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REVIEW

An overview on source, mechanism and investigation approaches in groundwater salinization studies

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Abstract

Groundwater quality, as major source of freshwater, is an important factor in sustainable development and water resources management. Due to increase in water demand in developing countries and overexploitation, groundwater quality has decreased in many aquifers in the world. One of the most important factors which decrease the groundwater quality is salinization. The aim of this study is to comprehensively review the sources and mechanisms of salinization. Based on our review, the major sources of groundwater salinization consist of marine sources (e.g., connate saline groundwater, marine transgressions, incidental flooding by seawater, lateral seawater intrusion and seawater sprays), natural continental sources (e.g., evaporation, soluble minerals, membrane effects and geothermal origin), anthropogenic activities and multiplicity sources. Research approaches in groundwater salinization include hydrogeochemical and isotopic tracers, hydrogeochemical models and groundwater dating isotopes (radioisotopes). The simple and clear guideline presented in this paper can be applied to investigate the groundwater salinization by researchers in the world.

Keywords Salinization · Salinity source · Global hazard · Hydrogeochemistry · Environmental isotopes

Introduction

Groundwater quality is an important factor in sustainable development and water resource management (Mirzavand et al. 2014; Mirzavand and Ghazavi 2015). Groundwater salinization is one of the most important reasons of diminishing groundwater quality (Vengosh et al. 2002a, b). Salinization is a long-term process, and during the last decades many aquifers in the world have become unsuitable for human use due to overpumping and salinization. Future exploitation of aquifers in many water-scarce regions, such as the arid and semiarid environment, depends mainly on the rate of salinization. The term "groundwater salinization" is used to specify an increase in overall chemical content over background levels in groundwater (van Weert et al. 2009). Generally, the word "saline groundwater" includes brackish to brine groundwaters. The groundwater can be classified into four categories based on levels of salinity (Fig. 1) (Clark 2015; Freeze and Cherry 1979). Proper management of accessible groundwater resources is impossible without knowledge of the distribution of fresh and saline groundwater and the processes that lead to salinization (Clark 2015). Saltwater intrusion is a long-term process and could degrade groundwater system and restrict the availability of useable water for drinking, irrigation and industry (Vengosh 2014). Proximity of groundwater system to seawater, salt lake, mineral dissolution and anthropogenic activity (such as overpumping) in coastal aquifer could destroy freshwater resources (Vengosh 2003, 2014). Chemical composition of groundwater in a coastal aquifer is a function of the rate of fresh/saltwater mixing from different salinity sources such as water–rock interaction, cation exchange, redox reaction, carbonate and evaporate mineral dissolution, old salty water

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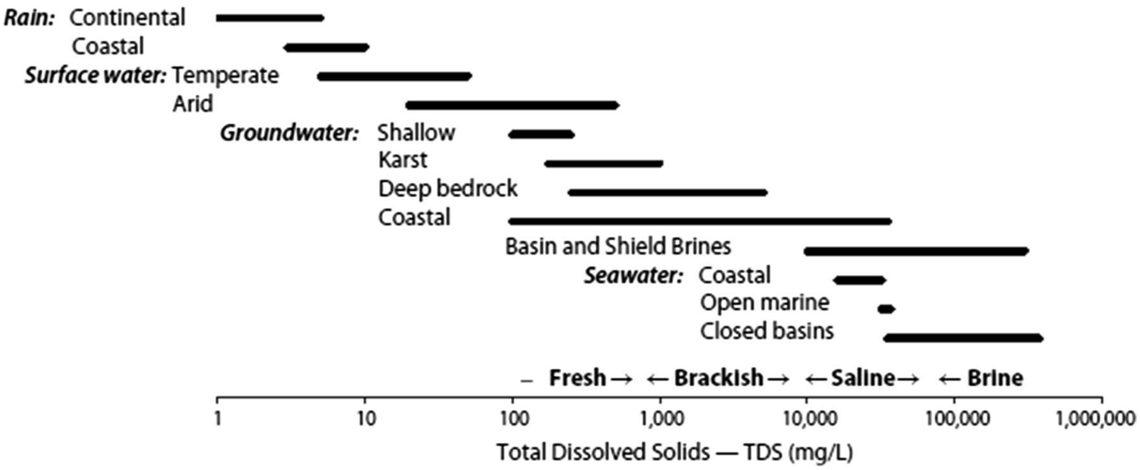

Fig. 1 Water quality classification based on TDS variation (Amiri et al. 2016b)

tapped in the aquifer and seawater/salt lake intrusion (Bagheri et al. 2014; Clark 2015; Mirzavand et al. 2018a, b; Nadri et al. 2014; Vengosh 2003). For the effective management of groundwater resources, especially in arid and semiarid regions, policies depend on understanding the sources and mechanism of groundwater system salinization (Bagheri et al. 2019; Clark 2015). Hence, many researchers all over the world use hydrogeochemical mixing diagrams, geoelectric modeling and isotopic techniques for determining the origin and mechanism of groundwater salinization (Zarroca et al. 2011; Tomaszkiewicz et al. 2014; Amiri et al. 2016a, b, c).

Numerous summits and conferences are held every year around the world to deal with the problem of aquifers salinization, especially coastal aquifers. The most important meeting on the influx of saltwater intrusion (SWIMs) into groundwater systems was established in 1968 (Mirzavand 2018). Recently, the SWIMs are more discussed about modeling of water resources, hydrogeology, hydrogeochemistry and isotopic studies of the groundwaters. Also, a special group in Cartagena was established since 2001 which called saltwater intrusion in coastal aquifers (SWICA) to investigate the issue of saltwater intrusion on a global scale. (Mirzavand 2018). So, as could be seen, the issue of groundwater salinization is a global concern (Vengosh et al. 2002a, b; van Weert et al. 2009) and a serious problem especially in arid and semiarid areas, where the ground water is a vital resource. Not only will many job opportunities disappear due to groundwater salinization, but also many species of wildlife will be extinct. Therefore, with regard to harmful effects of groundwater salinization as a global concern, this paper aims to provide a comprehensive overview of the sources and mechanisms of groundwater salinization and to provide better insight for the interested readers. Hence, the review aims to summarize the sources and mechanism of saltwater intrusion and provides an overview of hydrogeochemical and isotopic techniques for groundwater salinization. Based on this review, the researchers would be able to know and study the groundwater salinization process and dating.

