	529007	3798177	-16.3	-4.5			
W29	516837	3810692	-55.1	-7.7			
W31	524052	3803221	-55.6	-6.9			
W35	530225	3811130	-19.7	3.6			
W37	540169	3803080	-3.5	4.2			
W40	533052	3791659	-52.3	-7.1			
W42	580600	3744492	-55.4	-8.4			

3.2. δ^{18} O and δ^{2} H and Salt effect correction

According to the results of the study, enrichment, and depletion of δ^{18} O occurred the most in W10 (6.00‰) and W42 (-8.4‰), respectively. Also, the highest level of enrichment and depletion of δ^{2} H was found in W10 (25.5‰) and W21 (- 56.4‰), respectively. Such high enrichment of δ^{18} O and δ^{2} H in sample W10 could be attributed to the effect of evaporation. The results of the study also indicated that by moving towards the Playa Lake (northeast of KPA) (Figure 1), water

samples are enriched in terms of ¹⁸O and ²H isotopes.



Figure 2 shows the results of $\delta^{18}O$ and $\delta^{2}H$ variations before and after salt effect correction. According to the findings, δ^{18} O values before and after salt effect correction ranged between -8.4 to 6 and -8.38 to 6.48 ‰, respectively. The average δ^{18} O values before and after salt effect correction vary from -4.58 to -4.49 ‰. Figure 2 illustrates the disparity between measured and corrected δ^{18} O in all samples, indicating the impact of MgCl₂ and CaCl₂ salts on δ^{18} O, which is in line with Horita et al. (1993), Sofer and Gat (1972), and Benetti et al. (2017). The obtained results also suggest that as the salinity of the water sample increases, the difference between the measured ¹⁸O value and the corrected value increases, indicating that the activity of ¹⁸O in saline waters decreases with an increase in salinity. However, Figure 2 shows that except for sample GW37 (which shows a very slight difference between the measured and corrected values), there is no difference between measured and corrected δ^2 H, indicating that the activity of

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²H in saline waters does not change with an increase in salinity. This finding is consistent with the one reported by Benetti et al. (2017), reiterating that ²H remains constant across varying salinity levels (Benetti et al., 2017). Thus, there is no need to correct the salt effect on δ^2 H in saline/brine water samples.

4. Conclusion

The complex nature of saline waters requires correction of the salt effect on isotopic values, considering the impact of ion hydration and salt deposition on the measurements. The correction of "activity" was performed using established equations to recalibrate the isotopic values from the activity scale to the concentration scale. The results of the study provided insights into the general hydrogeochemistry of the Kashan aquifer, revealing an evolution from Ca-HCO₃ in the recharge zone to Na-Cl in the discharge zone. The isotopic analysis (δ^{18} O and δ^{2} H) indicated significant enrichment and depletion patterns, with the influence of evaporation being observed in some samples. Furthermore, the salt effect correction for δ^{18} O showed variations in the isotopic values before and after correction, highlighting the necessity of addressing the impact of salinity on measurements. However, for δ^2 H, the results suggested that salt correction was not necessary. This study contributes valuable information to the field of isotope hydrology, particularly in the context of saline/brine groundwater resources. The findings offer a foundation for future research and can be useful for researchers and specialists working on saline/brine groundwater resources.

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