Origins And Processes of Groundwater Salinization Beneath Playa Lake Aquifers In Iran: A Chemical And Stable Isotope Approach

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Abstract

Groundwater salinization and interaction between Playa Lake and regional groundwater was investigated using multi-chemo-isotopic evidences. Forty groundwater and 26 Kashan Playa Lake (KPL) water samples collected and analyzed for their geochemical compositions. The evolution of hydrochemical facies in Kashan Plain Aquifer (KPA) to KPL is Ca-HCO_3 (19%), Mix Ca-Cl (9%), Ca-Cl (17%), and Mix Na-Cl and Na-Cl (55%). Also, the Hydrochemical Facies Evolution Diagram (HFE-D) proposed cation exchange as the main process of salinization in KPA. Based on the binary hydrogeochemical diagrams of $(\text{Na}^+/\text{Cl}^-)/\text{Cl}^-$, $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-+\text{SO}_4^{2-}$, and Cl/Br , dissolution of halite and gypsum in the Miocene marlstone in the KPA is the main source of salinity. The isotopic composition $\delta^{18}\text{O}$ in aquifer and playa water samples varies from -10.03 to 7.03‰ (VSMOW) with an average of -6.95‰ and -60.73 to 25.08‰ with average of -45.82‰ for $\delta^2\text{H}$. Based on the result, the relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$, and $\delta^{18}\text{O}$ and Br , approve discharge of saline water from KPA to KPL. Likewise, the isotopic composition of $\delta^{34}\text{SO}_4$, varies from 5.95 to 22.55‰ CDT in KPA, and 5.95 to 9.99‰ CDT in KPL. Also, the relation between $\delta^{18}\text{O}-\delta^{34}\text{SO}_4$ and $\text{Cl}-\delta^{34}\text{S}$ were non-linear, indicating that sulphur concentration in KPA and KPL changed due to sulphide oxidation and sulphate reduction in the freshwater and deep brines in the aquifer and mixed during the over-pumping in the KPA. Oxidation of sulphide minerals such as galena (PbS), and Chalcopyrite (CuFeS_2) may have been the source of sulfur in Dore mine in western part of the aquifer (recharge zone) leached by seasonal runoff. In general, water–rock interaction, ion exchange, and hydraulic gradient have been the dominating factors in changing the water chemistry between aquifer and playa leading to saline groundwater discharged to the playa.

Introduction

Groundwater salinization is a major environmental problem affecting water resources while causing restriction of accessibility to suitable water especially in arid and semi-arid regions and coastal zones (Gomez et al., 2021; Vengosh, 2014). The processes responsible for the development of salinization of water are complex and intimately related to the transport of dissolved mass in groundwater flow systems. The concentration of continental lake constituents can rise significantly in confined bodies of water due to evaporation, leading to precipitation of various minerals and dynamic chemical processes (Ghazban, 2018).

Chemical composition of groundwater could be change due to potential sources of salinity like Ion exchange, water-rock interaction, carbonate and evaporite mineral dissolution, redox reaction, connate waters, seawater intrusion (Richter and Kreitler, 1993). As such, the presence of different sources of salt can complicate the process of determining the source of salinity in the aquifer.

Hydrogeochemical characterization of groundwater Ion ratios Cl/Br , $(\text{Na}/\text{Cl})/\text{Cl}$, Ca/HCO_3 , Ca/SO_4 , and $(\text{Ca} + \text{Mg})/(\text{SO}_4 + \text{HCO}_3)$ have been used to distinguish possible sources and mechanisms for increasing groundwater salinity (Ben Ammar et al., 2020; Cartwright et al., 2009; Gopinath et al., 2019). Isotope can be used as tool for source identification. The stable isotopic composition of water (^{18}O and ^2H) were employed to determine groundwater sources (Mazor, 2003), as well as distinguishing between process such as evaporation, clay filtration, and mineral dissolution (Clark and Fritz, 1997). Sulfur isotopes have been used for determine the source of sulphate, salts, mixing and upconing process in the aquifer (Chivas et al., 1991). Hence, using hydrogeochemical and isotopic information could greatly improve our understanding of the groundwater system.

The severity of water crisis in central Iran is significant in Kashan Plain Aquifer (KPA) which is one of the critical aquifers. In addition to water level declining due to over pumping, groundwater salinization is the main dilemma in area. There are number of potential sources of salinity in the area (Jamshidzadeh and Mirbagheri, 2011; Mirzavand et al., 2020b), but Kashan's playa Lake (KPL) while the major source of salinity in vicinity of KPA has not been studied lacking good resolution and comprehensive sampling. This study focuses on the hydrogeochemical composition of KPA, KPL, origin and mechanism of groundwater salinization, and Kashan playa-groundwater interaction. Therefore, the main aims of this study are groundwater salinization and playa-groundwater interaction investigation in Kashan plain using multi-chemo-isotope data. Also, this research is the first study aims to investigate the interaction between aquifer and Salt lake playa in Iran using isotopic, hydrogeochemical and geophysical investigations.

Materials And Methods

2.1. Geology and Hydrogeology setting of study area

Kashan plain is located in Central Iran, covering total area of about 2410 km² (Fig.1). The area is a part of the arid and desert regions with temperatures ranging from 5°C to 48°C and mean annual rainfall of about 133 mm.

KPL is situated within the Qom watershed, with inflow from three streams that head into the Zagros- the Ghareh Chay, Rud-e-Shur and Qom Rud (Fig.2). The rocks cropping in the area consist of evaporites of the Qom Formation. The formation comprise thick successions of marine marls, limestones, gypsum and siliciclastics, ranged from the Early Oligocene to the Early Miocene with the thickness ranging from 600 to 800 meters. The Qom Formation bounded by the underlying Lower Red Formation and the overlying Upper Red Formation, both consisting of continental redbeds

(Stöcklin and Setudehina, 1991). The base of the formation is dominated by brown, gray and red marls, and by argillaceous limestones. The transition of the Qom Formation into the Upper Red Formation is gradual and characterized by a drastic increase of siliciclastics.

Ghareh Chay river originate from Shazand heights and flow to the north and extends west to east to the salt lake and its excess water enters the salt lake. The flow of the Ghareh Chay is the most intensive, with a resultant inundation of the northwestern part of the playa.