It is needed to mention that this is the first overview of groundwater salinization in this view, and the previous overview (Werner et al. 2013) focused on coastal saltwater intrusion and numerical models. But, in this paper, we describe and interoperate all kinds of salinity sources and mechanisms, hydrogeochemical, isotopic (stable and radioactive) and geophysical approaches, which are important in groundwater salinization studies.

Results and discussion

Groundwater salinization

The main sources of groundwater salinization which commonly deteriorate fresh groundwater include three major classes of natural continental sources, marine sources and anthropogenic sources (Fig. 2) (Mirzavand 2018; van Weert et al. 2009). In the following, the different salinity sources are discussed in details.

Saline groundwater with marine source

The marine source can salinize the groundwaters via different mechanisms such as connate saline water and seawater spray mechanism (Fig. 2).

- Connate (residual) saline groundwater

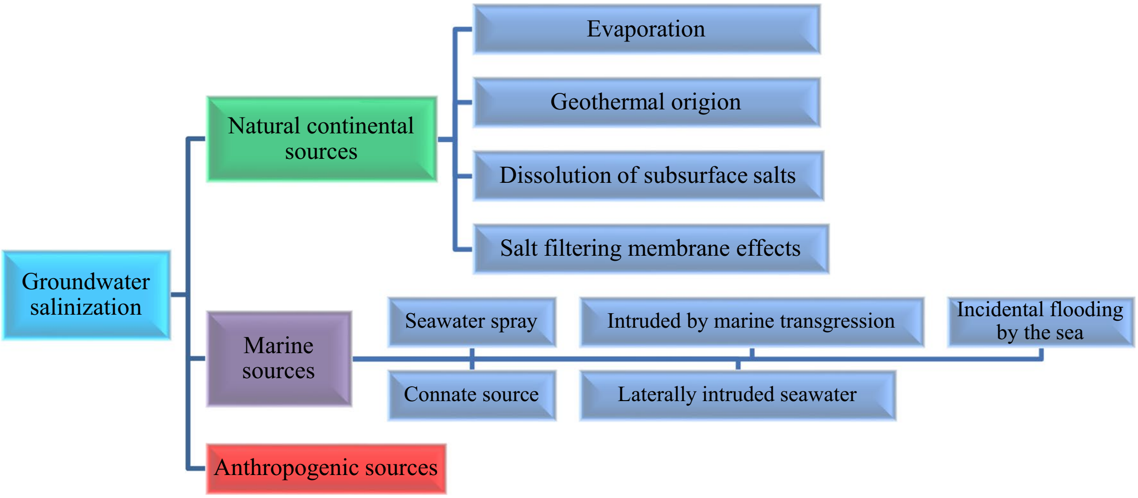

Fig. 2 The potential sources of groundwater salinization

The origin of saline groundwater in deep sedimentary environments can be residual waters that are stored simultaneously with sedimentation in a saline environment (Monjerezi 2012). However, the saline groundwater is intrinsically connate because of various chemical and physical changes that occur after sedimentation (Bagheri et al. 2013). Residual brines can be part of evaporated continental or marine waters that have been buried or infiltrated into the ground (Freeze and Cherry 1979; Jones et al. 1999). In polar areas, connate brines can be derived from isolated continental surface waters and freezing of seawater (Bein and Arad 1992; Bottomley et al. 1999; Herut et al. 1990; Marison et al. 1999; Matsubaya et al. 1978; Nelson and Thompson 1954; Richardson 1976; Stein et al. 1997; Yaqing et al. 2000). Fluids from these sedimentary and crystalline environments are usually characterized as Na–Cl, Na–Ca–Cl, Ca–Na–Cl or Ca–Cl_2 brines (Bottomley et al. 1999; Davisson and Criss 1996; Wilson and Long 1993; Yaqing et al. 2000). Residual brines are often not found in shallow subsurface due to natural flushing in the formations by precipitation over time. Normally, natural salinity in groundwater increases with the depth due to residence time, chemical reactions and mixing process (Clark 2015).

- Saline groundwater originating from marine transgressions

Seawater intrusion is one of the main causes of groundwater quality degradation in coastal aquifers (Kim et al. 2003; Vengosh et al. 2002a, b; Wicks and Herman 1996). Normally in coastal aquifers, groundwater flows toward the sea/ocean water due to the hydraulic gradient and dynamic equilibrium between freshwater and seawater (Hubbert 1940; Kohout 1960). But, due to changing in sea/ocean level or water table decline, this hydraulic gradient and dynamic equilibrium can be changed over geological time. As a result, coastal aquifers become submerged with the advent of seawater. In these conditions, saltwater penetrates the groundwater system, and as long as this trend continues, coastal aquifers remain salinize (Monjerezi 2012).

- Incidental flooding by seawater

Like groundwater, which has become saline as a result of seawater level rising, this origin is also caused by the rise of seawater level (Monjerezi 2012). But this happens over a shorter period of time. When the sea level is exceptionally high, like when the tsunami phenomenon occurs, or as the coastal walls are degraded as a result of tide, the salt water intrudes the coastal plains. Even though the flooding time is short relative to the rise of seawater level during the seawater rising, a greater region of coastal aquifers may be affected by flood. Consequently, flushing the sea salt on the surface of the floodplain can increase the salinity of groundwater in coastal aquifers. As this process is repeated, not only surface water is salted, but also salty water infiltrates deep parts of the aquifers (Monjerezi 2012). This can happen in coastal aquifers in arid and semiarid regions which are close to inland salt lakes. In this case, as a result of historical flood, the salt lake water level rises and sedimentation will occur in a wider area. Finally, evaporative minerals can be deposited on the margin of these lakes and penetrate the deep layers of adjacent aquifers by flushing process (Mirzavand 2018).

- Laterally seawater intrusion

This type of salinization happens in coastal zones due to interaction between sea and coastal aquifer. Lateral intrusion may be enhanced through surface and groundwaters that flow to the sea (van Weert et al. 2009).

- Seawater spray

  In coastal areas, atmospheric moisture may be rich in sea salts through seawater sprays. These salty aerosols are mixed by the rain and are absorbed in recharge regions of groundwater causing groundwater salinization (Monjerezi 2012).

Groundwater salinization with natural continental sources

This class of saline groundwaters subdivides into four classes:

- Evaporation at or near land surface

  Evaporation is the most important process for soil and groundwater salinization (Deverel and Gallanthine 1989) in areas with the shallow water table depth (<5 m) and high evaporation potential (Yechieli and Wood 2002; Sowayan and Allayla 1989). In closed basins, brines in evaporative minerals (e.g., calcite and halite) dissolve in recharge zone and increase the groundwater salinity over time. Due to overpumping and negative water balance, salinity content increases from recharge zone to discharge areas, and so hydrochemical faces change from Ca–HCO_3 to Na–Cl (Monjerezi 2012). The differences in chemical component are mainly due to alterations and reactions through flow direction in aquifer (Berner and Berner 2012). Nevertheless, in most cases, the concentration of salts, especially chlorides, increases until halite saturation state (Richter and Kreitler 1993) with hydrochemical faces of Na–Mg-Cl–SO_4 (Jones and Vandenburgh 1969).
- Dissolution of naturally occurring soluble minerals

  In sedimentary basins, the dissolution of evaporative minerals is a known cause of salinization (Bagheri et al. 2014; Herczeg et al. 1991; McManus and Hanor 1993; Nesbitt and Cramer 1993; Vengosh et al. 2002a, b) and the reason is that many sedimentary basins have halite salt as bedrock of aquifer. However, the salt dome may develop as a result of the uplift of salt to the ground surface (Richter and Kreitler 1993). Depending on the date of deposition, halite deposits might be associated with other salts such as chloride salts (Carnalite $KMgCl_3{\cdot}6H_2O$) or sylvite (KCl), sulfates (polyethylene ($K_2Ca_2Mg(SO_4)\text{-}4{\cdot}H_2O$)), anhydrite ($CaSO_4$), gypsum ($CaSO_4{\cdot}2H_2O$), carbonates (such as dolomite ($CaMg(CO_3)_2$ and/or calcite ($CaCO_3$)). Halite and these salts can change the chemical composition and increase the salinity of groundwater (McManus and Hanor 1993; Richter and Kreitler 1993) (Bennetts et al. 2006). These types of brines may be discharged to the surface or become part of a groundwater system (Mirzavand 2018; Richter and Kreitler 1986, 1993). In arid and semiarid regions where evaporation is higher, evapotranspiration increases the concentration of salt in surface water bodies and shallow groundwaters. As a result, seasonal rainfall flushes these salts into groundwater resources (Mirzavand 2018).
- Membrane effects

  The principle of reverse osmosis membrane filtration was applied to describe the salinity source of deep brines in sedimentary basins (Richter and Kreitler 1993). This process involves the formation of a hydraulic fluid flow from brines through a semipermeable environment such as shale and clay sediments (Graf 1982; Manheim and Horn 1968). As a result, the neutral water molecules pass easily over the shale or clay layers in comparison with dissolved ions. This salt filtration is due to electrostatic repulsion of dissolved ions as a result of double electrical layers around clay particles (Kharaka and Hanor 2005). In this case, as the fluid passes through the membrane, filtration of the selected cations and anions causes one side of the membrane to become gradually more saline from the other side (Bagheri et al. 2019; Mirzavand et al. 2018a, b). In deep alluvial basins, clay or shale layers may be very compact and act as semipermeable membranes (Berry 1973; Hanshaw and Hill 1969; Kharaka and Berry 1973; McKelvey and Milne 1969). Although the reverse osmosis mechanism in deep brine sedimentary basins has been investigated as a salinization mechanism (Berry 1973; Graf 1982), the significance of membrane filtration in the modification of chemical compounds of groundwater is still controversial (Hanor 1987).
- Geothermal activity

  In some areas where igneous rocks are dominant, groundwater can become highly mineralized. In such cases, these water sources are rich in minerals and called thermo-mineral waters. Therefore, these types of hydrothermal water-based systems can convey saline and hot groundwater to the surface. In addition to chloride content, hot springs are often rich in bromine, fluoride, sodium, arsenic and other pollutants that threaten the quality of freshwater (Edmunds et al. 2003; Vengosh et al. 2002a, b).