The playa has a triangular shape, with the apex pointing approximately due north. The maximum dimensions in both the north-south and east-west directions are approximately 50 km. The KPL consist of dry pan surface (crust broken into polygons) in the center and evaporation media in around, which indicate the desiccation stage in evolution process of saline pan.

The water from this aquifer is pumped from different wells, resulting in a yearly groundwater level drop of about 1m (Mirzavand and Ghazavi, 2014). With increasing water withdrawals, water balance has been negative (-52 Mm^3) in the KPA. Generally, in KPA, groundwater flow from the west to the northeast.

2.2. Sampling

Forty water samples from Qanats, deep and shallow wells in KPA, and twenty-six samples from KPL were collected for geochemical and stable isotopes analysis in November of 2018 (See the sampling location in Fig.1). Physical and chemical parameters including temperature, pH, and electrical conductivity were determined using portable HACH-150 and Metrohm in the field. Prior to analysis for cations and sulfur isotopes the water samples were filtered ($0.45 \mu\text{m}$) and later acidified by pure HCl ($\text{pH} < 2$) and stored at 4°C .

2.3. Analysis

2.3.1. Geochemical analysis methods

Major and trace elements, were analyzed at geochemistry lab using Ion Chromatography (IC), and Inductive Couple Plasma-Mass Spectrometry (ICP-MS), respectively. Analyzed samples showed that the value of the computed ionic charge balance error (CBE) is within the acceptable range of $\pm 5\%$.

Total Dissolved Solid (TDS) was calculated using the results of the chemical analyses. Sampling and analysis carried out using methods introduced by Clark (2015). Due to high salinity in most of water samples, 1g of Activated Charcoal and pure copper added to the vials for precipitation of organic material and chloride. After that, samples stored for a week (at 25°C).

$\delta^{18}\text{O}$, $\delta^2\text{H}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ of water samples measured in the Ján Veizer Laboratory of advanced research complex (ARC) in the University of Ottawa, Canada. Analyze by Gasbench+DeltaPlusXP and EA/IRMS $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results are reported based on Vienna standard mean ocean water (VSMOW). Also, $\delta^{34}\text{S}$ are reported relative to the Vienna Canon Diablo Troilite (VCDT). The analytical precision is $\pm 0.2 \text{ ‰}$. for decrease the salinity effect on $\delta^{18}\text{O}$, and $\delta^2\text{H}$, correction was done using the following equations (1 and 2) (Sofer and Gat, 1972, 1975; Clark and Fritz, 1999).

$$\delta^{18}\text{O}_{\text{corrected}} = \left[\frac{(1.1m\text{Mg} + 0.47m\text{Ca} - 0.16m\text{K})}{1000} \right] \times (\delta^{18}\text{O}_{\text{meas}} + 1000) + \delta^{18}\text{O}_{\text{meas}} \quad (\text{Eq.1})$$

$$\delta^2\text{H}_{\text{corrected}} = \left[\frac{(-0.4m\text{Na} - 5.1m\text{Mg} - 6.1m\text{Ca} - 2.4m\text{K})}{1000} \right] \times (\delta^2\text{H}_{\text{meas}} + 1000) + \delta^2\text{H}_{\text{meas}} \quad (\text{Eq.2})$$

Where, in both equations, m is molality of ion concentration.

2.3.2. Geophysical methods

To determine the saline/freshwater distribution in KPA, the subsurface and bedrock geology of KPA, geoelectric technique carried out with 396 electrical sounding harvested with a flow line length of 800 m with Schlumberger arrangement. A direct electric current were injected into the ground through two electrodes at relatively long distances from each other. Subsurface anomalous conductivity in the middle of two current-transmitting electrodes were measured by a high-noise, low-noise magnetometer perpendicular to the line between the two electrodes, using a secondary magnetic field from the current passing through the ground.

The measurements are based on a series of transverse and longitudinal profiles at the desired area. The distance between each measuring point to the next point adjusted to cover the entire area. The probes are located along 42 profiles (41 latitudinal profiles and 1 longitudinal profile) (Fig. 3). Due to abundant data base, only the longitudinal and the transverse cross sections have been presented in Fig. 4.

Fig. 3. Geoelectric profiles in Kashan plain

2.4. Hydrogeochemical methods

In order to evaluate hydrochemical facies, Hydrochemical Facies Evolution (HFE) Diagram (Giménez-forcada, 2010) have been employed. Such diagram provides information on salinization and freshening processes, determined by the scattering of anion and cation in the model. To assess the influence of CaSO_4 and NaCl dissolution on groundwater salinization, binary plots of $(\text{Na}/\text{Cl})/\text{Cl}$, and $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-+\text{SO}_4^{2-}$ ratios are used (Richter and Kreitler, 1993).

Examination of water-rock interaction is carried out using the saturation index (SI). The SI is calculated by PHREEQC version 3.3 (Parkhurst and Appelo, 1999) which is a suitable method for evaluating the interaction of groundwater and solid-phase minerals and determines the thermodynamic equilibrium of groundwater samples.

The Sulphur compounds from different sources contribute in the geochemical reactions in groundwater. Sulur isotopes is a useful tracer for investigation of changes in the groundwater characteristics (Wallin and Ab, 2011) and upconing investigation. To determine the source of Sulphate and assessment upconing and mixing processes, water samples were selected for $\delta^{34}\text{S}_{\text{SO}_4}$ analysis, including KPL and groundwater samples.

Results And Discussion

4.1. Geoelectrical resistivity

The geo-electric resistivity method (GRM), including vertical electrical sounding (VES) surveys, was applied using the schlumberger array. For study the subsurface formations, deposits, and salinization, longitudinal (green line) and transverse (pink line) geoelectric cross sections shown in Fig. 4. As shown in Fig. 4A, the apparent resistance (AR) of the subsurface materials varies from 1 to 90 OA(m), along the longitudinal cross section (from the south to north of KPA (Fig. 3). Based on the results, layers with $\text{AR}<20$ OA(m) would have saline water or thin soil particles. Based on the mineralogy map, the bedrock of KPA consist of Qom formation, Upper and Lower Red Formation, and Miocene Marl, which in present of water, would produce saline groundwater. As shown in Fig. 4A, by moving toward the bedrock, AR decreases. Likewise, AR decrease by moving from west to east of KPA (Fig. 4B) which probably is due to mentioned formations and discharging saline groundwater from aquifer to the east of Kashan plain.