Groundwater salinization due to anthropogenic activities

Significant examples of salinization of groundwater resources due to anthropogenic activities include domestic, agricultural and industrial effluents; desalinization plants; road salt; and oil and gas field brines (Clark and Fritz 1997; Hanor 1987; Mirnejad et al. 2011; Vengosh et al. 2002a, b). These types of activities often lead to local salinization of groundwater resources. The dissolution of the salts used on the road surface in order to deice (defrost) the roads is an important source of salinity of surface water (Richter and Kreitler 1993). Another major concern is the salinity of domestic wastewater caused by the use of detergents and salts (Vengosh et al. 1994). In areas where there is water crisis, most of these polluted water sources are used for irrigation, which ultimately leads to soil and groundwater salinity (Beltran 1999; Ronen et al. 1987; Zalidis et al. 2000). Agricultural activities may cause groundwater and soil salinity due to the degradation of natural vegetation cover and farm irrigation with salt water. The soil salinization of irrigation and dryland area occurs when the water table of the saline groundwater is close to the surface (Jenkin 1981; Peck and Williamson 1987; Ruprecht and Schofield 1991). As a result, due to the property of capillarity, salt is transported to the surface and the concentration of salt increases during evaporation (George et al. 1997). In fact, the salinity of agricultural wastewaters depends on (1) the balance between the input and the output salt of the soil, (2) salinity of the soil, (3) the quality of irrigation water and (4) the rate of application of manure and fertilizers in agricultural lands (Hern and Feltz 1998).

Naturally, in arid and semiarid regions, the irrigation of saline soil lands could lead to the flushing of salts into groundwater resources (Monjerezi 2012). The contamination of groundwater by the oil and gas field's brines happens during the mixing between brine and freshwaters due to oil or gas extractions. Disposal approaches such as surface disposal, uncoated surface pits and injection wells may also result in salinization (Richter and Kreitler 1993). Salt flushing from such pits and long-term use of them leads to the introduction of brines into groundwater resources and, consequently, salinization of aquifers. Of course, it should be noted that the salinization of water resources by injectable wells in oil and gas fields occurs only when the hydraulic connection between oil and gas and aquifer is established (Richter and Kreitler 1993). Another anthropogenic activity that affects the salinity of water resources is land use changing and excessive pumping from coastal aquifers. By increasing the depth of agricultural wells and overpumping of groundwater resources, the hydraulic gradient between surface water and groundwater changes, and as a consequence, deep groundwater brines will mix with freshwater through upcoming process (Mirzavand 2018).

Saline groundwater produced as a result of multiplicity source

The origin of groundwater salinization may be multiplicity source. In this type of salinization, a combination of above sources is simultaneously affecting the groundwater salinization (Mirzavand 2018). Given the characteristics of resident time of groundwater, when the source of saline water is determined, the effect of time should not be ignored. In other words, groundwater dating should be done in order to identify and distinguish different sources of salinization (Weert et al. 2009).

Groundwater salinization investigation approaches

The multiplicity of salinity sources makes delineation of origin and mechanism of groundwater salinization highly complex (Richter and Kreitler 1993). Study of spatiotemporal distribution of stable and radioactive isotopes (O, H, C, S, Sr, Br, B, Sm, Nd, U, Th, Cl and I) is a useful tool in determining the sources and mechanism of groundwater salinization (Banner et al. 1989; Clark 2015; Mirzavand 2018; Sheppard 1986; Vengosh et al. 2002a, b). The basic principle in isotopic and chemical techniques used for tracing salinity sources is based on the hypothesis that the fingerprint of the original source is conserved during the salinization process. However, processes such as evaporation, water–rock interaction and membrane filtration could change the original isotopic and chemical composition of the salinity source. As such, the combination of isotopic and hydrogeochemical techniques provides imperative and integrated information in identifying the source and mechanism of groundwater salinization (Mirzavand 2018; Vengosh et al. 2002a, b). Beside the hydrochemical and isotopic approaches, the geophysics technique could also be useful in groundwater salinization study.

Geochemical tracers

The main principle in all the hydrogeochemical techniques is that the chemical properties of the source of salinity are assumed to be maintained during the process of groundwater salinization. However, the water–rock interaction may change the composition of the source of salinity, and consequently, determination of the source and mechanism of salinity becomes rather complicated (Mahmoodzadeh and Karamouz 2019; Vengosh 2005). Composite plots of minor and major ions such as Na^+/Cl^-, Br^-/Cl^-, I/Cl^-, $SO4^{2-}/Cl^-$, Ca^{2+}/Cl^-, B/Cl^-, Mg^{2+}/Cl^-, Cl^-/NO_3^-, K^+/Cl^- and $(Ca^{2+}+Mg^{2+})/SO_4^{2-}$ could be used to separate the major sources of salinity and determine the mechanism of groundwater salinization (Alcalá and Custodio 2008; Bagheri et al. 2013; Bennetts et al. 2006; Harkness et al. 2017; Isawi et al. 2016; Lai et al. 2017; Mirzavand 2018; Naseem et al. 2017; Petalas et al. 2009; Raju et al. 2015; Sridharan and Senthil Nathan 2017; Zarei et al. 2013). The minor and major elements exist in distinct ratios in diverse sources of salinity. Nevertheless, these composite plots can be used as geochemical tracers once there is insignificant impact of geochemical reactions after mixing between fresh groundwater and particular salinity sources.

As such, these composite plots are useful tools at high salinity content (Richter and Kreitler 1993). In other cases, relatively conservative chemical parameters such as bromide, lithium, chloride and iodide are normally used. Cl–Br relationships are normally applied to separate nonmarine and marine origins of salinity (Bagheri et al. 2014). Cl is preferentially partitioned over Br into Na, K and Mg halogen salts throughout precipitation (Siemann and Schramm 2000). Hence, brines made by the dissolution of NaCl are associated with low Br/Cl ratios (Bagheri et al. 2013; Hanshaw and Hill 1969; Mirzavand 2018; Worden 1996).

In other words, brines produced from evaporated seawater are categorized by high Br/Cl (Bagheri et al. 2013). The seawater evaporation trend (SET) has been extensively used to determine the origin of the salinity in different basins (Bagheri et al. 2014; Kharaka and Hanor 2005). Normally, waters affected by halite dissolution and mixing between halite dissolution brine and freshwaters fall above the SET, while the saline water originated from the evaporated seawaters lies on the SET (Bagheri et al. 2013; Carpenter 1978; Mirzavand 2018). The Na/Cl molar ratio anticipated from the salt dissolution would be about 1 (Bagheri et al. 2013; Richter and Kreitler 1993). While the Na/Cl and Na versus Cl molar ratios of investigated water samples vary close to this value, suggesting that halite dissolution is a likely origin of salinity. Water samples with high Cl concentrations yet with Na/Cl molar ratios less than 1 may have experienced cation exchange (Bagheri et al. 2014).