4.2. General Hydrogrochemical Characteristics

The geochemistry of groundwater samples in KPA and KPL provides visions into the source and mechanism of salinization, and KPA and KPL interaction in the study area. The following interpretations effort to determine the source and mechanism of salinization in KPA, and assessment the KPA/KPL interaction (Table 1).

Table 1. Physicochemical parameters, saturation indices, and hydrogeochemical parameters in KPA and KPL (chemical elements in mg/L and EC in $\mu\text{S}/\text{cm}$).

ID	depth (m)	pH	TDS	Ec (µS/cm)	Na	K	Ca	Mg	Cl	ALK (HCO3)	SO4	Br
KA1	35	7.16	7,391	13,000	1775	0.01	723	69	4047	130	770	3.32
KA2	35	7.12	8,751	4,330	2408	0.01	881	123	4473	300	848	4.73
KA3	120	7.04	5,061	2,100	729	0.01	846	189	1775	150	1,512	1.92
KA4	25	7.1	6,405	4,250	1523	0.01	523	96	2556	79	1,702	2.09
KA5	150	7.36	1,084	1,783	202	0.01	179	48	287	600	576	0.55
KA6	100	7.55	2,790	3,380	559	0.02	255	103	607	250	1,249	1.12
KA7	150	7.72	2,693	3,630	530	0.01	281	77	1180	87	619	0.71
KA8	90	7.87	1,509	2,210	368	0	167	59	177	720	726	0.52
KA9	38	7.85	896	1,462	250	0	84	45	71	660	433	0.39
KA10	0.5	8.11	3,937	4,420	1041	0	223	55	1034	170	1,573	0.81
KA11	50	7.44	3,030	4,000	768	0.01	204	89	1172	120	788	0.84
KA12	0.5	6.88	137,600	150,200	35472	0.17	10718	2,655	87935	14	890	29
KA13	100	7.38	6,778	10,100	1890	0.01	341	41	2689	42	1,813	1.93
KA14	1.5	7.68	4,002	6,620	984	0.07	207	61	1300	130	1,440	1.52
KA15	80	7.68	3,561	5,150	863	0.02	350	126	1053	190	1,155	1.66
KA16	35	7.25	4,881	7,500	1042	0.01	625	56	2026	31	1,129	2.37
KA17	300	7.58	1,604	2,300	371	0.01	228	74	390	900	600	0.59
KA18	200	8	1,276	1,872	413	0.01	119	40	355	840	328	0.63
KA19	30	7.41	10,210	13,510	2383	0.03	849	337	4592	130	2,035	3.09
KA20	60	7.36	8,393	13,290	1400	0.02	1081	325	4810	64	773	1.64
KA21	80	7.33	8,970	11,720	2046	0.02	885	272	3510	150	2,247	2.77
KA22	80	7.57	10,636	14,250	2812	0.04	854	225	5259	140	1,477	4.7
KA23	170	7.43	2,686	3,290	465	0.01	327	88	720	230	1,071	0.99
KA24	120	7.48	1,667	2,270	482	0.01	173	57	377	210	563	0.63
KA25	150	7.35	3,603	3,930	842	0.01	440	79	1739	100	494	1.43
KA26	25	5.16	24,726	27,200	1941	0.03	867	730	11244	0.56	9,945	14.7
KA27	18	7.43	11,587	14,470	2897	0.03	1569	49	5680	63	1,390	2.49
KA28	50	7.58	4,935	6,560	1030	0.01	482	102	1474	62	1,841	2.17
KA29	80	7.78	2,003	1,619	538	0.01	94	86	745	150	528	0.66
KA30	40	7.19	6,635	10,420	1944	0.01	533	63	2867	100	1,220	1.56
KA31	140	7.99	2,298	1,923	765	0	99	10	816	190	594	0.57
KA32	15	7.66	3,099	2,730	796	0.02	204	111	994	230	978	1.19
KA33	52	7.52	4,182	6,350	1114	0.01	358	70	1680	85	954	1.47
KA34	14	6.95	4,581	6,720	1159	0.01	656	25	2733	24	530	1.95
KA35	0.5	5.76	292,500	204,000	74223	0.87	962	2438	204800	17	10,080	37
KA36	15	7.19	7,602	12,280	2200	0.01	137	9.49	3627	48	1,625	1.96
KA37	23	4.57	26,700	37,400	8284	0.09	1369	369	13710	0.5	2,976	12
KA38	14	4.17	20,315	28,800	3686	0.13	2848	677	11999	0.5	1,110	17
KA39	80	6.9	10,733	14,020	1818	0.03	1261	467	6009	1.6	1,169	2.58
KA40	60	7.37	6,650	7,660	2226	0.02	427	313	2291	1.3	1,385	1.57

PL1	0.5	6.66	235000	215000	87000	2600	440	19000	224000	104	12100	96
PL2	0.5	6.7	228000	203000	81300	3000	390	23800	202000	261	24000	113
PL3	0.5	6.66	245000	197000	83500	3200	240	26000	211000	240	29400	139
PL4	0.5	6.82	252000	219000	93700	1400	340	11900	193000	136	18500	87.4
PL5	0.5	6.57	251000	198000	79700	3200	230	24400	201000	200	26800	103
PL6	0.5	6.63	239000	215000	79900	2200	900	21600	209000	169	6600	93.7
PL7	0.5	6.48	229000	224000	86400	1800	1600	16200	207000	124	3900	81.4
PL8	0.5	6.71	248000	212000	85600	2700	380	19500	203000	188	15200	1.6
PL9	0.5	6.65	260000	207000	85700	2700	310	22800	200000	224	19600	113
PL10	0.5	6.63	208000	202000	86500	2600	250	22300	202000	324	27600	134
PL11	0.5	6.72	225000	220000	89600	2300	630	17200	209000	100	7900	66.7
PL12	0.5	6.69	219000	200000	81000	3100	270	25200	204000	278	24500	97.7
PL13	0.5	6.64	249000	203000	84600	2700	260	22600	1970000	313	25900	124
PL14	0.5	6.63	273000	205000	88200	2300	250	19500	2110000	309	25900	107
PL15	0.5	6.7	248000	205000	89300	2400	260	19500	200000	359	27200	120
PL16	0.5	6.53	163000	220000	81600	2600	2000	19700	218000	64	2500	54.8
PL17	0.5	6.73	275000	203000	85200	2700	250	20700	208000	233	28700	108
PL18	0.5	6.47	219000	214000	72700	3000	2800	24400	213000	61	1700	56.3
PL19	0.5	6.81	247000	219000	94600	1600	380	14500	208000	258	16700	70.1
PL20	0.5	6.75	251000	216000	110000	2100	400	15500	204000	183	23700	61.4
PL21	0.5	6.63	236000	210000	74900	3000	710	25500	219000	202	7300	90.5
PL22	0.5	6.71	234000	211000	83200	2600	360	21800	209000	155	14800	76.5
PL23	0.5	6.98	250000	213000	83800	2600	570	21300	211000	250	11600	67.6
PL24	0.5	6.41	2130000	209000	66100	3000	4900	27200	207000	64	11100	68.3
PL25	0.5	6.3	181000	204000	61600	3700	4300	32300	219000	55	11100	67.9
PL26	0.5	6.63	164000	231000	92200	1500	1900	11200	198000	66	30000	47.9

Table 2. Saturation indices of Calcite, Dolomite, Gypsum, Anhydrate, Halite and Aragonite in water samples of KPA and KPL

ID	SI _{Cal}	SI _{Dol}	SI _{Gyp}	SI _{Anh}	SI _{Hal}	SI _{Ara}	ID	SI _{Cal}	SI _{Dol}	SI _{Gyp}	SI _{Anh}	SI _{Hal}	SI _{Ara}
KA1	0.05	-0.57	-0.51	-0.81	-4	-0.09	KA34	-0.66	-2.38	-0.61	-0.91	-4.33	-0.8
KA2	0.45	0.4	-0.47	-0.77	-3.85	0.31	KA35	-0.75	-0.52	-0.04	-0.17	-0.24	-0.89
KA3	0.19	0.06	-0.15	-0.45	-4.72	0.04	KA36	-1.12	-3.06	-0.85	-1.15	-3.94	-1.26
KA4	-0.32	-1.05	-0.29	-0.59	-4.25	-0.47	KA37	-2.41	-5.03	-0.13	-0.43	-2.99	-2.56
KA5	0.29	0.34	-0.87	-1.18	-6	0.15	KA38	-1.98	-4.2	-0.16	-0.46	-3.25	-2.12
KA6	-0.04	-0.15	-0.55	-0.85	-5.27	-0.18	KA39	-1.7	-3.46	-0.28	-0.58	-3.82	-1.84
KA7	-0.38	-0.99	-0.75	-1.05	-4.99	-0.53	KA40	-2.2	-4.2	-0.53	-0.83	-4.15	-2.35
KA8	0.3	0.48	-0.85	-1.15	-5.96	0.16	PL1	-1.11	0.03	-0.69	-0.83	-0.3	-1.25
KA9	0.04	0.14	-1.25	-1.55	-6.5	-0.1	PL2	-0.82	0.72	-0.49	-0.64	-0.41	-0.97
KA10	-0.31	-0.91	-0.56	-0.86	-4.78	-0.46	PL3	-1.1	0.41	-0.61	-0.75	-0.33	-1.25
KA11	-0.41	-0.84	-0.8	-1.11	-4.84	-0.55	PL4	-0.9	0.3	-0.59	-0.75	-0.44	-1.05
KA12	-0.23	-0.58	-0.2	-0.44	-1.38	-0.38	PL5	-1.18	0.25	-0.67	-0.83	-0.42	-1.32
KA13	-0.78	-2.16	-0.43	-0.73	-4.13	-0.93	PL6	-0.65	0.69	-0.72	-0.87	-0.41	-0.79
KA14	-0.45	-1.11	-0.62	-0.92	-4.71	-0.59	PL7	-0.42	0.76	-0.62	-0.77	-0.4	-0.57
KA15	-0.03	-0.18	-0.5	-0.81	-4.85	-0.18	PL8	-0.91	0.48	-0.67	-0.83	-0.4	-1.05
KA16	-0.6	-1.9	-0.32	-0.62	-4.5	-0.74	PL9	-0.98	0.49	-0.67	-0.83	-0.39	-1.13
KA17	0.53	0.91	-0.83	-1.14	-5.62	0.38	PL10	-0.89	0.75	-0.61	-0.76	-0.38	-1.03
KA18	0.28	0.42	-1.27	-1.57	-5.6	0.13	PL11	-0.94	0.17	-0.72	-0.87	-0.36	-1.08
KA19	0.03	0	-0.18	-0.48	-3.84	-0.12	PL12	-0.98	0.59	-0.64	-0.8	-0.39	-1.12
KA20	-0.12	-0.41	-0.45	-0.75	-4.04	-0.27	PL13	-0.89	0.72	-0.63	-0.78	-0.41	-1.04
KA21	0.11	0.05	-0.09	-0.39	-4.01	-0.03	PL14	-0.85	0.76	-0.61	-0.76	-0.35	-1
KA22	0.08	-0.07	-0.3	-0.6	-3.71	-0.07	PL15	-0.77	0.9	-0.58	-0.74	-0.39	-0.91
KA23	0.06	-0.13	-0.49	-0.8	-5.26	-0.09	PL16	-0.72	0.18	-0.73	-0.88	-0.36	-0.86
KA24	-0.17	-0.49	-0.9	-1.21	-5.5	-0.31	PL17	-1	0.49	-0.57	-0.72	-0.37	-1.14
KA25	-0.16	-0.72	-0.73	-1.03	-4.64	-0.3	PL18	-0.69	0.18	-0.78	-0.94	-0.42	-0.84
KA26	-2.56	-4.87	0.25	-0.04	-3.6	-2.7	PL19	-0.65	0.86	-0.59	-0.74	-0.35	-0.79
KA27	-0.02	-1.19	-0.1	-0.39	-3.66	-0.16	PL20	-0.8	0.58	-0.43	-0.57	-0.24	-0.94
KA28	-0.47	-1.29	-0.26	-0.57	-4.62	-0.61	PL21	-0.75	0.69	-0.75	-0.9	-0.38	-0.89
KA29	-0.59	-0.89	-1.21	-1.52	-5.18	-0.74	PL22	-1.07	0.24	-0.72	-0.87	-0.38	-1.21
KA30	-0.19	-0.96	-0.41	-0.71	-4.09	-0.33	PL23	-0.66	0.86	-0.62	-0.77	-0.37	-0.8
KA31	-0.49	-1.65	-1.14	-1.44	-5	-0.64	PL24	-0.49	0.39	-0.75	-0.91	-0.47	-0.64
KA32	-0.16	-0.26	-0.75	-1.06	-4.91	-0.31	PL25	-0.72	0.09	-0.82	-0.98	-0.43	-0.86
KA33	-0.37	-1.11	-0.57	-0.87	-4.54	-0.51	PL26	-0.49	0.37	-0.6	-0.76	-0.43	-0.64