Isotope tracers

Due to the stability of stable isotopes over time, they are valuable tracers for determining the source and mechanism of salinization (Clark 2015). For this purpose, the most widely used isotopes in the hydrogeological studies are presented. The variations in δ^{18}O and δD of water are used to trace sources of water (Ayadi et al. 2016; Bagheri et al. 2013; Bouchaou et al. 2009; Clark 2015; Farid et al. 2015; Gil-Márquez et al. 2017; Isawi et al. 2016; Li et al. 2011; Mirzavand 2018; Nunes et al. 2017; Tweed et al. 2011), but the original values of water molecules isotopes are usually modified by dilution during mixing (Banner et al. 1989; Clark and Fritz 1997; Hanor 1994). Also, δD-δ^{18}O relationships can be used for calculating mixing ratio between fresh groundwater and saline or brines during saltwater intrusion (Yechieli and Wood 2002) or investigating irrigation return flows (Mirzavand 2018; Vengosh 2014). The δD-δ^{18}O relationships may also be used for studying the water–rock interaction (Bagheri et al. 2013; Vengosh 2014) and investigation of seawater evaporation effect (Bagheri et al. 2013), direct seawater intrusion (Najib et al. 2017) and upconing process (Amin Sharaf et al. 2001; Marandi and Vallner 2010; Mirzavand 2018). These isotopes may also be used to study the effect of evaporation and membrane filtration on groundwater salinization (Bagheri et al. 2013; Mirzavand 2018; Vengosh 2014).

The ^{11}B/^{10}B ratio can be used to separate natural fresh and saline waters (Barth 1998; Bassett et al. 1995; Bouchaou et al. 2008; Harkness et al. 2017; Hogan and Blum 2003; Mahlknecht et al. 2017; Warner et al. 2013). Boron has a tendency to be adsorbed by oxides and clay minerals, mainly in high saline settings. The δ^{10}B is preferentially incorporated into adsorption settings, while the remnant dissolved B is enriched in the δ^{11}B (Barth 1998). The δ^{7}Li may be used to separate natural fresh and saline waters (Harkness et al. 2017; Hogan and Blum 2003). ^{87}Sr/^{86}Sr are used to identify weathering processes and the origins of strontium (Andrew et al. 2005, 2017; Bagheri et al. 2013; Bouchaou et al. 2008; Harkness et al. 2017; Lyons et al. 1995; Mahlknecht et al. 2017; Warner et al. 2013; Wiegand 2009), mixing process of groundwater in a basin with diverse geology formations and flow-paths (Bagheri et al. 2013; Jones et al. 1999). ^{87}Sr/^{86}Sr can also be used to delineate salinization process by return flow from farms (Böhlke 2002).

Several projects have been carried out related to $\delta^{34}S_{SO4}$ signature in groundwater system (Han et al. 2011; Hosono et al. 2015; Jakóbczyk-Karpierz et al. 2017; Kaown et al. 2009; Li et al. 2011; Mirzavand 2018; Nunes et al. 2017; Samborska et al. 2013; Tostevin et al. 2016) with the aim of determining the origin of sulfate and salinization. Generally, sulfate reduction and sulfide oxidation make enrichment and depletion in $\delta^{34}S_{SO4}$, respectively (Deverel and Gallanthine 1989).

δ^{37}Cl is preferentially fractionate into the solid phase by deposition of halite from seawater evaporation; hence, δ^{37}Cl of the remnant brines and of subsequently deposited halite would be lighter. (Bagheri et al. 2013; Hanlon et al. 2017). Meteoric chloride is then considered by a high ^{37}Cl/Cl signature that is conserved through evaporative concentration and salts recycling through precipitation–dissolution (Bagheri et al. 2013). In contrast, additional saline and brine sources such as oilfield brines and road salts are significantly depleted in ^{37}Cl/Cl ratios. Likewise, modern meteoric water (MMW) is projected to be enriched in ^{129}I/^{127}I than fossil waters (Clark 2015; Monjerezi 2012).

δ^{81}Br is used for salt precipitation investigation (Bagheri et al. 2013). The ^{143}Nd/^{144}Nd isotopes are used to separate multiple salinity sources and determine the amount of water–rock interaction, mixing processes and mixing history in aquifer (Négrel et al. 2000, 2001).

Salt effect correction on the measurement of δ^{18}0 and δ^{2}H

In saline waters, the hydration of the ion results in the depletion of the water isotopes. Simultaneously with the deposition of salts, water crystallization has a greater effect on the process. On the other hand, by analyzing deuterium and oxygen-18 by the Gasbench + DeltaPlusXP method, oxygen-18 and deuterium are measured in carbon dioxide and hydrogen equilibrated with water. Therefore, these measured isotope values represent the deuterium and oxygen-18 activity. The isotope activity of saline waters decreases with increasing salinity while the concentration remains the same. Hence, the amount of activity obtained should be modified so that it can be expressed as a concentration (Clark and Fritz 1997; Sofer and Gat 1972). The equations are presented below:

$$\delta^{18}\mathrm{O}_{\mathrm{corrected}} = \left(\frac{1.11\ \mathrm{mMg} + 0.47\ \mathrm{mCa} - 0.16\ \mathrm{mK}}{1000}\right) \cdot \left(\delta^{18}\mathrm{O}_{\mathrm{meas}} + 1000\right) + \delta^{18}\mathrm{O}_{\mathrm{meas}} \tag{1}$$

$$\delta^{2}\mathrm{H}_{\mathrm{corrected}} = \left(\frac{-0.4\ \mathrm{mNa} - 5.1\ \mathrm{mMg} - 6.1\ \mathrm{mCa} - 2.4\ \mathrm{mK}}{1000}\right) \cdot \left(\delta^{2}\mathrm{H}_{\mathrm{meas}} + 1000\right) + \delta^{2}\mathrm{H}_{\mathrm{meas}} \tag{2}$$

where m is molality of ion concentration.