The electric conductivity (EC) of the water samples varies from 1462 (freshwater end member (KA9)) to 231000 (brine end member (SL26)) $\mu\text{S}/\text{cm}$. The mean value of EC for KPA and KPL is about 16,818 and 210,577 $\mu\text{S}/\text{cm}$, respectively. The total solid dissolve (TDS) ranges from 896 to 292500 mg/l (Fig. 5). The mean value of TDS for KPA and KPL is about 16,949 and 100,551 mg/l, respectively. The variation of TDS shows that 1, 45, 9, and 45% of the samples classify as freshwater, brackish water, saline, and brine, respectively. Pursuant to Fig. 5, the salinity increase by moving toward the groundwater flow direction (southwest to northeast). The pH ranges between 4.17 and 8.11 with an average of 6.93. The average temperature of the groundwater samples in KPA was 26.4°C. Na^+ and Ca^{2+} are the dominant cations and Cl^- and SO_4^{2-} are the dominant anions in KPA. The Ca^{2+} , Na^+ and Cl^- concentration varies from 84 to 10718, 202 to 110000 and 71 to 211000 mg/L, respectively. The concentration of SO_4^{2-} varies from 328 to 29400 mg/L. The average concentration of HCO_3^- in KPA is 186 mg/L and the concentration decrease by moving from southeast

of KPA toward the KPL. Also, Bromide concentration varies from 0.39 (KA9) to 139 (PL3) mg/l, respectively. Likewise, the mean value of Br for KPA and KPL is about 4.22 and 36.11 mg/l, respectively.

4.3. Hydrochemical Facies Evolution

Hydrochemical Facies Evolution Diagram (HFE-D) has been employed in order to provide information on salinization and freshening processes. The HFE-D (Fig. 6) shows the rate of Cl^- , SO_4^{2-} , HCO_3^- , Na^+ and Ca^{2+} controlling the process of intrusion, while the aquifer is affected by two mechanisms; (1) direct cation exchange, and (2) reverse cation exchange. According to this figure, the mixing line (Saltwater intrusion phase) shows intrusion (brine endmember with Na-Cl face) by replacement of Sodium by Calcium that indicate Reverse Cation Exchange (RCE) and freshening (fresh endmember with Ca- HCO_3 face) with exchange of Ca by Na that indicate direct cation exchange (Giménez-Forcada, 2010).

Fig. 6 also shows that hydrochemical facies in KPA to KPL is Ca- HCO_3 (19%), Mix Ca-Cl (9%), Ca-Cl (17%), Mix Na-Cl, and Na-Cl (55%) and reverse cation exchange RCE is the main cause of salinization in KPA which lead to depletion in Na and enrichment in Ca concentration. In intrusion stage, bellow conservative mixing line (blue line) in HFE-D (red and black solid diamonds), groundwater slowly was being salinity from MixCa-Mix HCO_3 to Na-Cl.

4.4. Hydrogeochemical approach

Hydrochemical evaluations use Na/Cl, Br/Cl and I/Cl ion ratios as well as other major Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , HCO_3^- ions to distinguish salinity and mixing of saline and fresh water (Fontes and Matray, 1993; Mirzavand et al., 2020a; Richter and Kreitler, 1993). To assess the influence of CaSO_4 and NaCl dissolution on groundwater salinization, binary plots of $(\text{Na}/\text{Cl})/\text{Cl}$, and $(\text{Ca}^{2+}+\text{Mg}^{2+})/\text{HCO}_3^-+\text{SO}_4^{2-}$ ratios are used (Richter and Kreitler, 1993). The seawater evaporation trend (SET) has been broadly applied to identify the source of salinization in sedimentary basins (Hanor et al., 1988; Kharaka and Hanor, 2005).

Waters influenced by halite dissolution and mixing with freshwater and brine fall above the SET (Mirzavand et al., 2020b), however, the saline groundwater originated from the evaporated sea waters distribute along the SET (Carpenter, 1978). Also, the Na/Cl molar ratio projected from the salt dissolution would be around 1 (Richter and Kreitler 1993). Likewise, the correlation of $\text{Ca}^{2+}+\text{Mg}^{2+}$ versus $\text{HCO}_3^-+\text{SO}_4^{2-}$ could be useful for investigation of gypsum, calcite and dolomite dissolution effect on groundwater quality (Jahanshahi and Zare, 2017). The samples which signed by the line 1:1, show the gypsum, dolomite and calcite dissolution, nevertheless the samples distributed below and above the line 1:1, illustrate freshening, and intrusion processes, respectively (Ben Ammar et al., 2020).

The brine from the dissolution of evaporite formations increases the molar ratio of Na^+ and Cl^- ions in water (Leonard and Ward, 1962). Besides, an increase in the concentration of SO_4^{2-} and Ca^{2+} due to dissolution of gypsum and anhydrite minerals in these conditions is likely.