Geophysics groundwater investigation

The geoelectric resistivity measurement method was originally developed by Schlumberger, a professor of physics at the Paris School of Advanced Mine in 1912 (Sikdar et al. 2001). Typically, geophysical methods (for example, electrical and electromagnetic methods) are used to identify the extent of the aquifer and its thickness, the quantity and quality (the boundaries) of the reservoir water as well as the determination of the profile and depth of the aquitard (Mirzavand 2018). The electrical resistivity method is very sensitive to the salinity of water between pores beneath the surface of the ground and is therefore a suitable method for differentiating salty and freshwater sources and their interface (Banner et al. 1989; Ma et al. 2007). A disadvantage of geophysical methods is impossibility to determine the origin and mechanism of groundwater salinization (Mirzavand 2018).

Hydrogeochemical modeling techniques

Mass transfer models (MTM)

The thermodynamic method of mineral solubility and equilibrium speciation codes can be extended to include mass transfer models (MTM). These models allow us to simulate the effects of geochemical processes such as mineral dissolution and precipitation, groundwater mixing, cation exchange, gas exchange or degassing (Clark 2015). The concept of MTM is based on the speciation codes, with the loss or gain of mass controlled by precipitation or dissolution of minerals through gas exchange with the open atmosphere or soil (Clark 2015). One of these models is PHREEQE that let us model mixing and reaction pathways and includes effects of hydrodynamic dispersion (Parkhurst 1995). SOLMINEQ. 88 (Kharaka et al. 1988) and PHRQPITZ (Plummer et al. 1988) were developed to accommodate the Pitzer (1987) (Pitzer 1973) relations needed for speciation modeling of brines with high ionic strength.

Hydrogeochemical faces evolution diagrams

For hydrochemical facies evolution, different models have been proposed such as Piper (1944), Durov (1948), Stiff (1951) and hydrochemical facies evolution diagram (HFE-D) (Giménez-forcada 2010). The Piper and Durov diagrams were conceived to be diagrams for water classification, delineation of potential water mixing between salt/freshwater end-members and to aid in the determination of reactions controlling water quality (Shelton et al. 2018).

HFE-M gives more effective information about freshening and intrusion processes (Amiri et al. 2016a; Mirzavand 2018). The HFE-M provides an effective way to recognize intrusion/freshening phases during saltwater intrusion and freshening which are recognized by the distribution of cation and anion percentages in the square model (Fig. 3). The HFE-D reflects the percentage of the main anions (Cl^{-}, $SO4^{2-}$ and $HCO3^{-}$) and cations (Na^{+} and Ca^{2+}) which control the dynamics of intrusion (Amiri et al. 2016a, b, c). In this model, the groundwater system is affected through two processes: (1) reverse cation exchange (line II) and (2) direct cation exchange (line II'). The hydrogeochemical faces evolve from freshwater (Ca-HCO3) toward saline/saltwater (Na–Cl) (Giménez-forcada 2010).

Groundwater dating and discrimination of the role of different contaminations

Groundwaters can have fast (daily) or long recharge cycle (thousands or millions of years) according to aquifer characteristics, regional climate and geographical conditions (Clark 2015). Most of the aquifers have a short recharge time, but some of them, including deep aquifers and fossil groundwaters, have a high residence time, and the recharge time of these aquifers may be tens of million years (IAEA 2013). Also, in aquifers located in arid and desert regions,

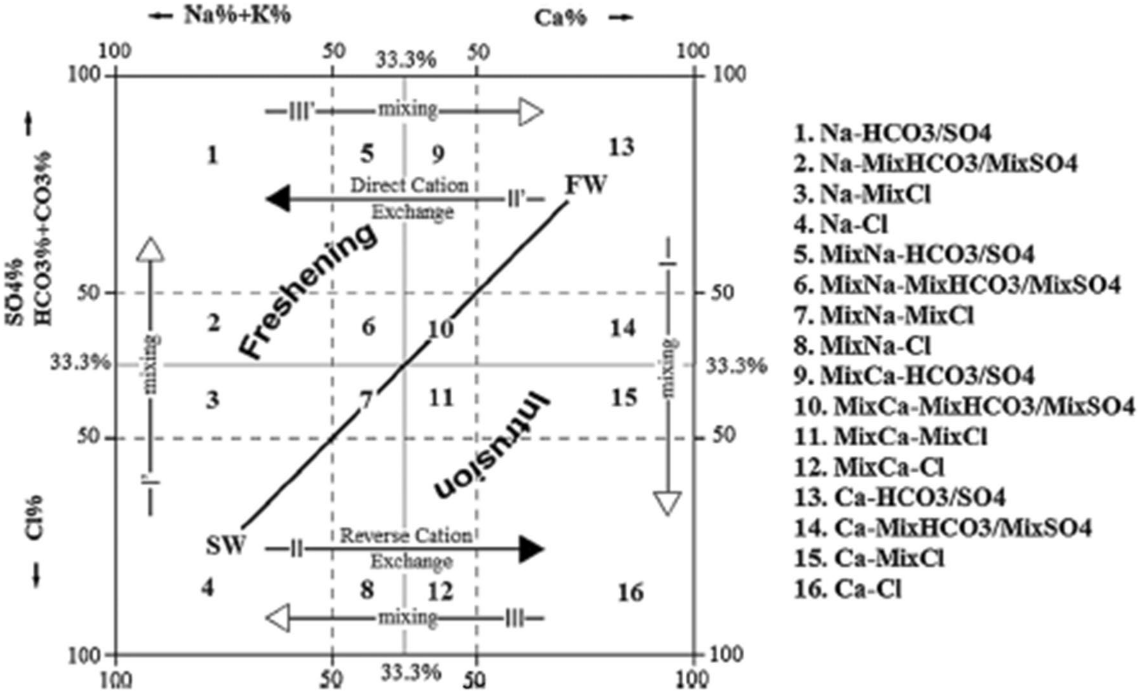

Fig. 3 HFE diagram (Warner et al. 2013)

due to climate changes from a moderate or high rainfall regime to very low rainfall and severe evaporation in these areas, the infiltrated part of the precipitation may be affected by evaporation and has no role in the water table, so virtually this type of aquifer will also have a high resident time (Mirzavand 2018) (Table 1).

Groundwater dating or the average residence time in the aquifer is important for several reasons. By determining the age of the groundwater, the aquifer's recharge cycle will be identified, and as a result, the management of groundwater and aquifer artificial recharge programs will be improved more efficiently. Also, it is possible to separate the role of different sources of contamination in the aquifer and to

Table 1 The most common stable environmental isotopes in groundwater investigation (Clark 2015)

Isotope	Ratio	Abundance%	Reference (abundance ratio)	Common sample types
D or ^{2}H	D/H	0.015	VSMOW (1.5575×10^{-4})	H_2O, CH_4, clays
^{13}C	^{13}C/^{12}C	1.11	VPDB (1.1237×10^{-2})	DIC, CO_2, $CaCO_3$, CH_4, organic C
^{18}O	^{18}O/^{16}O	0.204	VSMOW (2.0052×10^{-3})	H_2O, NO_3^-, SO_4^{2-}, O_2, minerals
^{34}S	^{34}S/^{32}S	4.21	CDT (4.5005×10^{-2})	SO_4^{2-}, H_2S, gypsum, sulfide minerals
^{3}He	^{3}He/^{4}He	0.000138	AIR (1.38×10^{-6})	Minerals, groundwater
^{6}Li	^{6}Li/^{7}Li	7.6	LSVEC (0.08215)	Minerals, brines, water
^{11}B	^{11}B/^{10}B	80.1	NBS 951 (4.044)	Minerals, brines, water
^{37}Cl	^{37}Cl/^{35}Cl	24.23	SMOC (0.324)	Brines, water, solvents
^{81}Br	^{81}Br/^{79}Br	49.314	SMOB	Brines, water, biocides

VSMOW, Vienna Standard Mean Ocean Water; VPDB, Vienna Pee Dee Belemnite, fossil carbonate; CDT, Canon Diablo Troilite; FeS from meteorite; LSVEC, lithium carbonate standard (Stiff 1951; Tamborski et al. 2017), now also used as a carbonate standard (Tomaszkiewicz et al. 2014); NBS-951, boric acid standard, also SRM 951, National Bureau of Standards; SMOC, Standard Mean Ocean Chloride (Ma et al. 2007) optimize management to prevent the occurrence of various contaminations by groundwater dating (Clark 2015). It should be noted that the determination of the method and technique of groundwater dating using radioisotopes depends on the characteristics of the aquifer (Clark 2015). Figure 3 and Table 2 provide valuable information on the half-life and other characteristics of the radioisotopes used in groundwater dating.

The most common isotopes in groundwater dating are: ^{224}Ra ($T_{1/2}=3.63$ day) and ^{222}Rn ($T_{1/2}=3.82$ day) (Tamborski et al. 2017), ^{14}C ($T_{1/2}=5730$ year) (Awaleh et al. 2017; Bhandary et al. 2015; Bouchaou et al. 2008, 2009; Carreira, et al. 2014; Han et al. 2011; He et al. 2013; Samad et al. 2017; Stewart 2012), ^{3}H ($T_{1/2}=12.32$ year) (Awaleh et al. 2017; Bouchaou et al. 2008, 2009; Carreira et al. 2014; Han et al. 2011; Nunes et al. 2017; Stewart 2012), ^{36}Cl ($T_{1/2}=301{,}000$ year) (Khaska et al. 2013; Louvat et al. 1999; Reich et al. 2008), ^{234}U/^{238}U ($T_{1/2}=245{,}500$ years) (Samad et al. 2017), T-^{4}He (Batlle-Aguilar et al. 2017), ^{20}Ne (Batlle-Aguilar et al. 2017), ^{40}Ar (Batlle-Aguilar et al. 2017), ^{129}I ($T_{1/2}=157.10^{5}$) (Clark 2015), ^{49}Ar ($T_{1/2}=170$ ms), ^{136}Xe ($T_{1/2}=2.4.10^{21}$ years), ^{81}Kr ($T_{1/2}=229.10^{3}$ year), ^{32}Si ($T_{1/2}=153$ years), ^{39}Ar ($T_{1/2}=269$ y), CFC, SF6, ^{85}Kr ($T_{1/2}=10.73$ years) and T-^{3}He, ^{35}S ($T_{1/2}=87.51$ day) (Clark 2015). Also, δ^{13}C is a stable isotope used with radioactive isotope of ^{14}C for groundwater dating (Bhandary et al. 2015; Carreira et al. 2014; Mirzavand 2018; Nunes et al. 2017). Different half-lives of various isotopes may confuse researchers, but researchers should select the best radioisotopes for dating according to hydrogeological and geological settings, regional climate and geographical conditions of study area. It means, for arid and semiarid regions with deep groundwaters such as Nubian Sandstone Aquifer System (NSAS), researchers should use the isotopes with long half-life such as ^{14}C and ^{81}Kr but for shallow groundwaters short half-life like ^{3}H should be use (Ayadi et al. 2016) (Fig. 4).