As shown in the geology map of the area (Fig.1), Miocene Marl, Qom, LR and UR formations contain significant evaporite minerals such as halite and gypsum. In order to determine halite dissolution in KPA and KPL causing salinization, the Na/Cl ratio was used (Fig. 7). The Na/Cl vs. Cl of the KPA samples varies close to Halite dissolution line 1:1 (Fig. 7) suggesting dissolution of halite is a probable source of salinity. High concentrations of Cl with Na/Cl vs. Cl ratios of more than 1 might have experienced ion exchange and KPL samples, shifting the results below the halite dissolution line, indicating reverse cation exchange process (Fig. 7). The Na/Cl vs. Cl diagram also indicates the enrichment in Cl ion from recharge zone of KPA toward the KPL due to high evaporation effect on discharge zone of KPA and KPL.

Also, for study the contribution of gypsum dissolution in salinization, correlation between $\text{Ca}^{2+}+\text{Mg}^{2+}$ and $\text{HCO}_3^-+\text{SO}_4^{2-}$ has been investigated (Fig. 8). Some of the samples lie on the line 1:1, representing the gypsum, calcite and dolomite dissolution effect on KPA and KPL samples, which indicates minor effect of this mineral on salinization. The samples that plotted above the equilibrium line revealed reverse cation exchange (salinization) and domination of gypsum dissolution while samples falling below the equilibrium line (dominant dolomite and calcite dissolution), confirm freshening process.

Plot of $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs. $\text{SO}_4^{2-}+\text{HCO}_3^-$ is a major indicator to identify ion exchange process (Fisher and Mullican, 1997). If ion exchange is the process, the points tend to shift to the right side of the plot due to an excess of $\text{SO}_4^{2-}+\text{HCO}_3^-$. While the reverse ions exchange tend to shift to the left side due to excess of $\text{Ca}^{2+}+\text{Mg}^{2+}$ over $\text{SO}_4^{2-}+\text{HCO}_3^-$. Samples falling along the equilibrium line (1:1) showed the dissolution of calcite, dolomite and gypsum. Dissolution of carbonates contributed greatly to the regional groundwater evolution, especially with respect to the origins of Ca^{2+} , Mg^{2+} , and HCO_3^- , because most samples plotted along the 1:1 line. High SO_4^{2-} in waters accounted for by weathering of soluble sedimentary minerals releasing Ca^{2+} , Mg^{2+} and SO_4^{2-} such as via dissolution of gypsum or anhydrite. The presence of some samples above the equilibrium line indicated the occurrence of inverse ion exchange in these samples. However, the dominant process in this graph was the reverse ion exchange. Fig. 8 also shows that some of the samples are clustered around the 1:1 line, indicating reverse-ion exchange. The imbalance of the ratio of sulfate and bicarbonate dissolution to calcium and magnesium may indicate that dissolution of carbonates and sulfates were not the only sources of calcium supply. The samples falling below the equilibrium line suggests significant contribution from non-carbonate sources and the excess would be

balanced by alkalis (Na and K). As shown in Na vs. Cl diagram, contribution samples on $\text{Ca}^{2+}+\text{Mg}^{2+}$ vs. SO_4^{2-} diagram, reject intrusion from KPL to KPA.

Cl^- vs. Br^- concentration was presented in Fig. 9. Due to preferential partitioning of Cl over Br into K^+ , Mg^{2+} , and Na^+ halogen salts during precipitation (Vengosh et al., 2002), brines produced by the halite dissolution, have low Br^-/Cl^- ratios (Hanshaw and Hill, 1969; Worden, 1996). Samples with high Cl^- concentration, are depleted in Br^- and unaffected by seawater evaporation as characterized by the SET (Carpenter, 1978; Kharaka and Hanor, 2005). Generally, samples affected by the dissolution of halite and mixing of fresh waters and brine shift to the upper part of the SET, while samples which effected by evaporated waters plotted on the SET. The analyzed KPA and KPL samples are plotted on the SET on a direct line and show a dilution or mixing trend. Also, the distribution of samples rejects intrusion from KPL to KPA and seawater sources for saline waters. Br^- vs. Cl^- plot shows that most of the KPA samples are aligned with seawater dilution line confirming that, while the KPL samples distributed along the SET, showing the dissolution of halite as major source of salinity.

4.5. Stable isotopes

Stable isotopic compositions of the water are useful methods for identify the source and mechanism of salinization. The relationship between δD and $\delta^{18}\text{O}$ and $\delta^{18}\text{O}/\text{Br}$ has been used to investigate the groundwater salinization. Variations in δD and $\delta^{18}\text{O}$ of waters are used to identify the source of water (Bouchaou et al., 2009; Farid et al., 2015; Isawi et al., 2016; Gil-Márquez et al., 2017; Nunes et al., 2017), while the initial isotopes concentration are typically modified by dilution during the mixing process (Clark and Fritz, 1997).

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data of KPA and KPL with Global Meteoric Water Line (GMWL), Evaporation line (EL), and East Mediterranean Meteoric Water Line (EMMWL) are plotted in Fig. 10. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ varies from -10.03 to 7.03‰ with average of -6.95 ‰ for $\delta^{18}\text{O}$ and -60.73 to 25.08 ‰ with mean value of -45.82 ‰ for $\delta^2\text{H}$ (Table 3). Also, the $\delta^{34}\text{S}_{\text{SO}_4}$ varies from 5.95 to 22.55‰ in the study area (Table 3).