Table 2 The most common environmental radioisotopes in groundwater dating (Clark 2015)

Isotope	Activity (Bq)	Atmospheric ratio	Decay	Half-life (year)
^{85}Kr	1.5 Bq/ccKr	85Kr/Kr $=2.7\cdot10^{-11}$	−β	10.76
^{3}H or T	0.12 Bq/L	T/H $=10^{-17}$	−β	12.32
^{39}Ar	$1.8\cdot10^{-6}$ Bq/ccAr	39Ar/Ar $=8.2\cdot10^{-18}$	−β	269
^{14}C	0.226 Bq/gC	14C/C $=1.18\cdot10^{-12}$	−β	5730
^{81}Kr	$1.34\cdot10^{-6}$ Bq/ccKr	81Kr/Kr $=5.2\cdot10^{-13}$	EC	$229\cdot10^{3}$
^{36}Cl	10^{-6}Bq/L (10 ppm Cl)	36Cl/Cl $\sim10^{-13}$	−β	$301\cdot10^{3}$
^{129}I	10^{-4} Bq/L (1 ppm I)	129I/I $\sim10^{-8}$	−β	$157\cdot10^{5}$

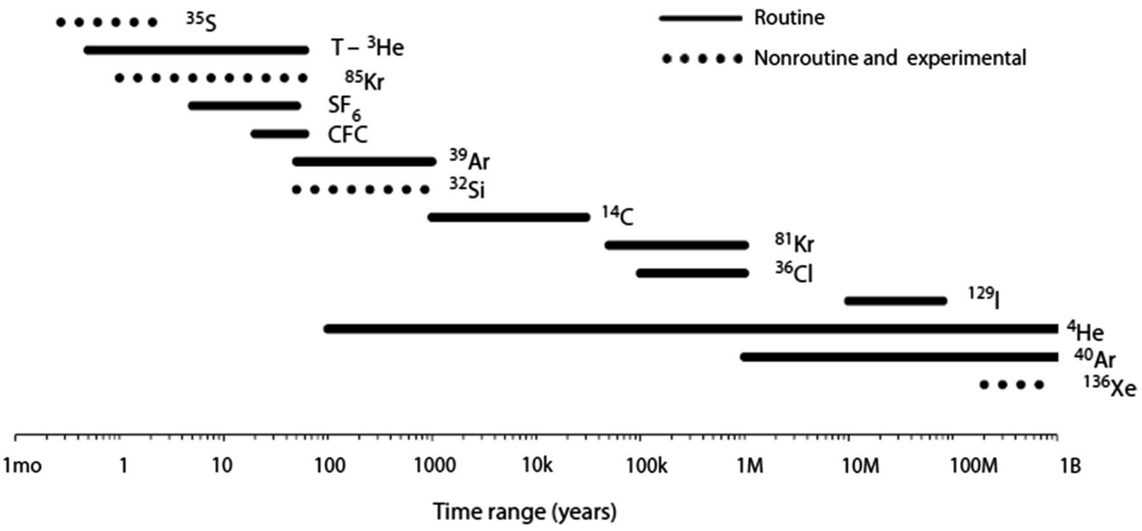

Fig. 4 Age range for groundwater dating by anthropogenic gases and experimental, routine and nonroutine radioisotopes (Clark 2015)

Conclusion

Groundwater is a finite resource, and it is becoming a scarce commodity in many parts of the world. One of the most important management programs in water resources is the conservation and sustainable development of these resources especially coastal aquifers. During the last decades due to low precipitation and changing precipitation regime, the groundwater in several aquifers of the world, especially coastal aquifers, has become unsuitable for human consumption due to overexploitation and salinization. The term of groundwater salinization is used to specify an increase in overall chemical content over background levels in groundwater. Adverse effects of groundwater overdraft include, uneconomic pumping conditions, water quality degradation through induced intrusion of saline or poor quality groundwater, land subsidence and gradual depletion of groundwater storage. The salinization risks limit the groundwater withdrawals from aquifer in some areas, threatening the future sustainable development of regions. Monitoring and identifying the origin of the salinity and salinization mechanism are crucial for both water management and remediation. The multiplicity of salinity sources and the influence of geochemical reactions within the aquifers as well as groundwater mixing cause a high degree of complexity to the task of identifying the origin and mechanism of salinization. The most important sources of groundwater salinity in most aquifers are (1) marine sources (e.g., connate saline groundwater, marine transgressions, incidental flooding by seawater, laterally seawater intrusion and seawater sprays), (2) natural continental sources (e.g., evaporation, soluble minerals, membrane effects and geothermal origin) and (3) anthropogenic activities. Delineation of aquifer systems and gathering information on their hydrogeology and hydrogeochemistry is essential for planning strategies in development programs for future exploitation and effective management of the groundwater resources in many water-scarce regions. Apart from the chemistry of the aquifer water, stable and unstable isotopes can be used as conservative environmental tracers in order to better understand the origin of the water, its recharge mechanisms and the hydrodynamic behavior of the aquifers. The groundwater salinization mechanism can be described using hydrogeochemical and isotopic tracers and hydrogeology and hydrogeochemical evaluation modeling. Beside the hydrogeochemical and isotopic investigation, geological and geophysical information was described as useful tools in groundwater salinization investigation. Decreasing the exploitation of groundwater is an effective way to control and mitigate the risks of salinization for the sustainable management of the groundwater aquifer in the future. It is recommended to apply the comprehensive methods developed in this study to crucial aquifers with a deteriorating water quality, especially when they are located in arid and semiarid regions in order to improve our understanding of overexploitation hazards and salinization risks that pose threats to the environment.

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