Table 3. $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ (‰) values in KPA and KPL

ID	$\delta^{34}\text{S}_{\text{SO}_4}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	d-excess	ID	$\delta^{34}\text{S}_{\text{SO}_4}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	d-excess
KA1	—	-55.26	-7.84	7.46	KA22	12.8	—	—	—
KA5	—	-54.19	-8.81	16.29	KA23	—	-57.23	-9.09	15.49
KA3	9.2	—	—	—	KA24	—	-57.51	-9.47	18.25
KA6	—	-49.91	-8.62	19.05	KA25	—	-57.79	-9.35	17.01
KA7	—	-59.06	-9.59	17.66	KA27	15.67	—	—	—
KA8	12.36	-55.71	-8.91	15.57	KA28	—	-54.54	-8.5	13.46
KA9	22.55	-60.73	-9.41	14.55	KA29	—	-58.04	-9.77	20.12
KA10	—	-50.44	-8.54	17.88	KA31	—	-56.19	-8.16	9.09
KA11	—	-56.88	-8.7	12.72	KA32	—	-59.65	-10.03	20.59
KA13	—	-56.18	-8.99	15.74	KA33	—	-58.89	-9.06	13.59
KA16	11.55	—	—	—	KA37	12.43	—	—	—
KA17	8.52	-56.11	-9.11	16.77	KA38	13.87	—	—	—
KA18	10.38	—	—	—	KA40	15.85	—	—	—
KA19	11.78	—	—	—	KPL3	5.95	21.78	6.03	-26.46
KA20	—	-56.36	-9.33	18.28	KPL12	9.99	25.08	7.03	-31.16
KA21	—	-53.74	-8.54	14.58	KPL26	8.84	22.68	6.48	-29.16

The fresh and saline groundwater samples plotted near the GMWL, with a lesser shift to the right due to membrane filtration, representing that the modern precipitations are the main source of groundwater. The brine samples collected from the wells in discharge zone of KPA, and KPL are plotted to the right side of the GMWL displaying enrichment in ^{18}O and ^2H due to evaporation effect. During the evaporation, solution preferentially depleted from lighter isotopes (Clark and Fritz, 1997) and enrichment in heavier isotope. This is compatible with the arid climatic condition in Kashan area situated in a desert region, where most of the precipitations evaporate prior to reaching the groundwater aquifer. In addition, over-pumping of the aquifer and groundwater is pumping from static storage.

The rocks forming the aquifer are mainly composed of marlstones, carbonates and evaporites which contain halite and gypsum. Thus, the source of salinity could be attributed to the deep brine waters that intruded into the aquifer during upconing and mixing process. Likewise, the saline groundwater is discharging to the northeast of the aquifer (discharge zone) and to the KPL which have been affected by intensive evaporation.

The relation between ^{18}O and Br^- (conservative parameter) could be used to investigate evaporation effect on water samples (Eissa, 2018). Fig. 11 shows increase in Br corresponds to the ^{18}O enrichment, indicating evaporation process is one of the main causes of enhancing isotopic values in KPL.

4.6. Water-rock Interaction

The SI is a valuable measure to conclude whether the groundwater is under-saturated, saturated, or super-saturated with respect to halite, gypsum, calcite, dolomite, aragonite, and anhydrite. The saturation indexes (SI) quantify the deviation of water samples from balance state with respect to minerals. Six Saturation indexes are applied to determine the varies geochemical processes and reactions that change the chemistry of water (Clark, 2015).

Based on the results (Table. 2 and Fig. 12) saturation indices in KPA and KPL indicate different trend and pathways. In KPA, the SI regarding calcite and dolomite are supersaturated in the recharge zone of aquifer, while these minerals shown under-saturation conditions in the discharge zone. Gypsum and halite showed under-saturated state for all the groundwater samples.

According to Fig. 12, by moving toward the discharge zone, gypsum and halite, tends to be in saturation state, because of reverse ion exchange process. Also, the saturation of dolomite and calcite was typically related to carbonate dissolution through the groundwater flow path. As shown in Fig.12, all the KPL samples, display saturated state with regard to calcite and dolomite. Also, KPL tends to be in saturation state regarding to gypsum and halite. During the salinization process, due to reverse ion exchange, depletion in Na^+ and Mg^{2+} , and enrichment in Ca^{2+} occur leading to conditions favorable for further gypsum and halite dissolution. While, during the freshening, because of direct cation exchange, enrichment in Na^+ and Mg^{2+} , and depletion of Ca^{2+} occurs and lead to conditions suitable for more calcite and dolomite dissolution.

4.7. $\delta^{34}\text{S}$ stable isotope as tracer for upconing and mixing Assessment

Fractionation of $\delta^{34}\text{S}$ isotopes between sulphur compounds is a useful approach to understand the biological cycling and sulphate reduction in natural systems (Wallin and Ab, 2011). The $\delta^{34}\text{S}$ value of SO_4^{2-} in modern seawater is close to 21‰ VCDT (Robert and Seal, 2006), whereas ancient marine evaporites shows $\delta^{34}\text{S}_{\text{SO}_4}$ values from +10 to +36‰ VCDT (Han et al., 2011; Hosono et al., 2015; Massmann et al., 2003; Robert and Seal, 2006; Wallin and Ab, 2011). For Tertiary period, $\delta^{34}\text{S}_{\text{SO}_4}$ is greater than 20 ‰ VCDT (Clark and Fritz, 1997). Generally, S^{2-} oxidation and SO_4^{2-} reduction lead to depletion and enrichment in $\delta^{34}\text{S}_{\text{SO}_4}$, respectively (Clark and Fritz, 1997). The Sulphur compounds from different sources could have contributed to the geochemical reactions in groundwater. Hence, the $\delta^{34}\text{S}$ isotopes can be a useful tracer for investigation of changes in the groundwater characteristics (Wallin and Ab, 2011) and upconing investigation. For determine the source of Sulphate and assessment upconing and mixing processes, 15 water samples were selected for $\delta^{34}\text{S}_{\text{SO}_4}$ analysis, including three KPL samples, and twelve groundwater samples, three (see Table 4).

Based on the results, except sample KA9 (fresh end-member) with $\delta^{34}\text{S}$ of 22.6‰, other samples have $\delta^{34}\text{S}$ range between 5.95‰ and 15.85‰ (see Fig. 13 and 14). Knowing the Tertiary age of geologic Formations in KPA, $\delta^{34}\text{S}_{\text{SO}_4}$ is greater than 20‰ (Fig. 14) which is compatible with freshwater end-member ($\delta^{34}\text{S}_{\text{SO}_4}=22.55‰$), while all the samples shown depletion in $\delta^{34}\text{S}_{\text{SO}_4}$.

Thus, sulphide minerals Galena (PbS), and Chalcopyrite (CuFeS_2) in Dore mine in west of the aquifer (recharge zone) may have been the source of depleted $\delta^{34}\text{S}_{\text{SO}_4}$ produced by sulphide oxidation leached to the aquifer by seasonal runoff. Based on Fig.13, by moving to northeast of the aquifer pH decrease to 4.17, HCO_3^- decrease (Table 1). This is an indication that sulphide oxidation in KPA has occurred causing depletion of $\delta^{34}\text{S}_{\text{SO}_4}$. Sulphate and H_2S formed through oxidation of sulphides or bacterial reduction, respectively, are isotopically significantly lighter at about +10‰. The most effective isotopic fractionation is caused by microbial reduction of dissolved sulphate to sulphide. During sulphate reduction, H_2S and HCO_3^- are generated increasing the pH. Sulphate reduction (“rotten egg” odour) occurred in deep brine and mixing with sulphide oxidation in freshwater during upconing and moving by groundwater flow (southwest to northeast of KPA), $\delta^{34}\text{S}$ shown values less than Tertiary values ($\delta^{34}\text{S}<20‰$) (Fig.14).

Table 4. $\delta^{34}\text{S}_{\text{SO}_4}$ (‰ CDT) values in KPA and KPL

ID	KA3	KA8	KA9	KA16	KA17	KA18	KA19	KA22	KA27	KA37	KA38	KA40	KPL3	KPL12	KPL26
$\delta^{34}\text{S}_{\text{SO}_4}$	9.2	12.36	22.55	11.55	8.52	10.38	11.78	12.8	15.67	12.43	13.87	15.85	8.95	9.99	8.84

Alternatively, in some systems, $\delta^{34}\text{S}$ can contribute to the understanding of groundwater mixing, especially when $\delta^{34}\text{S}$ plot against conservative tracer such as dissolved Cl^- and $\delta^{18}\text{O}$ (Wallin and Ab, 2011). Oxidation of sulphide yields sulphate with $\delta^{18}\text{O}$ larger than that of the oxygen in water molecules by +4 to +20‰ (Taylor et al., 1984) observed here. The increase in $\delta^{34}\text{S}_{\text{SO}_4}$ values is commonly followed by an increase in $\delta^{18}\text{O}$ and Cl values (Wallin and Ab, 2011). Based on the results, this pattern cannot be determined from plot between $\delta^{18}\text{O}$ - $\delta^{34}\text{S}_{\text{SO}_4}$ and Cl - $\delta^{34}\text{S}$ (Fig. 15a,b). So, there are other processes which changed this pattern described by Laaksoharju (1995). The sulphur in KPA and KPL should be changed due to sulphide oxidation and sulphate reduction in the aquifer.

Conclusions

In spite of extensive study on the source and mechanism of groundwater salinization, only few studies are available for continental groundwater/playa lakes. Most of these studies are available for coastal aquifers. This research is the first study to delineate the interaction between aquifer and Salt lake playa in Iran using hydrogeochemistry and isotopic techniques.

Groundwater salinization is critical in KPA, a major source of water for about half a million people in Kashan City. Understanding groundwater salinization in KPA and interaction with KPL has important role for long-term aquifer management. The geologic map, geophysical information, hydrogeology data, and hydrochemistry and isotopes techniques of KPA and KPL indicate that saline groundwater discharge to the KPL and ruled out intrusion from Playa Lake to the aquifer. The mineralization of groundwater in KPA has a homogenous mechanism. The rock–water interaction is main factor which control the chemistry of deep groundwater. Shallow groundwater mainly controlled by upconing (Anthropogenic activity) and evaporation processes. However, groundwater salinization in the KPA seems to have natural origin (halite and gypsum dissolution in the bed rock of KPA), but exacerbated by anthropogenic activities like over-pumping and upconing. The discharge flow from KPA is also an imperative component in KPL mineralization control. The results show that the dehydration status of CaSO_4 in the KPL is affected by high evaporation and salinity related to the extreme aridity in the region. The potential sources of groundwater could be meteoric, present or paleo-groundwater.

The mechanisms controlling groundwater quality is important for implementing effective remediation and scientific paradigms for management of aquifer and controlling the groundwater salinization. It is suggested that an amalgamation of the above mentioned techniques, and further techniques such as groundwater dating (such as ^3H - ^4He), could be applied for determine groundwater dynamic in such complex aquifer, therefore decreasing the degree of uncertainty.

Declarations

-Ethical Approval and Consent to Participate

Not applicable

-Consent to Publish

Not applicable

-Availability of data and materials

All data and materials for this study are included in the manuscript.

-Competing Interests

The authors declare that they have no competing interests

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-Authors Contributions

MM contributed in sampling, analysis, interpretation, and writing of manuscript. Also, FGh contributed in interpretation and writing of manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1
Geologic map of the KPA and KPL and sampling locations

Figure 2
Hydrological network in Salt lake basin

Figure 3
Geoelectric profiles in Kashan plain

A

B

Figure 4

Longitudinal (Green line in Fig. 3) and transverse (Pink line in Fig. 3) geo-electric cross section in KPA

Figure 5

TDS variation in KPA and KPL

Figure 6

HFE-D of KPA and KPL (black diamonds) samples

Figure 7

Na/Cl vs. Cl concentrations of KPA samples (blue circles), and KPL samples (red diamonds)

Figure 8

Ca²⁺+Mg²⁺ vs. HCO₃⁻+SO₄²⁻ concentrations of KPA (Blue circles) and KPL samples (red diamonds)

Figure 9

Br vs. Cl of KPA (red diamonds) and KPL (blue triangular) water samples

Figure 10

The $\delta^{18}O$ vs. δ^2H isotopes of KPA (circles) and KPL (diamonds)

Figure 11

$\delta^{18}\text{O}$ vs. Br concentration in KPA and KPL water samples

Figure 12

Saturation indices of investigated minerals in water samples of KPA and KPL

Figure 13

Distribution map of SO42- concentration, pH contour line, and $\delta^{34}\text{SSO}_4^{2-}$ in KPA and KPL

Figure 14

$\delta^{34}\text{SSO}_4$ vs. SO_4^{2-} for KPA and KPL (solid red diamonds)

Figure 15

a,b. $\delta^{34}\text{SSO}_4$ vs. $\delta^{18}\text{O}$ (a) and $\delta^{34}\text{SSO}_4$ vs. Cl (b) for samples of KPA and KPL